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BINAR Y AND TERNARY TRANSITION METAL PNICTIDE NANOPARTICLES AND THEIR THREE-DIMENSIONAL ASSEMBLIES: TOWARDS PROMISING MAGNETIC REFRIGERATION MATERIALS

by

MALSHA ANURADHI HETTIARACHCHI

DISSERTATION

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2019

MAJOR: CHEMISTRY

Approved By

__________________________________________
Advisor Date
DEDICATION

To my beloved Parents

For all their love, efforts, and dedication towards me

To my loving Asanka

For all his unconditional love and sacrifices

To my little Akain

For all the happiness he brings to life
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# TABLE OF CONTENTS

Dedication ........................................................................................................................................... ii

Acknowledgements .............................................................................................................................. iii

List of Tables ........................................................................................................................................ ix

List of Figures ......................................................................................................................................... x

Chapter 1  Introduction .......................................................................................................................... 1

  1.1 Nanomaterials ................................................................................................................................ 2

  1.2 Solution-phase Synthesis of Nanoparticles .................................................................................... 3

  1.3 Anisotropic Growth of Colloidal Nanoparticles .............................................................................. 5

  1.4 Magnetic Properties of Materials .................................................................................................. 6

  1.5 Magnetic Behavior of Nanomaterials .............................................................................................. 12

  1.6 Magnetic Refrigeration .................................................................................................................. 15

  1.7 Materials for Room Temperature Magnetic Refrigeration ............................................................. 19

  1.8 Nanoparticle Assembly .................................................................................................................. 23

  1.9 Thesis Statement ............................................................................................................................ 27

Chapter 2 - Experimental and Materials Characterization Techniques ................................................ 30

  2.1 Materials ...................................................................................................................................... 30

  2.2 Experimental techniques .............................................................................................................. 31

  2.3 Characterization techniques .......................................................................................................... 33

Chapter 3 – Synthesis of Colloidal MnSb Nanoparticles: Consequences of Size and Surface
Characteristics on Magnetic Properties ................................................................................................. 53

  3.1 Introduction .................................................................................................................................. 53

  3.2 Experimental ................................................................................................................................ 55

  3.3 Results and Discussion ................................................................................................................... 56
3.4 Conclusions...........................................................................................................72

Chapter 4 – Anisotropic Manganese Antimonide Nanoparticle formation by Solution-Solid-Solid Growth Mechanism: Consequence of Sodium Borohydride Addition Towards Reduced Surface Oxidation and Enhanced Magnetic Moments.................................................74

4.1 Introduction...........................................................................................................74

4.2 Experimental......................................................................................................76

4.3 Results and Discussion......................................................................................78

4.4 Conclusions.......................................................................................................95

Chapter 5 – Synthesis of Ternary Phase MnAs_xSb_1-x Nanoparticles: Consequences of Compositional Inhomogeneity, and Magnetic Properties.................................................97

5.1 Introduction........................................................................................................97

5.2 Experimental......................................................................................................98

5.3 Results and Discussion......................................................................................99

5.4 Conclusions......................................................................................................110

Chapter 6 – Three-Dimensional Assembly of Discrete Nanoparticles and Evaluation of Their Composite Magnetic Properties..............................................................112

6.1 Introduction........................................................................................................112

6.2 Experimental......................................................................................................113

6.3 Results and Discussion......................................................................................114

6.4 Conclusions......................................................................................................127

Chapter 7 – Conclusions and Prospectus.................................................................129

7.1 Conclusions......................................................................................................129

7.2 Prospectus.........................................................................................................132

Appendix A .................................................................................................................135

Appendix B................................................................................................................138

References...............................................................................................................143
Abstract……………………………………………………………………………………………………158

Autobiographical Statement……………………………………………………………………..160
LIST OF TABLES

Table 1.1: Common examples of transition metal pnictides and their MCE (in terms of $\Delta S_M$) and $T_c$ .................................................................20

Table 4.1: The crystallite size of MnSb and Sb nanoparticles, synthesized using different NaBH$_4$ amounts, calculated by Scherrer equation......................................................80

Table 5.1: Differences between the target and the actual compositions of MnAs$_x$Sb$_{1-x}$ nanoparticles determined by XRF.................................................................105

Table 5.2: Refined lattice parameters of hexagonal crystal structures of MnAs$_{0.1}$Sb$_{0.9}$ to MnAs$_{0.8}$Sb$_{0.2}$ ............................................................................................................106

Table 6.1: The elemental composition analysis of post-heat treated Fe$_{1.2}$Ni$_{0.8}$P aerogels by EDS .................................................................................................................123
## LIST OF FIGURES

**Figure 1.1** Schematic illustration of La Mer’s model for nucleation and growth of nanoparticles in solution ................................................................. 3

**Figure 1.2:** Electron orientation and associated types of magnetism ........................................... 6

**Figure 1.3:** Typical M vs H and $\chi$ vs T plots of diamagnetic materials ....................................... 7

**Figure 1.4:** Typical M vs H and $\chi$ vs T plots of paramagnetic materials ..................................... 8

**Figure 1.5:** Plot of reciprocal susceptibility vs temperature for paramagnetic material .............. 8

**Figure 1.6:** Typical M vs H and $\chi$ vs T plots of antiferromagnetic materials ......................... 9

**Figure 1.7:** Typical magnetization (M) vs applied magnetic field curve (H) of a ferromagnetic material ........................................................................................................ 10

**Figure 1.8:** Different types of magnetic hysteresis curves ............................................................. 11

**Figure 1.9:** Typical $\chi$ vs T curve for ferromagnetic materials ..................................................... 12

**Figure 1.10:** Alignments of magnetic moments in a bulk multidomain material demonstrating domain wall migration and in a single domain nanoparticle demonstrating coherent spin rotation .................................................................................................................. 13

**Figure 1.11:** (a) Illustration of change in coercivity ($H_c$) with particle diameter ($D$) (b) M vs. H curve for superparamagnetic material. $D_c$ defines critical diameter ........................................... 14

**Figure 1.12:** Magnetization as a function of temperature measured under ZFC and FC conditions ................................................................................................................................. 15

**Figure 1.13:** Schematic illustration of a magnetic refrigeration cycle ............................................. 17

**Figure 1.14:** Magneto-structural phase transition of MnAs .............................................................. 18

**Figure 1.15:** Mn occupancy sites of hexagonal bulk MnSb structure ............................................. 21

**Figure 1.16:** The proposed gelation mechanism for CdSe nanoparticles ....................................... 22

**Figure 1.17:** Possible mechanisms for Ni$_2$P gelation ................................................................. 25
Figure 2.1: Phase diagram of CO₂ ................................................................. 34
Figure 2.2: Schematic diagram of a filament X-ray tube .............................. 35
Figure 2.3: Illustration of generation of Kα X-rays. .....................................36
Figure 2.4: Derivation of Bragg’s law ............................................................ 36
Figure 2.5: Schematic diagram of a typical TEM ....................................... 39
Figure 2.6: Ray diagram of (a) bright-field mode (b) dark-field mode of TEM ......................................................................................... 40
Figure 2.7: Schematic diagram of HAADF-STEM ........................................ 41
Figure 2.8: Common electron transitions associate with peaks in EDS .......... 42
Figure 2.9: Schematic diagram of ICP-MS .................................................... 45
Figure 2.10: Instrumentation set up for XRF ................................................. 46
Figure 2.11: Six basic types of adsorption isotherms .................................... 49
Figure 2.12: Schematic diagram of superconducting coil in SQuID ............ 51

Figure 3.1: PXRD patterns of MnSb nanoparticles synthesized using an Mn:Sb precursor concentration of 1:1 at (a) 3 h at 330 °C and (b) 12 h at 330 °C by the slow heating method ....... 57
Figure 3.2: PXRD patterns of MnSb nanoparticles synthesized with Mn:Sb precursor ratio of 1:1 under different reaction temperatures and reaction times by the slow heating method ........... 58
Figure 3.3: (a) PXRD pattern (b) TEM image obtained of the product isolated from an attempt to synthesize MnSb nanoparticles at 200 °C for 3 h ........................................................................................................ 59
Figure 3.4: PXRD patterns obtained for MnSb nanoparticle synthesis by the slow heating method using different Mn₂(CO)₁₀ amounts. The % excess corresponds to the extra molar equivalents of Mn₂(CO)₁₀ relative to Ph₃Sb ........................................................................................................ 60
Figure 3.5: TEM image of MnSb nanoparticles synthesized using 80% mole excess Mn₂(CO)₁₀ by the slow heating method ........................................................................................................ 61
Figure 3.6: (a) PXRD pattern and (b) TEM image obtained for MnSb nanoparticles synthesized by slow heating with larger solvent volume (1-ODE) (MnSb- PDF #: 03-065-0388) at 280 °C for 5 h with 80% excess Mn₂(CO)₁₀ by mole (c) Particle size distribution histogram (d) SAED pattern of the MnSb nanoparticles synthesized by slow heating ........................................................................................................ 62
Figure 3.7: PXRD patterns of MnSb nanoparticles synthesized using an Mn:Sb precursor concentration of 1:1 under different reaction temperatures and reaction times by the cannulation method, cannulated at 200 °C .................................................................63

Figure 3.8: (a-d) HAADF-STEM of MnSb nanoparticles synthesized by the cannulation method and EDS mapping of Mn, Sb, and O, respectively. The scale bar corresponds to 100 nm. (e) Line scan elemental analysis of a single MnSb nanoparticle: .................................................................64

Figure 3.9: MnSb nanoparticles synthesized by the slow heating method before and after purification by repeated CHCl₃ dispersion, ethanol precipitation .................................................65

Figure 3.10: PXRD patterns of two different MnSb nanoparticles syntheses reacted at higher temperature and longer reaction times other than the optimized temperature (280 °C) and time (5 h) .................................................................................................................................67

Figure 3.11: Temperature dependence of the DC molar magnetization (M) (normalized to Mn moles) recorded under Zero-Field-Cooled (ZFC) and Field-Cooled (FC) conditions (collected at 100 Oe) for MnSb nanoparticles synthesized by the slow heating method at 280 °C for 5 h .......68

Figure 3.12: Field dependence of the DC molar magnetization (M) (normalized to Mn moles) recorded at different magnetic fields (H) at (a) 300 K and (b) 50 K for MnSb nanoparticles synthesized by the slow heating method at 280 °C for 5 h. The inset shows an enlarged image of the loop of the hysteresis curve obtained at 50 K .................................................................69

Figure 3.13: Field dependence of the DC molar magnetization (M) (normalized to Mn moles) recorded at different magnetic fields (H) at 50 K for MnSb nanoparticles synthesized by the slow heating method at 280 °C .............................................................................................................70

Figure 3.14: Magnetic properties of MnSb nanoparticles synthesized by the cannulation method (a) Temperature dependence of the DC molar magnetization (M) (normalized to Mn moles) recorded under Zero-Field-Cooled (ZFC) and Field-Cooled (FC) conditions (collected at 100 Oe) Field dependence of the DC molar magnetization (M) (normalized to Mn moles) recorded at different magnetic fields (H) recorded at (b) 300 K and (c) 50 ...........................................................................................................71

Figure 4.1: PXRD data of the product of MnSb synthesis carried out in the absence and in the presence of NaBH₄ (0.53 mmol). The corresponding peaks for Sb, (012) at 2θ=28.7 and (110) at 2θ=42, are marked with asterisks for comparison .................................................................78

Figure 4.2: PXRD data of the product of MnSb synthesis (1 mmol Sb and 1.2 mmol Mn) as a function of added NaBH₄ ..................................................................................................................79

Figure 4.3: TEM images of MnSb syntheses in the presence of different amounts of NaBH₄ (0.53-0.92 mmol) and associated histograms corresponding to the head diameter, tail length, and tail width ........................................................................................................81
Figure 4.4: TEM images of MnSb syntheses in the presence of different amounts of NaBH₄ (1.06-2.64 mmol) and associated histograms corresponding to the head diameter, tail length, and tail width ..........................................................................................................82

Figure 4.5: (a) HAADF-STEM of MnSb nanoparticles synthesized in the presence of NaBH₄ (2.64 mmol) and EDS mapping of (b) Sb and (c) Mn (d) O and (e) P; (f) Bottom mount image of a portion of the tail part of a MnSb nanoparticle showing lattice fringes; (g) line scan elemental analysis of a single head-tail MnSb nanoparticle .................................................................83

Figure 4.6: HAADF-STEM of MnSb nanoparticles synthesized in the presence of NaBH₄ and EDS mapping for B .................................................................84

Figure 4.7: TEM image of MnSb nanoparticles reminiscent of peas in a pod synthesized in the presence of 2.64 mmol NaBH₄ .................................85

Figure 4.8: HAADF-STEM of a MnSb nanoparticle with a ‘swollen tail’ synthesized in the presence of 2.64 mmol of NaBH₄ and line scan elemental analysis (a) axial (b) vertical scan across the tail .................................................................86

Figure 4.9: (a) TEM images (b) PXRD patterns of the fractions obtained at different time intervals (30, 60, 90, 120, 180 min) and quenched in cold chloroform from the reaction using near-stoichiometric Mn₂(CO)₁₀ and 0.92 mmol NaBH₄ .................................................................87

Figure 4.10 (a-c): TEM images of MnSb nanoparticles synthesized in the presence of NaBH₄ (0.79 mmol), using 0.7, 0.9, 1.5 mmol (40, 80, 200% mole excess) of Mn₂(CO)₁₀ ................................................89

Figure 4.11: PXRD patterns of MnSb nanoparticles synthesized in the presence of NaBH₄ (0.79 mmol), using (a) 0.7 (b) 0.9 (c) 1.5 mmol (40, 80, 200% mole excess) of Mn₂(CO)₁₀ ................................................90

Figure 4.12: Low and high magnification TEM images showing the transformation of initial elongated head-tail nanorods, [(a) (low mag), (b) (high mag)] into mixed head-tail nanorod and spherical nanoparticles 3h after adding 0.9 mmol of Mn₂(CO)₁₀ [(c) (low mag), (d) (high mag)] and into spherical nanoparticles after 5 h total [(e) (low mag), (f) (high mag)] ...........................91

Figure 4.13: PXRD patterns of near-stoichiometric Mn₂(CO)₁₀ containing reaction mixture and upon the introduction of excess Mn₂(CO)₁₀ to the near-stoichiometric Mn₂(CO)₁₀ containing the reaction mixture after 3 and 5 h carried out in the presence of 1.59 mmol NaBH₄ .......................92

Figure 4.14: (a) Low magnification and (b) high magnification TEM images (c) PXRD pattern of the MnSb nanoparticles synthesized under near stoichiometric Mn₂(CO)₁₀ amount with NaBH₄ (1.59 mmol) after heating for a total of 8 h ...........................................................................92

Figure 4.15: Field dependence of the DC molar magnetization (M) (normalized to Mn moles) recorded at different magnetic fields (H) at 50 K for MnSb nanoparticles synthesized (a) with near-stoichiometric Mn₂(CO)₁₀ amount (0.6 mmol) and (b) with excess Mn₂(CO)₁₀ (1.5 mmol) in the presence of 1.0 mmol of Ph₃Sb and 0.79 mmol NaBH₄ (250 °C for 3 h) .................................................................94
Figure 5.1: PXRD pattern of initial synthesis of MnAs_{0.5}Sb_{0.5} nanoparticles (target composition) using 1.1 mmol of Mn and heating the reaction mixture at 250 °C for 3 h ........................................100

Figure 5.2: PXRD patterns of the syntheses showing the effect of reaction time when heated at 250 °C in the presence of 1.1 mmol of Mn .................................................................100

Figure 5.3: PXRD patterns of the syntheses showing the effect of reaction temperature towards the MnAs_{0.5}Sb_{0.5} nanoparticles (target composition) synthesis in the presence of 1.1 mmol of Mn and heated for 3 h .................................................................................................................................101

Figure 5.4: Effect of NaBH₄ addition towards the MnAsₙSb₁₋ₙ nanoparticle synthesis ............101

Figure 5.5: PXRD patterns of MnAs_{0.5}Sb_{0.5} (target composition) synthesized using different amounts of Mn ..........................................................................................................................102

Figure 5.6 (a): PXRD pattern of MnAsₙSb₁₋ₙ (x=0.1-0.8) nanoparticles ........................................103

Figure 5.6 (b): TEM images of MnAsₙSb₁₋ₙ (x=0.1-0.8) nanoparticles ........................................104

Figure 5.7: (a) PXRD pattern (b) TEM image of MnAs₀.₉As₀.₁ nanoparticles .........................104

Figure 5.8 Graphical representation of target composition vs actual composition ..................105

Figure 5.9: The refined lattice parameters of target compositions MnAsₙSb₁₋ₙ (x=0.1-0.8) (a) a axis (b) c axis (c) cell volume ..........................................................................................................................106

Figure 5.10 HAADF-STEM of MnAs_{0.5}Sb_{0.5} nanoparticle and elemental mapping analysis of Mn, As, Sb, O, (O+As), (Mn+As), and (Mn+Sb) .........................................................................................108

Figure 5.11: (a) Temperature dependence of the DC molar magnetization for the target nanoparticle composition of MnAs_{0.5}Sb_{0.5}. ................................................................................................................109

Figure 6.1: TEM images of Fe₁.₂Ni₀.₈P nanoparticles/nanorods (a-c) before and (d-f) after 3-D assembly (thiolate exchanged with 11-MUA). The inset on each image shows the corresponding monoliths obtained after supercritical drying of the 3-D assemblies ...........................................115

Figure 6.2: The PXRD images corresponding to the aerogels in Fig. 6.1 (e-f) of the Fe₁.₂Ni₀.₈P composition synthesized by using (a) 2.0 mL of oleylamine and 3.0 mL of TOP (b) 2.0 mL of oleylamine and 5.0 mL of TOP (c) 1.0 mL of oleylamine and 5.0 mL of TOP, and thiolate exchanged using 11-MUA .........................................................................................................................116

Figure 6.3: Nitrogen adsorption/desorption isotherms of aerogels relevant to Fig. 6.2 (d-f). Insets indicate pore size distribution ..............................................................................................................................117
Figure 6.4: (a) TEM image (b) PXRD pattern of the Fe$_{1.2}$Ni$_{0.8}$P nanoparticles, thiolate exchanged with 1-DDT, after 3-D assembly. The inset on Fig. 6.4 (a) shows a high magnification image of the corresponding aerogel sample

Figure 6.5: (a) About 1 min after EDTA addition into Fe$_{1.2}$Ni$_{0.8}$P +11-MUA aerogel (b) supernatant of Fig. 6.4 (b) (c) EDTA addition into Fe$_{1.2}$Ni$_{0.8}$P +1-DDT aerogel

Figure 6.6: PXRD patterns of the Fe$_{1.2}$Ni$_{0.8}$P aerogels (thiolate exchanged with 11-MUA) heat treated under different conditions

Figure 6.7: TEM images of Fe$_{1.2}$Ni$_{0.8}$P aerogels (thiolate exchanged with 11-MUA) treated under different conditions: (a) heated at 250 °C under Ar for 1 h; (b) heated at 250 °C under H$_2$ (5%) for 1 h (c) heated at 400 °C under Ar for 1 h (d) heated at 400 °C under H$_2$ (5%) for 1 h

Figure 6.8: TGA analysis of Fe$_{1.2}$Ni$_{0.8}$P aerogel post-heat treated at 400 °C for 1 h under 5% H$_2$

Figure 6.9: Nitrogen adsorption/desorption isotherms obtained for the Fe$_{1.2}$Ni$_{0.8}$P original aerogel thiolate exchanged with 11-MUA, and the same aerogel heated at 400 °C under H$_2$ (5%) for 1 h. The inset shows the pore size distribution

Figure 6.10: (a) TEM image and (b) PXRD relevant to the original gel and the aerogel heat treated under reducing conditions (5% H$_2$) at 400 °C for 1 h

Figure 6.11: ZFC and FC curves of (a) discrete nanoparticles of Fe$_{1.2}$Ni$_{0.8}$P (as-prepared, capped with oleylamine and TOP) (b) aerogels prepared from nanoparticles thiolate-capped with 11-MUA, before and after heat treatment at 400 °C under 5% H$_2$ (c) aerogels prepared from nanoparticles thiolate-capped with 1-DDT, before and after heat treatment at 400 °C under 5% H$_2$
CHAPTER 1-INTRODUCTION

Nanoparticle research has achieved extensive scientific and public attention due to the uniqueness and importance of their applications in various fields such as catalysis, medicine, solar cells, fuel cells, magnetic recording, and agriculture. The transition metal pnictides (TMP) (group 15 elements) are emerging as a group of materials with many practical applications. The physical properties of these materials are highly dependent on the stoichiometry and the structure. Catalytic activity, superconductivity, magneto-caloric activity, semiconductivity, and magneto-optical activity are some of the important properties of TMP.

Owing to the distinct optical, magnetic, and catalytic properties compared to their macro-scale counterparts, nano-sized manganese arsenide (MnAs), manganese antimonides (MnSb) and their associated ternary phases have long been of interest due to strong magneto-structural coupling and associated large magneto-caloric effects. However, synthesis of discrete nanoparticles of these compounds is challenging owing to the phase separation and large size polydispersity.

The work presented in this dissertation is focused on synthesis of MnSb and ternary phase MnAs$_x$Sb$_{1-x}$ nanoparticles, and the assembly of discrete nanoparticles into three-dimensional architectures. The magnetic properties of these materials are evaluated towards promising magnetic refrigeration material(s). CHAPTER 1 introduces the background information relevant to this dissertation study. This includes; general properties of nanomaterials, magnetic properties of nanoparticles, and the basic principles of nanoparticle assembly.
1.1 Nanomaterials

Solids that have at least one dimension in the size range of 1-100 nm are known as nanomaterials. Nanomaterials can be divided into 3 classes; (1) nanoparticles: all dimensions are less than 100 nm, (2) nanowires: one dimension is larger than 100 nm (1-D), (3) thin films: two dimensions are larger than 100 nm (2-D). Nanophenomena are dominated by the surface, with the surface-to-volume ratio (A/V) playing an important role in nanomaterials. As an example, when comparing a spherical particle having the radius 1 mm (A/V = 3x10^3 m⁻¹) to a spherical nanoparticle of 10 nm (A/V=3x10^8 m⁻¹) the factor of 10^5 difference can be observed. Owing to the large A/V and changes in electronic/magnetic interactions, a material’s catalytic, mechanical, electronic, optical, magnetic, and dynamic properties can change on the nanoscale.

Nanomaterials can be produced by two main approaches; (1) Top-down approach, (2) Bottom-up approach. The top-down approach starts with bulk materials and nanostructures are produced when the starting bulk material undergoes milling and etching (eg: lithography). Nanomaterials produced by the top-down approach are vulnerable to imperfections, resulting in strain. In contrast, the bottom-up approach uses molecular precursors to produce nanomaterials (eg: self-assembly), enabling more control over the size and morphology. Nanomaterials can be fabricated by a physical or a chemical method. Physical methods for nanoparticle synthesis include ball milling, molecular beam epitaxy, and irradiation (microwave, X-ray and gamma rays). Chemical methods for nanoparticle synthesis include hydrothermal, solvothermal and solution-phase arrested precipitation techniques.

1.2 Solution Phase Synthesis of Nanoparticles

In this dissertation study, the Solution-Phase Arrested Precipitation (SPAP) technique is employed in nanoparticle synthesis using organometallic reactants, along with coordinating
ligands in high boiling point solvents. The SPAP method is one of the widely used chemical synthesis methods for nanoparticles due to the excellent control over nanoparticle size, morphology, polydispersity, surface functionalities and chemical composition that can be achieved.\textsuperscript{23-24}

The most commonly employed method of SPAP is rapid injection of the reaction precursors into a hot coordinating solvent. Rapid introduction of the reactants/regents leads to a burst of precursors causing a single and short nucleation event. On the other hand, SPAP can take place in a reaction mixture of reactants and the coordinating ligands that has been subjected to slow/gradual ramping of the temperature. In a gradual temperature change, the nucleation event takes place owing to the decomposition of the reaction precursors when the temperature attains a critical value. This dissertation study involves both types of SPAP techniques mentioned above.

![Figure 1.1: Schematic illustration of La Mer’s model for nucleation and growth of nanoparticles in solution (adapted from reference\textsuperscript{25})](image-url)
The formation of highly monodisperse nanocrystals in the solution-phase, upon the rapid injection of the reactant precursor, can be explained by La Mer’s model of nucleation and growth, as illustrated in Fig. 1.1. According to this model (Fig. 1.1), injection of reaction precursors into a hot solvent results in thermal decomposition, forming monomers. The concentration of the monomers then rises until the critical limiting super-saturation level is reached. The supersaturation of monomers results in a burst of nucleation, which then lowers the monomer concentration owing to a higher consumption rate of the monomers than the generation rate. When the monomer concentration is reduced below the nucleation threshold, the formation of new nuclei is discontinued, and the monomers add to existing nuclei, resulting in nanoparticle growth. As the nanoparticles grow, the concentration of the monomers is further decreased, resulting in saturation. At this point, the nanoparticles are continuing to grow at the expense of smaller particles, known as Ostwald ripening. Ostwald Ripening was first described by Wilhelm Ostwald in 1900. According to this mechanism, smaller particles in a solution with high solubility and high surface energy re-dissolve, facilitating the growth of larger particles. The longer Ostwald ripening goes on (i.e. longer the reaction time), the bigger the average particle size. This results in a high polydispersity in the size of the final product. Therefore, according to the La Mer’s model, high polydispersity can be controlled by arresting the reaction during the rapid growth stage before the start of Ostwald ripening.

SPAP provides control over the particle size and the shape by facilitating the tuning of various reaction conditions. Temperature control is essential to avoid additional nucleation, hence controlling the morphology and the size distribution of the nanoparticles in solution. The activation energy requirement for nucleation is higher than that of the particle growth. Therefore, ramping the temperature of the reaction provides a control over the relative rates of nucleation
and the growth of nanoparticles. Thus, a low nucleation temperature results in decreased monomer concentration, hence larger particles. On the other hand, the rate of the Ostwald ripening process can be increased by elevated temperatures, forming larger particles.

1.3 Anisotropic Growth of Colloidal Nanoparticles

Nanoparticle growth can be controlled either thermodynamically or kinetically. Thermodynamic control over a reaction usually results in spherical (the lowest-energy shape) or near-spherical nanoparticles, due to even growth of all facets. However, kinetically-controlled growth of the nanoparticles can lead to directional and/or preferential growth of some crystal facets, resulting in anisotropic growth. Kinetic control over a reaction can achieved by tuning the reaction parameters such as reaction temperature and time, type of stabilizer, precursor concentration...etc. Anisotropic growth results in elongated nanoparticles such as rods, wires, and tadpoles.

Surfactants play an important role in anisotropic growth, as they can preferentially bind to a facet inhibiting the growth of nanoparticle along this facet, and then lead to anisotropic growth. The surfactants/coordinating ligands have considerable influence on the reaction pathway and characteristics of the final product(s). Critical parameters include, surfactant-to-precursor ratio, strength of surfactant-monomer interaction, and the steric effects of the surfactants. Anisotropic growth in nanoparticles can be facilitated by many methods such as seed mediated growth, polyol synthesis, hydro/solvothermal synthesis, galvanic reactions, photochemical synthesis, electrochemical synthesis. Solution-Liquid-Solid (SLS) and Solution-Solid-Solid (SSS) growth mechanisms are also widely employed in the synthesis of 1-D nanorods and nanowires. More details about this growth mechanisms are described in CHAPTER 4.
1.4 Magnetic Properties of Materials

Magnetism is an intrinsic property of all materials. The magnetic strength of a material is determined by the presence or absence of unpaired electrons, and their combined interactions in the presence of an external magnetic field. The unpaired electrons are usually located on metal cations, therefore, non-diamagnetic behavior is usually found in to transition metals and lanthanides, having unpaired $d$ and $f$ electrons, respectively. Magnetic materials can be classified into five types depending on the orientation of magnetic moments in these materials (Fig. 1.2)

Magnetic susceptibility ($\chi$) is the ratio of the degree of magnetization (M) of a material towards the applied magnetic field (H), as shown in Equation 1.1.

$$\chi = \frac{M}{H}$$ (1.1)

![Diagram of magnetic susceptibility types](image-url)

**Figure 1.2:** Electron orientation and associated types of magnetism

1.4.1 Diamagnetism

Diamagnetism is an inherent property of all materials, except the hydrogen atom, and arises due to the presence of paired electrons. Materials classified as diamagnetic possess only paired electrons, hence their magnetic susceptibility ($\chi$) is negligibly small ($\sim 10^{-5}$) and typically
negative (-8x10^{-6} for Cu)\(^{38}\) compared to materials with unpaired electrons. The diamagnetic behavior is a result of the orbital motion of electrons, and the magnetic susceptibility is independent of temperature. The magnetization of diamagnetic materials as a function of magnetization (M) vs applied external magnetic field (H) is linear with a negative slope, and completely reversible (Fig. 1.3).

![Figure 1.3: Typical (a) M vs H and (b) \(\chi\) vs T plots of diamagnetic materials](image)

### 1.4.2 Paramagnetism

A material is classified as a paramagnetic material, when there are unpaired electrons and the magnetic moments are oriented randomly. The magnetic moments of paramagnetic materials do not cooperate in the absence of an external magnetic field. In the presence of an external magnetic field, the magnetic moments align with the direction of the applied field. The magnetization increases linearly with an applied external magnetic field, owing to the gradual orientation of the magnetic moments with the applied field (Fig. 1.5 (a)). For paramagnetic materials \(\chi\) is small (~10\(^{-3}\) -10\(^{-5}\))\(^{38}\) and positive. \(\chi\) is temperature dependent and in a case of increasing temperature, the \(\chi\) value decreases as the thermal energy facilitates spins to overcome
the orienting force of the external field (Fig. 1.4 (b)). Therefore, according to the Curie law (Equation 1.2), \( \chi \) is inversely proportional to temperature, related by C, the Curie constant.

\[
\chi = \frac{C}{T}
\]  

(1.2)

Fig. 1.5 shows the reciprocal susceptibility as a function of temperature.

Figure 1.4: Typical (a) \( M \text{ vs } H \) and (b) \( \chi \text{ vs } T \) plots of paramagnetic materials

Figure 1.5: Plot of reciprocal susceptibility vs temperature for paramagnetic material

1.4.3 Antiferromagnetism

In antiferromagnetic materials, the magnetization of neighboring moments is equal, but the alignment is opposite to each other. Similar to paramagnetism, antiferromagnetic materials
do not exhibit a magnetic response in the absence of an external magnetic field. However, in the presence of an external magnetic field the magnetization increases linearly with the increasing external magnetic field (Fig. 1.6 (a)). The $\chi$ value is positive ($\sim 0$ to $10^{-2}$), and for randomly oriented grains, the $\chi$ value first increases with increasing temperature, and then decreases after a certain point, called as Nèel temperature ($T_N$) (Fig. 1.6 (b)). Therefore, at $T_N$ the material transition from an antiferromagnetic to a paramagnetic material.

![Typical (a) M vs H and (b) $\chi$ vs T plots of antiferromagnetic materials](image)

**Figure 1.6**: Typical (a) $M$ vs $H$ and (b) $\chi$ vs $T$ plots of antiferromagnetic materials

### 1.4.4 Ferromagnetism

The magnetic moments of ferromagnetic materials interact with each other and align parallel in the same direction, producing a large net magnetization in the absence of an external magnetic field. Ferromagnetism is the most important class of magnetism, as ferromagnetic materials are utilized in various applications such as magnetic refrigeration, magnetic data recording and the data storage. In the presence of an external magnetic field, as the magnetic field grows, the magnetic moments align with the field, increasing the magnetization of the material until it reaches a point where further increase of the magnetic field does not affect the magnetization. The magnetization at this point is called the *saturation magnetization* ($M_s$). When magnetizing from a zero field value (first curve) the material follows a non-linear magnetization
curve, known as the *virgin curve*. Unlike in paramagnetic materials, when the applied external magnetic field is removed, the magnetic moments remain parallel to each other maintaining a residual magnetic moment. This is called *remnant magnetization* \( (M_R) \). In order to bring the magnetization to zero, an external magnetic field has to be applied in the opposite direction, i.e. *coercive field/ coercivity* \( (H_C) \).

**Figure 1.7:** Typical magnetization (M) vs applied magnetic field curve (H) of a ferromagnetic material

As the magnetic field increases in the opposite direction, the material reaches a point where it attains the saturation magnetization with the spins aligned in the opposite direction. Upon the removal of the applied external magnetic field, the material obtains remnant magnetization in the opposite direction. Cycling the field results in a *hysteresis loop*. The narrower the loop, the lower the extent of hysteresis, and smaller the coercivity. Ferromagnetic materials with different types of hysteresis, as shown in **Fig. 1.8**, are important in various types of magnetism-related applications.
In Fig. 1.8 (a), the size of the hysteresis loop and the remnant magnetization ($M_{R'}$) is larger, meaning that this type of ferromagnetic material retains a large fraction of the saturation magnetization when the applied external magnetic field is removed, making them desirable for permanent magnets, magnetic recording and memory devices. Narrow hysteresis loops (Fig. 1.8 (b, c)) are indicative of small amounts of dissipated energy in repeatedly reversing the magnetization. Transformers, motor cores, and magnetic refrigeration devices exhibit high energy efficiency with this type of ferromagnet as functional materials.

The $\chi$ value of a ferromagnetic material is positive and large ($\sim 5 \times 10^3$ for Fe)\textsuperscript{38}, hence these materials are strongly attracted to an external magnetic field. Upon the increase of the temperature, the thermal energy overcomes the ferromagnetic energy, and become paramagnetic. This transition point is called the Curie Temperature ($T_C$) (Fig. 1.9).
1.4.5 Ferrimagnetism

In ferrimagnetic materials, neighboring magnetic moments are opposite to each other but their magnitude is different. Therefore, there is always a net positive magnetization in this type of materials. Ferrimagnetic materials exhibit characteristic magnetic behaviors (spontaneous magnetization, Curie temperature, and hysteresis) analogous to ferromagnetic materials, but there is always a reduced magnetic moment. The $M$ vs $H$ and $\chi$ vs $T$ plots of ferrimagnetic materials are similar to those shown in Fig. 1.8 and 1.9, but the magnitude of $M$ and $\chi$ is smaller.

1.5 Magnetic Behavior of Nanomaterials

Nanoscale magnetic materials exhibit strong size and shape-dependent properties, and some of these properties are extremely beneficial in practical applications. Magnetic domains are small regions in which the magnetization is uniform in direction and is characteristic of ferro- and ferrimagnetic materials. Magnetic domains are separated from each other by domain walls. Magnetic domain walls possess a unique width and energy profile that corresponds to their formation and existence. In bulk materials when an external magnetic field is applied, the
magnetic domains align with the direction of the external field, and grow at the expense of neighboring domains that are not aligned with the external field by domain wall migration (Fig. 1.10 (a)). However, the formation of domain walls becomes energetically unfavorable at the critical particle size ($D_c$), and each particle has only one magnetic domain (Fig. 1.10 (b)). Below $D_c$, a coherent spin rotation is required to alter the spin orientation. Compared to domain wall migration, this is a high energy process. Therefore, nanoparticles can possess larger coercivity than the bulk material. However, as the size continues to decrease, the magnetic moments in the nanoparticles become sensitive towards thermal fluctuations, giving rise to superparamagnetism.

![Figure 1.10: Alignments of magnetic moments](image)

In a superparamagnetic state, the magnetic hysteresis disappears, and the material behaves similar to a paramagnetic material in the absence of an applied external magnetic field as shown...
in Fig. 1.11; saturation is observed, but the absence of coercivity means there is no permanent moment (relaxes rapidly upon removal of field).

![Diagram](image)

**Figure 1.11:** (a) Illustration of change in coercivity ($H_c$) with particle diameter ($D$) (b) $M$ vs. $H$ curve for superparamagnetic material. $D_c$ defines critical diameter

In a ferromagnetic material the temperature at which superparamagnetism appears is known as the *blocking temperature* ($T_B$). The $T_B$ for a certain material depends on the size of the nanoparticle and/or polydispersity, shape anisotropy, and time scale of measurement. $T_B$ can be determined experimentally using magnetization vs temperature measurements carried out under *Zero-Field Cooling* (ZFC) and *Field Cooling* (FC) conditions in a low applied field (~100 Oe). Under ZFC conditions, nanoparticles are cooled in a zero-magnetic field. Therefore, the magnetic moments freeze in random orientations. When an external magnetic field is applied and the temperature ramped up, the magnetic moments start aligning with the external magnetic field through coherent spin rotations, increasing the magnetization. At $T_B$, thermal fluctuations are capable of re-orienting the moments resulting in a decrease of magnetization. Under FC conditions, the nanoparticles are cooled in the presence of an external magnetic field, making the
moments orient in the direction of the magnetic field. When the temperature is ramped up, the magnetization remains regardless of the temperature until $T_B$ is drawing near. At $T_B$ the magnetic moments randomize, and magnetization decreases with increasing temperature. In a ZFC plot $T_B$ corresponds to a point of maximum magnetization. Above $T_B$ both ZFC and FC plots exhibit super paramagnetic behavior. Fig. 1.12 shows typical ZFC and FC plots of a ferromagnetic material.

![Magnetization vs Temperature](image.png)

**Figure 1.12:** Magnetization as a function of temperature measured under ZFC and FC conditions

Other important information that can be obtained by ZFC and FC plots is the Curie temperature. In order to be more accurate, $M$ vs $H$ measurements are carried out at different temperatures close to $T_c$, which is estimated from ZFC and FC plots. Then the plots of $M^2$ vs $H/M$ are obtained, which are called as Arrott plots. A linear curve that passes through the origin $(0,0)$, corresponds to $T_c$.

### 1.6 Magnetic Refrigeration

According to statistics, about 17% of the United States energy consumption is used by the refrigeration sector, which includes air conditioning. It is reported that even the best
performing Vapor Compression Refrigerators (VCR) have only a 5-10% Carnot cycle efficiency. VCR employs movable compressors to impart the compression and expansion processes, which are intrinsically inefficient. On the other hand, even though the ozone depleting substances in refrigerators are restricted by the Montreal Protocol, the emission of greenhouse gases like ammonia (used as a refrigerant gas) and carbon dioxide (emitted in producing the energy required to drive VCR) are largely unregulated. About 20% of the global-warming impact of refrigeration systems is due to direct emissions, i.e. leakage of fluorocarbons (CFCs, HCFCs, and HFCs) or ammonia, while the remaining 80% is caused by the indirect emissions of gasses produced during the electricity generation required to operate the systems by fossil fuels (www.iifiir.org/Publications/Informatory_Notes).

Unlike conventional refrigerators, the MR technique does not involve a gaseous substance as a working material. The functional material for MR is a magnetic, solid material whose magnetic moments alignment (magnetization) imparts the cooling process in the presence of an external magnetic field. Therefore, MR serves as an excellent alternative to conventional VCR in terms of energy efficiency (prototype MRs exhibit 30-60% Carnot cycle efficiency)\(^{40}\) and environmental friendliness.

1.6.1 First and Second Order Phase Transitions

Transition or Phase change refers to the transformation of a system/material from one phase to another, casing an abrupt alternation in one or more physical properties. In terms of a magnetic system, two phase transitions are identified; first order and second order phase transitions. First Order Phase Transitions (FOPT) generally can be observed in a system, in which two phases are in equilibrium. When one phase undergoes a structural change to another, a sudden, discontinuous entropy change occurs at the phase transition. Therefore, FOPT is also
called as first order magneto-structural phase transition, and this is associated with high magnetic entropy change/MCE in a narrow temperature range (Fig. 1.13 (a)). However, due to magneto-structural phase transition, FOPT endures hysteresis, which reduces the efficiency of the system. In contrast, Second Order Phase Transition (SOPT) is continuous over a broad temperature change (Fig. 1.13 (b)). Therefore, compared to FOPT, SOPT possesses lower magnetic entropy change/MCE.

Figure 1.13: Magnetic entropy dependence of temperature for a ferromagnetic material with (a) first order phase transition (b) second order phase transition for a particular field change $\Delta H$

1.6.1 Magnetic Refrigeration Cycle

The typical MR cycle consists of two adiabatic steps and two isomagnetic steps as shown in Fig. 1.14. The total entropy of a magnetic material can be explained by Equation 1.4.

$$S_T = S_M(H, T) + S_E(T) + S_L(T)$$  \hspace{1cm} (1.4)

According to Equation 1.4, the total entropy of a magnetic material depends on the magnetic entropy ($S_M$), the electronic entropy ($S_E$) caused by the material’s free electrons, and the lattice entropy ($S_L$) from the vibration of the crystal lattice.\(^{41}\) All these three components depend on temperature, while only $S_M$ depends on an applied external magnetic field. At a constant pressure, the total entropy of a magnetic material is also a constant.
As shown in Fig. 1.14 (A), the MR cycle starts with the material at temperature $T_0$, and the magnetic moments are randomly aligned as there is no applied external magnetic field ($B=0$). When an external magnetic field is applied adiabatically, the moments align with the direction of the magnetic field decreasing the randomness of the system, hence $S_M (A \rightarrow B)$. Therefore, in order to maintain the $S_T$ at a constant value, terms $S_E$ and $S_L$ collectively increase. Because of the increased lattice vibrations (major contributor) and free electron motions the temperature of the material increases ($T_0 + \Delta T$). The high heat is expelled by the system using a pump and a coolant fluid (Fig. 1.14 (B)). This coolant fluid can even be water at 273 K. Once the excess heat is expelled by the system, the temperature of the material approaches to its original value, $T_0$ (Fig. 1.14 (B)).

Figure 1.14: Schematic illustration of a magnetic refrigeration cycle.
In order to maintain the efficiency of the step $B \rightarrow C$ the applied magnetic field is held at a constant value, in an isomagnetic process. As shown in Fig. 1.14 (C), the applied external magnetic field is next removed; therefore, the magnetic moments align back randomly, increasing the term $S_M$. The second adiabatic Step, $C \rightarrow D$, is exactly the reverse of step $A \rightarrow B$. For that reason, the temperature of the material decreases to $T_0 - \Delta T$. By design, the temperature at this level (Fig. 1.14 (D)) is lower than the temperature of the refrigerator. Consequently, the excess heat from the refrigerator flows into the material by a coolant fluid, making the refrigerator interior cooler than the outside (environmental) temperature. After absorbing the heat, the material’s temperature increases back to the initial temperature, $T_0$. Step $D \rightarrow A$ is also maintained at constant external magnetic field (isomagnetic). When the cycle reaches level Fig. 1.14 (A) again, this completes one MR cycle and the material is ready for another cycle.

1.7 Materials for Room Temperature Magnetic Refrigeration

Ferromagnetic materials with a large magneto-caloric effect (MCE) near-room temperature are desired for room temperature MR. MCE is the reversible change of the thermodynamic variables of a sample, i.e. magnetic entropy and temperature, in the presence of an external magnetic field, and express by either magnetic entropy change ($\Delta S_M$) or adiabatic temperature change ($\Delta T_{ad}$). For practical near-room temperature applications, it is important to have the $T_c$ of the MR material close to room temperature. Further, the material should be workable in a broad temperature range in the vicinity of room temperature. The presence of minimum/near-zero magnetic hysteresis (occurs during an alternating magnetic field) and thermal hysteresis (occurs during heating and cooling) is important to gain high operating frequency and to minimize the energy loss, thereby obtaining a large cooling power. Materials with low specific heat and high thermal conductivity allow large changes in the temperature
facilitating the process of heat transfer, and thereby increasing the efficiency of the heat transfer process.\textsuperscript{41} Environmental friendliness, and lower manufacturing costs are also necessary for commercial viability and sustainability of the product.

Early prototype MR materials were mostly based on gadolinium (Gd) and Gd-based intermetallic compounds such as Gd\textsubscript{0.5}Dy\textsubscript{0.5},\textsuperscript{42} Gd\textsubscript{0.74}Tb\textsubscript{0.26},\textsuperscript{43} Gd\textsubscript{5}Pd\textsubscript{3},\textsuperscript{44} Gd\textsubscript{5}(Si\textsubscript{x}Ge\textsubscript{1-x})\textsubscript{4} where x=0.5,\textsuperscript{45} 0.505\textsuperscript{46} and Gd\textsubscript{5}(Si\textsubscript{1.985}Ge\textsubscript{1.985}Ga\textsubscript{0.03})\textsubscript{2}\textsuperscript{47}. Elemental Gd undergoes a second order paramagnetic to ferromagnetic phase transition at a T\textsubscript{c} of 294 K for a magnetic field of 5 Tesla (T), giving the $\Delta S\textsubscript{M}$ value of ca. 10.2 J kg\textsuperscript{-1}K\textsuperscript{-1}.\textsuperscript{48} At the magnetic field of 5 T, the MCE of most of these Gd compounds is considerably larger (ca. 10-40 J kg\textsuperscript{-1}K\textsuperscript{-1}), and the T\textsubscript{c} is either at room temperature or close to room temperature. However, Gd and its associated compounds suffer from low abundance, high cost and easy oxidation.\textsuperscript{41} A number of transition metal based compounds emerge as promising MR materials due to their large MCE and their T\textsubscript{c} being close to room temperature. Moreover, unlike Gd, transition metal compounds are highly abundant and less expensive.\textsuperscript{49-50} Table 1.1 shows some common examples of transition metal pnictides and their MCE (in terms of $\Delta S\textsubscript{M}$) and T\textsubscript{c}.

**Table1.1:** Common examples of transition metal pnictides and their MCE (in terms of $\Delta S\textsubscript{M}$) and T\textsubscript{c}

<table>
<thead>
<tr>
<th>Magnetic Material</th>
<th>$\Delta S\textsubscript{M}$ (J kg\textsuperscript{-1}K\textsuperscript{-1})</th>
<th>T\textsubscript{c} (K)</th>
<th>$\Delta H$ (T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnAs\textsuperscript{51}</td>
<td>30.0</td>
<td>318</td>
<td>5.0</td>
</tr>
<tr>
<td>MnAs\textsubscript{0.9}Sb\textsubscript{0.1}\textsuperscript{52}</td>
<td>30.0</td>
<td>286</td>
<td>5.0</td>
</tr>
<tr>
<td>MnFeP\textsubscript{0.45}As\textsubscript{0.55}\textsuperscript{13}</td>
<td>18.0</td>
<td>300</td>
<td>5.0</td>
</tr>
<tr>
<td>Ni\textsubscript{52.6}Mn\textsubscript{23.1}Ga\textsubscript{24.3}\textsuperscript{53}</td>
<td>18.0</td>
<td>300</td>
<td>5.0</td>
</tr>
<tr>
<td>La\textsubscript{1-x}Ca\textsubscript{x}MnO\textsubscript{3}\textsuperscript{54-57} x=0.2</td>
<td>5.5</td>
<td>230</td>
<td>1.5</td>
</tr>
<tr>
<td>x=0.33</td>
<td>6.4</td>
<td>267</td>
<td>3.0</td>
</tr>
<tr>
<td>x=0.35</td>
<td>5.2</td>
<td>255</td>
<td>3.0</td>
</tr>
<tr>
<td>x=0.4</td>
<td>5.0</td>
<td>263</td>
<td>3.0</td>
</tr>
<tr>
<td>La\textsubscript{0.75}Ca\textsubscript{0.15}Sr\textsubscript{0.10}MnO\textsubscript{3}\textsuperscript{16}</td>
<td>2.8</td>
<td>327</td>
<td>1.5</td>
</tr>
<tr>
<td>La\textsubscript{2/3}(CaPb)\textsubscript{1/3}MnO\textsubscript{3}\textsuperscript{58}</td>
<td>7.5</td>
<td>296</td>
<td>7.0</td>
</tr>
</tbody>
</table>
1.7.1 Manganese arsenide (MnAs)

MnAs exhibits a large MCE of 30 J kg\(^{-1}\) K\(^{-1}\) at 5 T and a \(T_c\) of 318 K. This exceeds the \(\Delta S_M\) of Gd\(_5\)Si\(_2\)Ge\(_2\) by a factor of 2. Bulk MnAs undergoes a first order magneto-structural phase transition at 318 K, transforming from a high-spin ferromagnetic hexagonal NiAs-type (\(\alpha\)-MnAs) to low-spin paramagnetic orthorhombic MnP-type phase (\(\beta\)-MnAs). Upon further increase of temperature, \(ca.\) 400 K, MnAs undergoes a second order phase transition from low spin paramagnetic to high spin paramagnetic, reverting back to hexagonal NiAs-type \(\alpha\)-MnAs (Fig. 1.15).

**Figure 1.15:** Magneto-structural phase transition of MnAs (Adapted from Billinge\(^{59}\))

However, bulk MnAs suffers from a large thermal hysteresis of \(ca.\) 7 K, and the transition occurs over a small temperature window, which reduces its desirability as a promising MR material.\(^{51}\) Nanostructuring is helpful to minimize the thermal hysteresis, while both cation and anion doping can fine-tune the transition temperature.
1.7.2 Manganese antimonide (MnSb)

MnSb adopts the hexagonal NiAs-type structure. At the $T_c$ of 572 K, MnSb undergoes a second order phase transition from ferromagnetic to paramagnetic. In the structure of MnSb, Mn occupies the regular octahedral sites, however, it is possible to reside additional Mn in trigonal bipyramidal sites. (Fig. 1.16).

![Mn occupancy sites of hexagonal bulk MnSb structure](image)

Because of this, Mn$_{1+\delta}$Sb adopts a broad homogeneity range: $0<\delta<0.3$. When $\delta$ deviates from 0, the structure adopts the Cu$_2$Sb-type structure. The magnetic properties of bulk MnSb is highly dependent on the $\delta$ value. For example, when $\delta=0$, MnSb acts as a ferromagnet, transitioning into ferrimagnetism when $\delta>0$. Moreover, $T_c$ is highly dependent on the $\delta$ value, dropping from ca. 600 K to ca. 300 K as $\delta$ increases from zero.

1.7.3. Manganese arsenide antimonide (MnAs$_x$Sb$_{1-x}$)

Introduction of Sb into the anion sub-lattice of MnAs forms a solid-solution over all $x$. According to these data, no structural transformation from the NiAs-type is observed for $x \leq 0.1$. Therefore, for the concentration range of $0.1 \geq x \geq 0$ the transition from the FM hexagonal phase to the PM orthorhombic phase is first-order, but upon increasing the Sb amount from $x=0$ to $x=0.1$, the transition temperature shifts from 315 K to 280 K. Further, it is also reported that for $x=0.1$ and $x=0.05$ no thermal hysteresis behavior is observed in a magnetic field of 1 T. In
contrast, for \( x > 0.1 \), the transition is second order and there is no structural change. Intriguingly, the \( x > 0.1 \) phases exhibit a high \( \Delta S_M \), hence a large MCE, despite the absence of FOPT, with \( T_c \) decreasing to \( ca \) 200 K at \( x = 0.3 \) where upon it begins to increase again up to 587 K.\(^{52}\) Nanostructuring of \( \text{MnSb}_x\text{As}_{1-x} \) is expected to lead to improved functionality for magnetic refrigeration. Reducing the size of the material down to the nano scale is expected to reduce the thermal hysteresis,\(^{62}\) whereas cation and anion substitution of \( \text{MnAs} \) nanoparticles is expected to tune the FOPT temperature, producing a range of materials with FOPT’s spanning the temperature of interest.\(^{51-52, 62-63}\)

### 1.8 Nanoparticles Assembly

Nanoparticle assembly has arisen as a trending-area of nanoscience. The assembled complex multi-particle systems have become technologically attractive due to their wide range of applications in the areas of biosensing\(^{64-65}\), energy storage devices\(^{66}\), drug delivery\(^{67-68}\), and optoelectronic devices.\(^{69-70}\) Some nanoparticles can self-assemble spontaneously, by releasing energy and maintaining an equilibrium between the individual nanoparticles and the assembled components. In addition, the self-assembly can be promoted by an external force (i.e. *externally directed self-assembly*) like magnetic field, electric field, and a flow field. Chemical modification(s) of nanoparticle surfaces is one of the common and reliable methods of nanoparticle assembly.

For functional MR based on nano magnets, we need a method to integrate the nanoparticles to form a macro-scale structure. Phase-pure, size-controlled nanoparticles can be assembled to build up porous three-dimensional (3-D) architectures such as aerogels and xerogels. These composites are expected to yield coupled magnetic properties when compared to the individual nanoparticles. In terms of MR, porous 3-D architectures encourage the
practical application of the material in a device by providing a high surface area of contact with the heat transfer fluid, possible mechanical stability during the refrigeration cycling and reduction of the magnetic hysteresis owing to the small size of the primary particles.

1.8.1 Sol-gel Assembly

Sol-gel assembly is based on nanoparticles undergoing a series of hydrolysis and condensation reactions to form a wet gel. When a wet-gel in a solvent dries under ambient conditions, dense and low porosity xerogels can be obtained. The existence of strong capillary forces between the gel and the solvent makes pores collapse resulting in low surface area. Drying a gel with supercritical CO₂ (supercritical drying) avoids the presence of a liquid-vapor interface; hence, preserving the original pore structure in the wet-gel. The formed aerogels are low density and have high surface areas. However, an additional solvent exchange step is required before the supercritical drying due to the immiscibility of liquid CO₂ with alcohols and water. Aerogels possess continuous micro (< 2 nm in diameter) to meso (2-50 nm in diameter) pore structures, and these pore-structures provide an easy pathway/channel for molecules to reach the nanostructure surface. Traditional sol-gel approaches are more ‘oxo’ centered, limiting the chemical constituents and the practical applicability of these materials. In contrast, usage of either sulfides, selenides, or telurides provide increased covalency, making them suitable for diverse applications.

The Brock group has pioneered the sol-gel assemblies of binary chalcogenide nanoparticle compositions of CdTe, CdSe, PbTe, PbS, Bi₂Te₃, ZnS and phosphides of InP, Ni₂P by surface oxidation, Ni₂P by metal assisted bridging based on solvated Ni²⁺ ions crosslinking carboxylation and CdS, CdSe, PbTe and PbS by covalent-metal (Sn⁴⁺) assisted crosslinking. In the case of oxidation-induced gelation, the nanoparticles are
first surface ligand exchanged with a thiolate followed by the addition of an oxidant (e.g., \( \text{H}_2\text{O}_2 \), tetranitromethane (TNM)). The proposed gelation mechanism for CdSe is shown in Fig. 1.17.

**Figure 1.17:** The proposed gelation mechanism for CdSe nanoparticles (adapted from Brock\(^\text{87}\) )

According to the gelation mechanism of CdSe nanoparticles, in the presence of an oxidizer the surface thiolates are oxidized and disengage from the nanoparticle forming disulphides or sulphonates and releasing \( \text{Cd}^{2+} \) into the solution. These decomplexed \( \text{Cd}^{2+} \) are solvated by methanol or a carboxylate species often appended to the surface thiolate. This leaves a \( \text{Se}^{2-} \) rich surface, which is then further oxidized by the excess oxidizing agent forming diselenide or poly-selenide bonds, bringing the particles together, making a gel network. This gel network can be easily disturbed by adding a reducing agent, for an example a thiol, to cleave \( \text{Se}-\text{Se} \) bonds to make individual nanocrystals again.\(^\text{87}\)

However, according to the mechanism reported for InP nanoparticles in lieu of dichalcogenide, phosphate/phosphite bonds (P-O-P) interconnect these nanoparticles. Similar to the CdSe gelation, the addition of an oxidant to thiolate capped phosphide particles exposes P\(^3-\)
by elimination of disulfide. However, instead of P-P bond formation the phosphide reacts with a reactive oxygen source, and a phosphate/phosphite layer forms followed by hydrolysis and condensation leading to formation of P-O-P bonds. Hence, InP gelation is only possible in the presence of an oxygen transferring oxidant such as H₂O₂. Gelation attempts carried out with a non-oxygen transferring oxidant (eg: TNM) under oxygen free environments were unsuccessful. In contrast to CdSe gels, InP gels can not be cleaved/dispersed by adding a reducing agent. Gelation of Ni₂P nanoparticles has also studied. In addition to the oxidizing agent (oxygen transferring or non- oxygen transferring), the gelation of Ni₂P depends on the nature of the thiolate, which has been used to cap the nanoparticle surface. When Ni₂P is ligand exchanged by 11-mercaptoundecanoic acid (11-MUA), Ni₂P can undergo gelation either with oxygen transferring (eg: H₂O₂) or non- oxygen transferring (eg: TNM) oxidant. However, when the Ni₂P nanoparticles are ligand exchanged by either 4-fluorothiophenol or 1-dodecanethiol, gels form exclusively in the presence of an oxygen transferring oxidant. These observations paved a way for proposing another possible mechanism for Ni₂P gelation based on ion crosslinking originally put forth by Eychmüller and co-workers. Fig. 1.18 explains two possible mechanisms of Ni₂P gelation.

According to Fig. 1.18 path 1, Ni₂P gelation is similar to the InP gelation that occurs through P-O-P bond formation, and is independent of the nature of the thiolate. However, when the nanoparticles are capped with a surface ligand having a pendent binding group (eg: 11-MUA), metal ions in the solution (eg: Ni²⁺) can bring the nanoparticles together, making gels by binding through the functional group(s) (either S⁻ or COO⁻ functionalities in MUA). Therefore, Fig. 1.18 path 2 is known as metal-assisted gelation. In the cases of 1-dodecanethiol and 4-
fluorothiophenol the carboxylate functionality is replaced by alkyl and fluoro functionalities, respectively, and the metal assisted gelation is not supported by these ligands.

**Figure 1.18:** Possible mechanisms for Ni$_2$P gelation (adapted from Brock$^{85}$)

1.9 Thesis Statement

Magnetic Refrigerators (MR) have received increased scientific and public attention during the past two decades in terms of energy efficiency and the environmental friendliness, as an alternative to the conventional vapor compression refrigerators. Magnetic materials with large Magneto-Caloric Effect (MCE), lower hysteresis, and broader working temperature are recognized as prospective magnetic refrigerant materials.

Transition metal based MR materials have distinct advantages over the traditional MR materials of gadolinium and its associated compounds. Transition metal based MR materials exhibit high MCE, low cost, and high abundance. Bulk MnAs has been recognized as a potential MR material with large MCE associated with its First Order Phase Transition (FOPT). Unfortunately, the magnetic transition of MnAs suffers from a large thermal hysteresis of 6 K$^{51}$
precluding efficient MR cycling, and the magnetic entropy change associated with the FOPT is limited to a narrow temperature range, making the temperature control window very small. Solid solutions of MnAs, synthesized by both cation and anion doping, are reported to reduce the hysteresis, enabling tuning of the optimal temperature range.\textsuperscript{13, 52} Reducing the materials’ dimensions to the nano scale has the potential to enable formation of nano 3-D graded macrostructures thereby greatly expanding the temperature window. Moreover, 3-D assembly of nanoparticles into macro-structures provides advantages over the heat transfer through high surface area,\textsuperscript{71} possible mechanical stability during the refrigeration cycling,\textsuperscript{72} and reduction of the magnetic hysteresis owing to the small size of the primary particles.\textsuperscript{73}

This dissertation research was focused on two major goals. The first goal was to develop a synthetic protocol to solid-solution MnAs\textsubscript{x}Sb\textsubscript{1-x} nanoparticles over all x, with low polydispersity and phase-purity, via a solution phase methodology. At the outset, understanding the corresponding binary phases, \textit{i.e.} MnAs nanoparticles and MnSb nanoparticles, is important before stepping into the ternary phase synthesis. The Brock group has expertise in MnAs nanoparticle syntheses,\textsuperscript{90-92} however, to the best of our knowledge, there have been no reports of the synthesis of MnSb nanoparticles with controlled phase, size, and morphology. Therefore, in order to achieve the first goal, a solution phase synthetic methodology was developed to MnSb nanoparticles and the magnetic properties were evaluated. The synthetic procedure enabled synthesis of phase pure, low polydispersity MnSb nanoparticles, and the synthetic levers leading to successful MnSb nanoparticles synthesis were identified. However, the synthesized MnSb nanoparticles possess low saturation magnetization (CHAPTER 3). The synthesis of MnSb nanoparticles was further modified by adding a mild oxidizing agent NaBH\textsubscript{4}, to achieve enhanced saturation magnetization. This resulted in a significant change in the reaction
mechanism and MnSb nanoparticle morphology with an enhanced saturation magnetization (CHAPTER 4). Then the solution-phase methodology employed in CHAPTER 3 and 4 were further developed to synthesize a solid-solution of MnAs\textsubscript{x}Sb\textsubscript{1-x} nanoparticles of over all x, targeting x=0.1 to 0.9. The magnetic properties of representative sample of MnAs\textsubscript{0.5}Sb\textsubscript{0.5} nanoparticles are discussed as a context of elemental distribution (CHAPTER 5).

The second dissertation goal was to assemble discrete nanoparticles into three-dimensional architectures by oxidative sol-gel assembly, and evaluate the magnetic properties of these assemblies. At the outset, nanoparticle compositions of Fe\textsubscript{1.2}Ni\textsubscript{0.8}P and CoFeP were selected since the systems of Fe\textsubscript{2-x}Ni\textsubscript{x}P (0≤x≤2) and Co\textsubscript{2-y}Fe\textsubscript{y}P (0≤y≤2) nanoparticles are well-established. CHAPTER 6 and APPENDIX B describe and discuss the oxidative sol-gel assembly of these nanoparticle compositions and consequences of nanoparticle assembly towards the magnetic properties.
CHAPTER 2 – EXPERIMENTAL AND MATERIALS CHARACTERIZATION TECHNIQUES

This chapter discusses the materials, synthetic procedures, nanoparticle assembly methods, working principles and the concepts of the instruments employed in this dissertation research. Binary and ternary transition metal phosphide nanoparticles (MnSb, MnAs\textsubscript{x}Sb\textsubscript{1-x}, Fe\textsubscript{2-y}Ni\textsubscript{y}P, Co\textsubscript{2-z}Fe\textsubscript{z}P) were synthesized by the slow heating method and the rapid precursor injection method under an inert gas (argon) atmosphere. The synthesized compounds were characterized using Powder X-Ray Diffraction (PXRD), Transmission Electron Microscopy (TEM), Energy Dispersive Spectroscopy (EDS), Inductively Coupled Plasma-Mass spectrometry (ICP-MS), X-Ray Fluorescence Spectroscopy (XRF), Thermo Gravimetric Analysis (TGA), Nitrogen physisorption, and magnetometry.

2.1 Materials

2.2.1 Metal Precursors

Manganese(0) carbonyl \([\text{Mn}_2(\text{CO})_{10}]\) (98%), triphenyl antimony(III) \((\text{Ph}_3\text{Sb})\) (99%), triphenyl arsine oxide \([\text{Ph}_3\text{As}=\text{O}]\) (97%), iron carbonyl \([\text{Fe}(\text{CO})_5]\) (99%), cobalt octacarbonyl \([\text{Co}_2(\text{CO})_8]\) (>90%) were purchased from Sigma-Aldrich. Nickel acetylacetonate \((\text{Ni}(\text{acac})_2\) (95%)), was purchased from Alfa-Aeser.

2.2.2 Solvents

1-octadecene (1-ODE) (90%, technical grade), hydrogen peroxide \((\text{H}_2\text{O}_2)\) (30%\((\text{v/v})(\text{aq})\)), trioctylphosphine oxide (TOPO) (90%, technical grade), 11-mercaptoundecanoic acid (11-MUA) (95%), 1-dodecanethiol (1-DDT) (≥98%), acetone (99.5%) were purchased from Sigma-Aldrich. Tri-n-octylphosphine (TOP) was purchased from STREM. N-octyl ether (97%) and oleylamine (C18, 80-90%) were purchased from Acros America. Tetramethylammoniumhydroxide pentahydrate (TMAH) (99%), and octylether (90%) were purchased from TCI America. Ethyl
acetate (99.9%), hexane (technical grade) and chloroform (99.9%) were purchased from Fisher. Ethanol (200 proof) was purchased from Decon laboratories. TOPO was purified by the fractional distillation method. All other chemicals were used as received.

2.2 Experimental Techniques

2.2.1 Glove Box

A glove box provides an air and moisture free environment to handle and store air and moisture sensitive compounds, radioactive elements, and hazardous chemicals. A typical laboratory glove box is composed of three main components; (1) main chamber, (2) antechamber, (3) gloves. The main chamber is always maintained at a positive pressure to avoid air leakages from outside. The main chamber is the working area of a glove box. All the chemical reactions, handling, and storage are done in the main chamber. A photohelic pressure gauge controls the pressure inside the main-chamber. The antechamber is attached to the main-chamber, and equipped with vacuum and inert gas purge valves. All materials that transfer in and out to the main chamber should go through the antechamber to avoid any possible contamination by air. Gloves are attached to the main chamber and are used for handling the chemicals inside the glove box.

An inert atmosphere is maintained inside a glove box by a continuous passage of argon gas. This gas is pumped through a series of treatment-devices to remove water and air (oxygen) from the gas. Heated Cu metal is a widely employed catalyst that removes oxygen from the circulating gas, while molecular sieves adsorb water in the gas. In the presence of oxygen, the catalyst turns into CuO, which can be regenerated to remove oxygen by passing a mixture of hydrogen and nitrogen at high temperature. The catalyst regenerates back to Cu metal, forming water as a by-product. This water is adsorbed by molecular sieves and removed from the system.
by heat and evacuation. This dissertation study used a Vacuum Atmosphere VAC-HE 493 glove box model for handling and mixing air and water sensitive chemicals.

### 2.2.2 Schlenk line

A Schlenk line is an alternative and complementary technique to the glove box for performing air sensitive reactions under inert conditions. A Schlenk line is composed of two manifolds, one for gas and the other for vacuum. The manifold that is connected to the inert gas supply (N\textsubscript{2}, Ar…ect) is used to provide an inert atmosphere for the experiments. The manifold that connects to the vacuum used to remove air from the system is associated with a cold trap. The cold trap is usually filled with liquid N\textsubscript{2} before a reaction, and this is necessary to prevent the solvent vapors and reaction by-products entering the vacuum pump. The Schlenk line also contains several ports to attach the Schlenk flask via rubber tubing. A set of bubblers is attached to the Schlenk line to avoid back-flow of air. These bubblers are also important for releasing additional pressure inside the Schlenk flask.

The nanoparticle syntheses associated with this dissertation study were carried out on a Schlenk line under inert (Ar) atmosphere. Reaction precursors were mixed in a Schlenk flask in the glove box, sealed and brought to Schlenk line. The flask was attached to the Schlenk line through a rubber tubing, and the content of the Schlenk flask was subjected to vacuum followed by Ar purging to degas the mixture. The Schlenk flask was then heated using a heating mantle. The temperature of the heating mantle is controlled by a programmable temperature controller with either an internal probe (thermocouple placed directly in the solution) or an external probe (thermocouple placed in between the Schlenk flask and the heating mantle underneath the solution).
2.3 Synthetic Methods

2.3.1 Synthesis of Binary and Ternary Transition Metal Pnictides Nanoparticles, Ligand Exchange and Assembly

Detailed descriptions of the synthesis of MnSb and MnAs$_x$Sb$_{1-x}$ nanoparticles are given in CHAPTER 3-5. CHAPTER 6 describes the ligand exchange and sol-gel assembly of the ternary phases of transition metal phosphide nanoparticles (Fe$_{1.2}$Ni$_{0.8}$P), under normal atmospheric conditions. The resultant wet gels were then supercritically dried to produce aerogels.

2.3.2 Supercritical Drying of Wet Gels

The removal of liquid from a wet gel takes place in several steps.

1. The pores shrink by an equivalent volume to that occupied by the solvent. Then the solvent starts to flow from the gel to the surface.

2. The flow volume is even further decreased as the drying proceeds, increasing the rigidity of the gels. In turn, this can increase the surface tension of the gel network leading to cracking the gels.

3. The collapse of the gel network takes place upon further drying of the gel. Under these conditions, ambient-drying results in about 90% gel volume loss. However, supercritical drying avoids the gel collapse since there is no liquid/gas interface in a supercritical state.

The phase diagram of CO$_2$ is shown in Fig. 2.1. CO$_2$ is ideal for supercritical-drying due to its lower critical temperature (31.1 °C). The wet gel is first solvent exchanged thoroughly 3-4 times over 3 days using acetone (3-5 mL aliquots), without disturbing the gel network. This additional solvent exchange step is necessary due to the immiscibility of the solvents that are used in the wet gel formation with CO$_2$. The solvent-exchanged step is further helpful in removal
of by-products in the gel solution. Then the vial is placed in a chamber filled with a drying solvent (eg: ethanol), and the chamber is maintained at 19 °C.

![Phase diagram of CO₂](image)

**Fig 2.1:** Phase diagram of CO₂ (adapted from Pajonk)⁹⁴

The solvent exchange of the drying solvent for CO₂ is carried out several times within the total of four hours. Once all the drying solvent is replaced by liquid CO₂, 2/3 of the chamber is filled with liquid CO₂, and the temperature of the chamber is increased to 39 °C. Upon this temperature rise, the pressure inside the chamber increases to 89-103 atm, enabling the acquisition of supercritical state. The gel is maintained under these conditions for about 1 h and pressure is released slowly (over ca. 30 min time) to dry the gel.

The gels produced in this dissertation were dried supercritically using a SPI-DRY model CO₂ critical point drier equipped with an ISOTEMP 10065 recirculating temperature bath.

### 2.4 Characterization Techniques

#### 2.4.1. Powder X-Ray Diffraction (PXRD)

Powder X-Ray Diffraction patterns serve as a ‘finger prints’ for identifying crystalline materials. The phase purity of the material, type of the unit cell, and unit cell parameters are the main types of information that can be obtained from a basic PXRD pattern. The X-rays are
produced in an X-ray tube, composed of three main parts; (1) a cathode, (2) an anode, and (3) an evacuated chamber, as shown in Fig. 2.2. The chamber windows are made out of Be, which help X-rays to leave the tube.

**Figure 2.2:** Schematic diagram of a filament X-ray tube (adapted from West)

A W filament serves as the cathode. When it is heated by a voltage supply, electrons are produced and those electrons are accelerated towards the anode, a piece of fixed Cu metal in the present case, by a potential difference of *ca.* 30 kV. When the electrons strike the target, a spectrum of X-rays is emitted. In general, the resultant X-ray spectrum has two components; (1) white radiation, (2) monochromatic X-rays. Some of the accelerated electrons from the cathode to the anode slow down on their way or are stopped by collisions, losing their energy in the form of white radiation. The monochromatic X-rays are used in diffraction experiments are produced as shown in Fig. 2.3. When the high energy electrons hit the Cu cathode, the incident electrons have adequate energy to ionize some 1s (K shell) electrons, leaving a vacancy. Then, an electron at a higher energy level (2p or 3p) immediately drops down to fill this vacancy. Upon this descent, the excess energy is released in the form of X-ray. When this electron transition takes place 2p→1s, $K\alpha$ X-rays are produced, having a corresponding wavelength of 1.5418 Å. This transition is the most frequent and it is much more intense than the other transitions. In fact, in an unrefined diffraction pattern at low angle, $K\alpha$ appears as a doublet, $K\alpha_1$ (1.54051 Å) and $K\alpha_2$
(1.54433 Å) owing to the electron transition arising from two different possible spin states of $2p$ electrons ($J=1/2, 3/2$). The electron transition from $3p\rightarrow1s$ produces $K_\beta$ radiation having the wavelength of 1.3922 Å.

Figure 2.3: Illustration of generation of $K_\alpha$ X-rays. When a $1s$ electron is ionized a higher energy $2p$ electron falls into the empty level (shown as □) releasing the excess energy as X-rays.

Bragg’s law explains the principles of X-ray diffraction. Bragg’s law assumes that the crystals are made out of semi-transparent layers of atoms, so that some of the incident X-rays can reflect off at an angle equal to the incident angle, while the others can transmit to succeeding planes to be reflected subsequently. The derivation of Bragg’s law is shown in Fig. 2.4.

Figure 2.4: Derivation of Bragg’s law
In Fig. 2.4, the X-ray radiations 1 and 2 are incident and reflect as 1’ and 2’, respectively, by crystal planes, A and B. The incident angle is $\Theta$ for both 1 and 2, and both beams reflect by the same angle. The incident angle is called as Bragg angle. The planes A and B are separated by a distance $d$, called the $d$-spacing. In order to create constructive interference, beam 1’ and 2’ should be in phase, therefore, beam 2-2’ travels an additional distance (path difference) of $xyz$, and must be an integer. The relationship between the Bragg angle, path difference and the incident angle are given by **Equation 2.1**.

$$xy = yz = d \sin \Theta \quad (2.1)$$

Therefore,

$$xyz = 2d \sin \Theta \quad (2.2)$$

However,

$$xyz = n\lambda \quad (2.3)$$

Where $n$ is an integer and $\lambda$ is the wavelength of the incident X-ray beam.

Therefore, Bragg’s equation can be written as

$$2d \sin \Theta = n\lambda \quad (2.4)$$

Upon satisfying Bragg’s law X-ray beams constructively interfere to result in a PXRD pattern. The intensity of the PXRD pattern corresponds to the specific arrangement of the atoms in space and their relative electron density. The peak positions are determined by the size and the shape of the unit cell.

The PXRD patterns of nanoparticles are broader compared to bulk crystalline materials due to a fewer number of planes. Therefore, the beams undergo partial interferences around the ideal Bragg angle making the peaks broader. Since a bulk material has more planes, complete cancellation of the beams that do not follow the Bragg’s law takes place. The size of the nanocrystal can be calculated by measuring the Full Width at Half Maximum (FWHM) of the peaks, and substituted it to the Scherrer equation\textsuperscript{96} given in **equation**.
2.5,

\[ D = \frac{0.9 \lambda}{\beta \cos \theta} \]  \hspace{1cm} (2.5)

Where \( D \) is the average size of the nanocrystal, \( \lambda \) is the wavelength of X-ray radiation, \( \beta \) is the FWHM in radians and \( \Theta \) is the Bragg angle.

In this dissertation study, room temperature PXRD patterns were acquired in the range of \( 2\Theta = 20^\circ - 70^\circ \) on a Bruker Phaser II model X-ray diffractometer equipped with a Cu anode. The X-rays are generated at the voltage of 40 kV and 150 mA current. Samples were placed on a zero background quartz holder for measurements. The acquired PXRD patterns are identified by comparing them with the phases in the International Center for Diffraction Data (ICDD) Powder Diffraction File (PDF) database.

### 2.4.2 Transmission Electron Microscopy (TEM)

Transmission Electron Microscopy provides details on nanoparticle shape, size and the structure (core-shell structure, amorphous vs crystalline nature). Most importantly TEM provides higher resolution imaging compared to the optical spectroscopy enabling nanoparticles to be imaged. The resolution is defined as the distance between two resolvable points (\( \delta \)), in which the smaller \( \delta \) leads to higher resolution. The relationship between the \( \delta \) and the wavelength (\( \lambda \)) of electromagnetic radiation is given in Equation 2.6, where \( \mu \) is the refractive index of the viewing medium and the semi-angle of the collection of the magnifying lenses is \( \beta \).

\[ \delta = \frac{0.61 \lambda}{\mu \sin \beta} \]  \hspace{1cm} (2.6)

On the other hand, the wavelength of electromagnetic radiation can be manipulated by changing the accelerating voltage as shown in Equation 2.7. According to this, the wavelength of
electromagnetic radiation ($\lambda$) depends on the kinetic energy (eV), the mass of the electron ($m_0$), and Plank’s constant ($h$).\(^{97}\)

$$\lambda = \frac{h}{(2m_0eV)^{1/2}}$$ \hspace{1cm} (2.7)

When a high voltage is applied, the electron gun (electron source) emits electrons. There are two types of electron guns; (1) thermoionic sources (LaB\(_6\) or W filament), (2) field emitter (fine W needle). The emitted electrons are then accelerated through a high voltage, usually 100-400 kV, in a vacuum. Electron acceleration in a vacuum avoids electron scattering. The electron beam is guided towards the specimen by three sets of lenses, (1) condenser lenses- control the size and the angular spread of the incident electron beam, (2) objective lenses- focuses the electron beam passing through the specimen, (3) intermediate and projector lenses- expand the beam onto the screen for viewing. \textbf{Fig. 2.5} represents a schematic diagram of a typical TEM.

\textbf{Figure 2.5}: Schematic diagram of a typical TEM (adapted from Goodhew)\(^{98}\)
A TEM can work under two modes: the bright field mode, and the dark field mode. In the bright field mode the objective aperture blocks the diffracted beam, and only the undiffracted/direct beam traverse. Therefore, the image of nanoparticles appears dark in a bright background (Fig. 2.6 (a)). In contrast, in the dark field mode, the diffracted beam is selected. Therefore, the nanoparticles appear in bright in a dark background (Fig. 2.6 (b)).

![Ray diagram of TEM modes](image)

**Figure 2.6:** Ray diagram of (a) bright-field mode (b) dark-field mode of TEM

Even though the conventional TEM has been identified as a powerful tool in characterizing materials at the nanoscale, it possesses some limitations in detecting extremely fine features of materials. However, recent advances in electron microscopy provide some novel analytical techniques with high sensitivity. High-Angle Annular Dark Field-Scanning Transmission Electron Microscopy (HAADF-STEM) is one such technique that is effective for nanomaterial characterization. In contrast to the conventional TEM, imaging in HAADF-STEM is based on incoherent scattering, and the *thermal diffuse scattering* (TDS) is the signal used to generate the image in the *high angle annular dark field* (HAADF) detector. In principle, each
atom in the specimen thermally vibrates at a frequency of $10^{12}$-10$^{13}$ Hz. The atomic vibrations are quantized as photons. However, in an electron microscope, electrons pass in a beam at a speed of 1.5x10$^{10}$ cm/s. Therefore, the time required to pass through a specimen with electron-transparent thickness (<300 nm) is $ca.7 \times 10^{-17}$ s. This passage time is much shorter than the oscillation time of the atoms. Nevertheless, the time between consecutive electrons in an incident electron beam is longer than the atomic oscillations, which causes electrons to scatter randomly. Considering all configurations of the atom, the average of the scattered intensity is off-directional or incoherent.$^{99}$ A schematic diagram of HAADF-STEM is shown in Fig. 2.7. The image contrast of HAADF-STEM is highly correlated to the specimen thickness and most importantly, the atomic number (Z-contrast images).$^{99}$ Therefore, the elements with a higher Z cause more electrons to scatter at higher angles because of the stronger electrostatic interactions between the nucleus and the electron beam. This produces a greater signal, hence the areas with higher Z appear brighter in the image.

![Figure 2.7: Schematic diagram of HAADF-STEM (adapted from Ewing)](image)

In this dissertation work a JEOL 2010 HR TEM located at Lumigen Instrument Center at Wayne State University was used at an accelerating voltage of 200 kV and the beam current 106-109 $\mu$A used to study the morphology of nanoparticles and aerogels. The electron source is LaB$_6$. 
The HAADF imaging elemental composition of individual nanoparticles determined by Energy Dispersive Spectroscopy (see section 2.4.3) was analyzed using an FEI Titan 80-300 HAADF-STEM with ChemiSTEM technology at 200 kV located at the Analytical Instrument Center at North Carolina State University. The nanoparticle and aerogel samples were prepared by dispersing the solid sample with sonication in chloroform and supporting the particles on a 200 mesh Cu grid coated with a carbon film.

**2.4.3 Energy Dispersive Spectroscopy (EDS)**

Energy Dispersive Spectroscopy is a qualitative and quantitative analytical technique that can be used to determine the chemical makeup of a compound or a material. EDS is usually associated with either a transmission electron microscope or a scanning electron microscope. When a primary electron beam impinges on a specimen, atoms can be ionized generating holes, followed by ionization of electrons from outer shells to fill the holes by releasing characteristic X-rays. These characteristic X-rays are named relative to the shell, in which the initial vacancy occurred, and the shell, in which the electron drops to fill the vacancy. Fig. 2.8 shows some common electron transitions associate with peaks in EDS.

![Figure 2.8: Common electron transitions associate with peaks in EDS](image)
EDS detectors are based on a semiconductor device such as lithium doped silicon or high purity germanium. When X-rays strike the detector it generates a charge pulse, which is proportional to the X-ray energy. Then this charge pulse is converted to a voltage by a pulse processor. The EDS spectrum is a plot of x-ray counts (intensity) vs energy in electron volt (eV). Elements are identified relative to the energy value where a peak appears.

In this dissertation study, an EDAX, Inc., detection unit associate with JEOL 2010 TEM was used to determine the elemental compositions of the nanoparticles and the aerogels. The atomic weight percentages were determined using EDAX Genesis software.

2.4.4 Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)

Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) is an analytical technique used for elemental analysis. Compared to the elemental analysis of EDS as described in section 2.4.3, ICP-MS provides high precision and selectivity. ICP-MS is capable of analyzing multiple elements simultaneously, and its lower detection limit for most of the elements is below parts per billion (ppb) level.

At typical ICP-MS instrument is composed of two parts, (1) the inductively coupled plasma (ICP) source, (2) the mass spectrometer. The ICP torch consists of concentric channels that facilitate the passage of argon (Ar) gas. The concentric tube tip is wrapped by an RF load coil, which is connected to a Radio-Frequency (RF) generator. When power is supplied to the RF coil, oscillating magnetic and electric fields are established at the end of the torch. Upon the application of a spark, the electrons are stripped off the Ar atoms forming Ar⁺. These ions collide with other Ar atoms due to the oscillating magnetic and electric fields, and form plasma. The plasma is at extremely high temperatures of ca. 6000-10,000 K.
The samples are usually introduced to ICP as an aerosol. Solid samples require complete digestion in a concentrated acid (usually in conc. HNO₃), and both liquid and digested solid samples require dilution, preferably down to ppb levels before the introduction. The elements in the aerosol are then converted into gaseous atoms and then ionized at the end of the plasma.

Interface cones unite ICP with MS. The sampler cone and skimmer cone transmit the ions into a low pressure (< 1x10⁻⁵ torr) region. Both sampler cone and skimmer cone are metal disks having a ca. 1 mm size hole in the center. These cones direct the ion beam towards the MS unit, and the small hole controls the total dissolved solids that enter into the MS region for the best instrumental performance and the stability. The ion beam is then focused by electrostatic lenses. The electrostatic lenses are positively charged, therefore, the lenses serve to collimate the ion beam (positively charged), and direct the ion beam towards the entrance of the MS.

The ions entering into the MS are separated by mass-to-charge ratio (m/e). A typical MS consists of a quadrupole mass filter. Alternating AC and DC voltages are provided to the opposite pairs of the rods. Upon the rapid switching of these voltages with an RF field, an electrostatic filter is established allowing only the passage of ions of a single m/e to the detector at a given time. Therefore, the quadrupole mass filter acts as a sequential filter. **Fig. 2.9** shows a schematic representation of a typical ICP-MS.
Elemental analysis by ICP-MS is mostly limited to the elements that prefer to form positive ions. Elements that prefer negative ion formation (e.g., F⁻, Cl⁻, I⁻… etc) are hard to detect by ICP-MS. The detection capabilities also depend on the sample matrix that affects the degree of ionization. Overlapping molecular singles can interfere the elemental composition determination. Some common interference includes, $^{75}$As with $^{40}$Ar$^{35}$Cl, $^{52}$Cr with $^{37}$Cl$^{16}$O, $^{87}$Sr with $^{87}$Rb… etc.

In this dissertation study, Agilent 7700x series ICP-MS instrument was used to determine the elemental composition of the nanoparticles. The solid nanoparticle powders (~1 mg, weighed on an analytical balance) were completely dissolved in concentrated nitric acid (2 mL) and then diluted to 100 mL in a volumetric flask with 2% nitric acid (HNO₃) (v/v). This was further diluted by taking a 0.10 mL aliquot and diluting to 100 mL using 2% HNO₃. 2% HNO₃ served as the blank solution. In order to calibrate the instrument, standard solutions (300, 500, 700, 1200, 1500, 1800, 2500 ppb) were prepared by a serial dilution of stock solutions.
2.4.5 X-ray Fluorescence Spectroscopy (XRF)

X-ray Fluorescence Spectroscopy (XRF) is a non-destructive method to determine the elemental composition of solids, liquids, thin films, bulk materials… etc. The detection range of XRF varies from ppm levels to 100% purity of a single material. The working principle for XRF is similar to the principle of EDS as described in section 2.4.3. However, the main difference between EDS and XRF is that the EDS uses a primary electron beam to eject an electron while XRF uses an X-Ray beam to eject electrons from the atom. The resultant X-rays have a specific energy depending on the element and the energy levels involved in fluorescence. Therefore, the elements can be identified by measuring the corresponding wavelength. Fig. 2.10 depicts the schematic diagram of XRF.

Figure 2.10: Instrumentation set up for XRF.

In this dissertation, the elemental composition (Mn, Sb and As) was analyzed by a SHIMADZU EDX-7000 energy dispersive X-Ray Fluorescence Spectrometer (XRF), with PCEDX-Navi software, operating under normal atmosphere (air) with the collimator size 10 mm. Solid samples were placed in the middle of a Mylar® cup, which was then placed on the beam window located on the sample plate. The X-ray generator was Rhodium target operated at 50 kV (Rh 50) under 26 μA current, and the detector was a silicon drift detector.
2.4.6 Thermogravimetric Analysis (TGA)

Thermogravimetric Analysis (TGA) provides information relative to the temperature-induced physical and chemical processes. These include, oxidation, decomposition, sublimation and vaporization. The sample can be treated under different conditions such as inert conditions (under Ar or N\textsubscript{2} gas), reducing conditions (under H\textsubscript{2} gas) with a programmed temperature profile, and then the change in sample mass as a function of temperature is measured. Sample weight loss or gain can be observed due to a variety of processes such as vaporization of water, the pyrolysis of organic ligands, or oxidation of solids.

In this dissertation study, a Perkin-Elmer Pyris 1 TGA was used to determine the temperature of ligand decomposition of aerogels. The aerogel was heat treated under 5\% H\textsubscript{2} from 25 to 500 °C in a ceramic crucible with a temperature ramp is 10°C/min. The purpose of the reducing atmosphere was to prevent nanoparticle oxidation during ligand pyrolysis.

2.4.7 Nitrogen Physisorption: BET Surface Area and Porosity Measurements

BET surface area analysis provides information about the specific surface area of materials. The Brunauer- Emmet- Teller (BET) theory was named after three scientists Steohen Brunauer, P.H. Emmet and Edward Teller in 1938. BET theory is based on adsorption and desorption of gas molecules onto a solid surface. This adsorption/ desorption can be either a chemisorption via chemical bond formation or a physisorption process via van der Waal forces. The adsorption/ desorption of a gas by a solid can be considered in several ways. The most commonly used chemisorption theory is the Langmuir theory while the BET theory is used to explain physisorption. Langmuir theory is based on several assumptions. It requires the gas molecules adsorption onto solids to be as a monolayer, and considers the collisions between gas
molecules and the solids to be inelastic. According to the Langmuir theory, the amount of gas adsorbed \((V_a)\) at pressure \((P)\) is given by **Equation 2.8**.

\[
V_a = \frac{V_m b P}{1 + b P} \tag{2.8}
\]

Where \(V_m\) is the amount of gas adsorbed to form a monolayer and \(b\) is a constant. Experimentally, \(V_m\) and \(b\) values can be calculated using a graphical method by re-arranging the **Equation 2.8** as **Equation 2.9**.

\[
\frac{P}{V_a} = \frac{1}{V_m b} + \frac{P}{V_m} \tag{2.9}
\]

Moreover, the specific surface area can be calculated by **Equation 2.10**, where \(\sigma\) is the area of the surface occupied by a gas molecule (for \(N_2\) gas this value is \(16.2 \times 10^{-20}\) m\(^2\)), \(N_A\) is the Avogadro constant (6.02214086 x \(10^{23}\) mol\(^{-1}\)), \(V_0\) is the molar volume of the gas (for \(N_2\) gas this is 22,414 cm\(^3\)), and \(m\) is the mass of the sample.

\[
S = \frac{V_m \sigma N_A}{m V_0} \tag{2.10}
\]

By substituting the above values **Equation 2.10** can be re-written as, **Equation 2.11**

\[
S = \frac{4.35 V_m}{m} \tag{2.11}
\]

BET theory is a modification of Langmuir theory achieved by incorporating the multilayer adsorption concept, and can be given by **Equation 2.12**.

\[
V_a = \frac{V_m c P}{(P_0 - P)[1 + (c-1)\frac{P}{P_0}]} \tag{2.12}
\]

In **Equation 2.12**, \(Ec\) is a constant and \(P_0\) is the saturation pressure of the gas. By re-arranging **Equation 2.12**, a plot of \(P/[V_a(P_0-P)]\) vs \((P/P_0)\) results a straight line, in which \(V_m\) is given by the intercept.
Pore size distribution can also be measured using Nitrogen physisorption using the BJH method. BJH method is based on the Kelvin equation, in which pores are considered as cylinders, and the pore-filling and pore-emptying take place in a gradual, step-wise order (Equation 2.13).

\[
\ln \frac{P^*}{P_0} = \left(\frac{2\gamma V \cos \theta}{RT r_m}\right) \tag{2.13}
\]

Where, \(P_0\) is the saturation pressure, \(P^*\) is the critical condensation pressure, \(\gamma\) is liquid surface tension, \(V\) is the molar volume of condensed absorptive, \(\theta\) is the contact angle between the solid and the condensed phase, \(T\) is the absolute gas constant, \(R\) is the ideal gas constant, and \(r_m\) is the mean radius of the curvature of the liquid meniscus.

There are six basic types of adsorption isotherms depending on the material (Fig 2.11).

**Figure 2.11:** Six basic types of adsorption isotherms (adapted from Zhang)\(^{100}\)
The Type I adsorption graph depicts monolayer adsorption, and can be easily explained by the Langmuir Adsorption isotherm. The type II isotherm shows a large deviation from the Langmuir model of adsorption. However, the intermediate flat region corresponds to monolayer formation. The type III isotherm also shows a large deviation from the Langmuir model of adsorption. This type of isotherm relates to multilayer formation. The type IV and Type V isotherms are common types of isotherms of mesoporous materials (pore size distribution is 2-50 nm), such as aerogels. The adsorption on mesoporous materials takes place through multilayer adsorption, and then by capillary condensation, which leads to the characteristic hysteresis loop. The type VI isotherm is an indicative of nonporous material.

In this dissertation study, a Micromeritics TriStarII 3020 surface area analyzer was used for the analysis of surface area and pore-size distribution of the aerogels. Prior to the measurements the aerogel samples were degassed for 14 h at 120 °C to remove any moisture trapped inside the pores.

2.4.8 Superconducting Quantum Interference Device (SQuID)

A Superconducting Quantum Interference Device is a sensitive and effective magnetometer used to measure a variety of magnetic properties. SQuID is sensitive to measuring magnetic fields as low as 5 aT (5 x 10^{-18} T).

SQuID consists of two superconductors separated by thin insulating layers to form two parallel Josephson Junctions. A weak superconductivity results at the Josephson Junctions compared to the rest of the superconductor loop. Therefore, the current flowing through the Josephson Junction is much lower than the current in the superconductor loop, resulting in a phase variation. The phase difference in the loop creates an alternating current in the application of a continuous voltage. The resulted alternating current is highly sensitive towards the magnetic
flux, allowing to obtain magnetic measurements with high precision. **Fig. 2.12** dictates a schematic diagram of the superconducting coil.

**Figure 2.12:** Schematic diagram of superconducting coil in SQuID.

The input coils and the SQuID are located inside a Nb shield. SQuID is operated under cryogenic environment, created by liquid He at 4.2 K. However, SQuID electronics are located at room temperature. The produced voltage variation in the conducting loop is analogous to the magnetic moment of the sample.

In this dissertation study, Magnetic measurements (Magnetization vs Applied magnetic field) were acquired by magnetometer (MPMS-5S) located in the department of physics and astronomy, Wayne State University, at 50 K and 300 K, sweeping fields from +10,000 Oe to -10,000 Oe. A PPMS 6000 system was used to record the temperature dependent DC magnetization data, Zero-Field Cooling (ZFC) and Field Cooling (FC), under 100 Oe DC field, between 10 K and 320 K. Solid nanoparticle powders and aerogel samples were stored in a silica gel capsule under inert conditions up until the time of measurement in order to avoid oxidation.
All the magnetic measurements were taken by Dr. Ehab Abdelhamid from the department of physics and astronomy, Wayne State University.
CHAPTER 3 - SYNTHESIS OF COLLOIDAL MNSB NANOPARTICLES: CONSEQUENCES OF SIZE AND SURFACE CHARACTERISTICS ON MAGNETIC PROPERTIES


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3.1 Introduction

Binary and ternary intermetallic compounds formed by combination of 3d transition metals and pnictogens X (X=P, As, Sb or Bi) are of special interest due to their various electronic and magnetic properties. Among transition metal pnictides, manganese arsenide (MnAs), manganese antimonide (MnSb), and their ternary phases have long been studied in the bulk phase due to strong coupling between the ferromagnetic properties and caloric, optical (Kerr effect) and/or structural changes, achievable at or near room temperature. Hence, these phases are of interest as magnetic refrigerant materials, data storage/processing devices, and magneto-optic readouts. The wealth of fundamentally interesting properties combined with potential applications has motivated the study of these materials on the nanoscale. However, the majority of published studies are on thin films and dots synthesized epitaxially on semiconductor supports and, to our knowledge, there are no reports of colloidal MnSb as narrow polydispersity samples that would enable the intrinsic size-property relationships to be established.

Reports of MnSb nanomaterials are limited to their growth on substrates. Formation of MnSb nanodisks on a Si (111) layer coated with a thin silicon nitride buffer layer by molecular beam epitaxy has been reported. The MnSb nanoparticles had average lateral diameters (<d>) from 5 to 30 nm with heights of 3.5-7.5 nm. It was found that these MnSb nanoparticles with <d> <9 nm are superparamagnetic, while the MnSb nanoparticles with <d> ≥ 15 nm are ferromagnetic at room temperature (Tc for MnSb = 587 K). Growth of nanoscale MnSb
dots having an average dot diameter 20-30 nm, on sulfur passivated GaAs substrate by molecular beam epitaxy is also reported.\textsuperscript{105} When the nominal thicknesses of the deposited MnSb films are in between 0.70 and 1.05 nm, cluster coalescence of MnSb dots takes place. This coalescence resulted in an increased saturation magnetization compared to the thin films of MnSb (thickness 5 nm), followed by increased polar magnetic dichroism, which is an indication of the active magneto-optical properties of these MnSb dots.\textsuperscript{105} Interestingly, this increased magnetic circular dichromism value is even higher than that of bulk MnSb at both room temperature and 4 K.\textsuperscript{105} The presence of MnSb nanoleaves and nanorods have also been reported in a MnSb film synthesized by physical vapor deposition on a Si substrate. These nanostructures comprise nearly 50\% of the MnSb film. These nanorods are approximately 20 nm in diameter and hundreds of nanometers in length, while the nanoleaves have a thickness of 20 nm and a width of 100 nm. However, these films were found to incorporate impurities in the form of Sb, antimony oxides and manganese oxides.\textsuperscript{107}

As mentioned above, while epitaxially-prepared MnSb nanoparticles exhibit potentially useful magnetic and magneto-optical properties, there have been no reports of synthetic methods that enable the synthesis of MnSb nanoparticles with controlled phase, size, and morphology as discrete colloidal particles. Further, when grown on a substrate the nanoparticles are subject to strain. For example, the lattice parameters of hexagonal MnSb are \(a=4.128\,\text{Å}\) and \(c=5.789\,\text{Å}\).\textsuperscript{108} However, when grown on GaAs(111) and Ge(111) surfaces, the epitaxial mismatch is 3.2\%, while the use of Si(111) increases the epitaxial mismatch to 7\%.\textsuperscript{108} This strain can potentially be avoided by synthesis of nanoparticles in the solution phase and these methodologies enable the necessary control of size and morphology, enabling the intrinsic size and shape-dependent properties to be ascertained. While the synthesis of colloidal transition metal phosphide particles
has become quite routine,\textsuperscript{109-123} and precedent exists for colloidal transition metal arsenide nanoparticles;\textsuperscript{90, 92, 124-128} examples of antimonide colloids that exhibit narrow size polydispersity are quite few and typically limited to main group semiconductors.\textsuperscript{129-131} In this chapter, we present a successful synthesis of manganese antimonide nanoparticles of 14-15 nm in diameter with no apparent crystalline secondary phase(s). The magnetic properties of these discrete nanoparticles are also reported and discussed in terms of the properties of bulk phases and supported nanocrystals.

3.2 Experimental

All the materials used in the synthesis of MnSb nanoparticles are given in \textbf{CHAPTER 2}.

3.2.1 Synthesis of MnSb nanoparticles

\textit{Slow heating method}

TOPO (4.0 g), Ph\textsubscript{3}Sb (1 mmol), Mn\textsubscript{2}(CO)\textsubscript{10} (0.5-0.9 mmol) and 1-ODE (10.0 mL) were combined together in a single Schlenk flask in the glove box and removed to a Schlenk line in a fume hood. The contents were evacuated for about 20 min at 60°C followed by argon (Ar) flushing. The flask was heated using a heating mantle controlled by a programmable temperature controller with a thermocouple placed directly in the solution. The contents were slowly heated (20°C/10 min) up to 180°C under Ar to avoid volatilization of Mn\textsubscript{2}(CO)\textsubscript{10}, and then the temperature was rapidly increased up to 250-330 °C and maintained for 3-12 h. Upon the slow heating, the initial light yellow color solution progressively turns into orange, red, dark red and black. The final black product was allowed to cool naturally to room temperature. The product was dispersed in chloroform and precipitated with ethanol followed by centrifugation. This process was repeated several times and then the product was dried under vacuum.
Rapid Injection method

Mn$_2$(CO)$_{10}$ (1 mmol) and 1-ODE (10-20 mL) were mixed together in a Schlenk flask in the glove box, removed to the Schlenk line and purged with Ar. This mixture was injected into another Schlenk flask containing TOPO (4.0 g) and Ph$_3$Sb (1 mmol) preheated at 100 or 200 °C under Ar. Before injection, the Mn$_2$(CO)$_{10}$ and 1-ODE mixture was slightly warmed with a heat gun until the Mn$_2$(CO)$_{10}$ powder was dissolved in the 1-ODE. Upon cannulation, the reaction mixture, which was initially light yellow in coloration, immediately turned black and the temperature was then rapidly increased to 250-330 °C where it was maintained for 3-12 h. The as-prepared nanoparticles were then cooled to room temperature, purified and dried following the procedure described above (slow heating method).

3.2.2 Characterization

The synthesized MnSb nanoparticles were characterized by Powder X-Ray Diffraction (PXRD), Transmission Electron Microscopy (TEM), Inductively Coupled Plasma – Mass Spectrometry (ICP-MS), High Angle Annular Dark Field-Scanning Transmission Electron Microscopy (HAADF-STEM), and magnetometry. The basic principles and the function of the above instruments are described in CHAPTER 2.

3.3 Results and Discussion

The protocols explored in our attempt to synthesize discrete MnSb nanoparticles are based on the methods developed by our group to synthesize MnAs nanoparticles and exploit reactions between organometallic Mn and Sb precursors. In our method, Mn$_2$(CO)$_{10}$ and Ph$_3$Sb were mixed together at the outset in a mixture of TOPO and 1-ODE, and then heated to 280-330 °C to induce nucleation, growth, and crystallization, by a reaction similar to that noted in Equation 3.1.
Mn₂(CO)₁₀ + 2(C₆H₅)₃Sb → 2MnSb + 3C₁₂H₁₀ (biphenyl) + 10CO  \hspace{1cm} (3.1)

3.3.1 Effect of Temperature and Time on MnSb Formation

Initial attempts to make MnSb nanoparticles by slow heating were carried out at 330 °C, as this was the optimized temperature for MnAs nanoparticle synthesis\(^9\) using stoichiometric precursors. As shown in Fig. 3.1 (a) and (b), at 3 h heating the crystalline product is dominated by Sb, with only a few small peaks suggestive of the presence of MnSb.

![Figure 3.1: PXRD patterns of MnSb nanoparticles synthesized using an Mn:Sb precursor concentration of 1:1 at (a) 3 h at 330 °C and (b) 12 h at 330 °C by the slow heating method (MnSb- PDF # 03-065-0388, Sb-PDF # 00-035-0732). The arrow indicates a smaller peak for MnSb, suggestive of the presence of minor MnSb phase.](image)

Moreover, increasing the heating time to 12 h leads to Sb as the exclusive crystalline product. We hypothesized that MnSb may decompose to form Sb at this temperature, so explored a lower reaction temperature (280 °C) whereupon peaks for MnSb became more prominent (3 h, Fig. 3.2 (a)) and then dominant (5 h, Fig. 3.2 (b)). Simultaneous with the increase in peaks attributed to MnSb, the sharp peaks indicative of large crystallites of Sb decreased in intensity. In an attempt to drive the reaction to completion, we increased the heating time. However, when the reaction
time exceeded 5 h, the peaks for Sb once again grew in intensity at the expense of MnSb (6.5 h, Fig. 3.2 (c)). When the reaction time was 12 h, only peaks for Sb were present in the PXRD pattern (Fig. 3.2 (d)). Thus, it appears that MnSb nanoparticles are not stable relative to Sb formation even at the relatively low temperature of 280 °C.

![PXRD patterns of MnSb nanoparticles synthesized with Mn:Sb precursor ratio of 1:1 under different reaction temperatures and reaction times by the slow heating method (MnSb-PDF #: 03-065-0388, Sb-PDF #: 00-035-0732).](image)

**Figure 3.2:** PXRD patterns of MnSb nanoparticles synthesized with Mn:Sb precursor ratio of 1:1 under different reaction temperatures and reaction times by the slow heating method (MnSb-PDF #: 03-065-0388, Sb-PDF #: 00-035-0732).

In an attempt to avoid the decomposition of the apparently metastable MnSb, the reaction temperature was decreased to 200 °C; However, neither MnSb nor Sb was evident in the PXRD pattern of the brick-red precipitate, the product isolated from the reaction (Fig. 3.3 (a)). Moreover, the corresponding peaks could not be identified as belonging to any Sb or Mn phases in the ICDD database. The TEM image revealed the presence of sheet-like structures, which may be a reaction byproduct or an intermediate phase (Fig. 3.3 (b)).
3.3.2 Use of Excess Mn$_2$(CO)$_{10}$

Based on these data, there appears to be an optimal temperature and time to stabilize MnSb, but there is insufficient Mn to drive the reaction to completion. Accordingly, we studied the effect of excess Mn on the reaction evolution. Fig. 3.4 shows the PXRD patterns obtained for MnSb nanoparticles synthesized using different excess amounts, (0.6, 0.8, and 0.9 mmol) of Mn$_2$(CO)$_{10}$ at 280 °C for 5 h. (representing 20, 60, 80% mole excess Mn$_2$(CO)$_{10}$).

![Figure 3.3: (a) PXRD pattern (b) TEM image obtained of the product isolated from an attempt to synthesize MnSb nanoparticles at 200 °C for 3 h.](image)

As shown in Fig. 3.4 (a) and (b), when the Mn$_2$(CO)$_{10}$ amount was in the range of 0.6 to 0.8 mmol, the PXRD patterns showed that the MnSb phase was present but was accompanied by peaks for Sb. However, the intensities of the Sb peaks decreased with increasing Mn$_2$(CO)$_{10}$. 
Accordingly, Mn₄(CO)₁₀ was increased further to 0.9 mmol, which corresponded to 80% mole excess of Mn₄(CO)₁₀, at which point no Sb peaks were observed (Fig. 3.4 (c)). The crystallite size calculated from the PXRD pattern using the Debye-Scherrer equation (using the Full Width at Half Maximum (FWHM) of the peak corresponding to the (101) reflection) was estimated to be 25 nm.

3.3.3 Controlling Polydispersity

Fig. 3.5 shows a representative TEM image of MnSb nanoparticles prepared with 80% mole excess of Mn₄(CO)₁₀ by the slow heating method. The discrete nanoparticles prepared by slow heating (at 280 °C for 5 h) are accompanied by dark, large aggregations making the particle size distribution highly polydisperse. Attempts to use size-selective precipitation or the filtration methods were not successful in eliminating the aggregates.
Figure 3.5: TEM image of MnSb nanoparticles synthesized using 80% mole excess Mn$_2$(CO)$_{10}$ by the slow heating method

In an attempt to produce more uniform particles, we sought to better control the nucleation by diluting the reaction, hence the quantity of 1-ODE was increased from 12 mL to 20 mL. The PXRD pattern and the TEM image obtained for MnSb nanoparticles synthesized with a solvent volume of 20.0 mL are shown in Fig. 3.6 (a) and (b), respectively. The Scherrer crystallite size is around 14 nm and the average particle size from TEM is 13±1.7 nm. (Fig. 3.6 (c)). The formation of MnSb nanoparticles was further confirmed by SAED. (Fig. 3.6 (d)) Thus, reagent dilution plays an important role in imparting better monodispersity, reducing aggregation and decreasing the average crystallite size.
Figure 3.6: (a) PXRD pattern and (b) TEM image obtained for MnSb nanoparticles synthesized by slow heating with larger solvent volume (1-ODE) (MnSb- PDF #: 03-065-0388) at 280 °C for 5 h with 80% excess Mn$_2$(CO)$_{10}$ by mole (c) Particle size distribution histogram (d) SAED pattern of the MnSb nanoparticles synthesized by slow heating.

3.3.4 Rapid Injection Method

An alternative synthetic method, the arrested precipitation or the cannulation method, was also evaluated in an attempt to reduce the need for excess Mn precursor and/or decrease the sample polydispersity. TOPO and Ph$_3$Sb were preheated to 100-200 °C, and a solution of Mn$_2$(CO)$_{10}$ in 1-ODE was rapidly introduced via a cannula, and then the temperature was rapidly increased to 280 °C. Experiments analogous to the slow heating method were carried out to determine the optimum reaction time, the reaction temperature, and the Mn$_2$(CO)$_{10}$ amount. However, no significant difference between the products were noted (Fig. 3.7). In some
cases volatilization of Mn$_2$(CO)$_{10}$ during the high-temperature was observed, evident as a yellow precipitate on the neck of the Schlenk flask, leading to lower product yield relative to the slow heating method.

Figure 3.7: PXRD patterns of MnSb nanoparticles synthesized using an Mn:Sb precursor concentration of 1:1 under different reaction temperatures and reaction times by the cannulation method, cannulated at 200 °C (MnSb- PDF # 03-065-0388, Sb-PDF # 00-035-07).

3.3.5 Chemical Nature of the Core and Shell of MnSb Nanoparticles & Mechanistic Insights

The elemental mapping of individual nanoparticles was conducted with HAADF-STEM imaging (Fig. 3.8 (a)) combined with elemental analysis (EDS). The elemental mapping images shown in Fig. 3.8 (b-d) reveals the presence of Mn and Sb as well as O co-localized in the particles. Careful examination of HAADF-STEM images (Fig. 3.8 (a)) revealed that the MnSb nanoparticles appear to have an amorphous shell about 2 nm in thickness, around the core, which is ca.12 nm in diameter. An EDS line scan across a single particle is shown in Fig. 3.8 (e).
Figure 3.8: (a-d) HAADF-STEM of MnSb nanoparticles synthesized by the cannulation method and EDS mapping of Mn, Sb, and O, respectively. The scale bar corresponds to 100 nm. (e) Line scan elemental analysis of a single MnSb nanoparticle: Mn (red), Sb (green), P (blue), and O (turquoise).

The data suggest an even distribution of Mn and Sb within the MnSb nanoparticle core, whereas Mn and O are present in the amorphous shell where no Sb is detected. The fall of the oxygen signal as the scan approaches the center of the core is consistent with localization of oxide on the surface. Based on these data, we presume that the shell comprises an amorphous manganese oxide. Consistent with this interpretation, ICP-MS data obtained on a sample of thoroughly washed MnSb nanoparticles reveals a ratio of 1.1:1.0 Mn:Sb, and the presence of a 10% excess of Mn relative to Sb was confirmed by ICP-MS. Although bulk-phase MnSb is capable of incorporating an excess of Mn to form Mn_{1+δ}Sb (0 ≤ δ ≤ 0.30) of Mn_{1+δ}Sb, clear evidence of surface oxidation suggests that the excess Mn is most likely present as oxide. Indeed, the formation of manganese oxide is evident in unpurified samples according to PXRD (Fig. 3.9) where there is a broad peak around 19° corresponding to cubic MnO₂.
The absence of any such peaks in the purified product suggests this is largely washed away, leaving only an amorphous shell around the particle. The formation of manganese oxide on the surface of the nanoparticles suggests that the excess Mn$_2$(CO)$_{10}$ (used to avoid Sb byproduct formation) is serving as a sacrificial oxygen getter. Finally, the line scan reveals that the P-content is low throughout the particle and background (Fig. 3.8 (e)), suggesting that there is no appreciable incorporation of P from the solvent, in contrast to what is observed in MnAs colloidal nanocrystals. The absence of P-incorporation was confirmed by ICP-MS analysis on isolated nanocrystals.

The formation of oxide suggests both an adventitious source of oxygen (which could even be from the TOPO solvent) and the strong preference of Mn for reaction with O over Sb. Control reactions in which Mn is not introduced lead to Sb precipitation, consistent with decomposition of Ph$_3$Sb to Sb is being thermodynamically favored under our reaction conditions when reactive (e.g., reduced) Mn is not available. It is well-established that formation of elemental Mn nanocrystals by solution-phase routes requires addition of strong reducing agents,
such as n-butyl Li.\textsuperscript{133} Unsurprisingly, when Mn\textsubscript{2}(CO)\textsubscript{10} is employed under optimized conditions, but in the absence of Ph\textsubscript{3}Sb, manganese oxides are formed in the mother liquor. The fact that MnSb appears to be unstable in the mother liquor at higher reaction temperatures or at longer reaction times relative to Sb formation (\textbf{Fig. 3.1} and \textbf{Fig. 3.2}) suggests that the reactivity with O is not exclusively occurring with the Mn precursor, but also with the formed MnSb nanocrystals (MnSb + O\textsubscript{2} $\rightarrow$ MnO\textsubscript{2} + Sb). Thus, initial gettering of oxygen by Mn\textsubscript{2}(CO)\textsubscript{10} to form phase-pure MnSb may not be sufficient to stabilize this phase in the presence of a continued supply of oxygen, and this will be apparent in reactions conducted at higher temperatures and longer times. Indeed, as shown in \textbf{Fig. 3.10} when the optimized reaction compositions, including 80\% mole excess of Mn\textsubscript{2}(CO)\textsubscript{10}, were allowed to react to higher reaction temperatures and longer reaction times, Sb starts to evolve again despite the presence of excess Mn\textsubscript{2}(CO)\textsubscript{10}. Based on these data, we presume formation of MnSb occurs by reaction of zero-valent molecular Mn species with Ph\textsubscript{3}Sb, with the reaction of the Mn precursor with adventitious oxygen occurring as a competing reaction, along with the reaction of MnSb with oxygen, both of which lead to precipitation of Sb and formation of Mn oxides. Therefore, the best protocol for the synthesis of MnSb involves balancing the low reactivity of Sb towards Mn with the high oxophilicity of Mn.
3.3.6 Magnetic Properties of MnSb Nanoparticles Synthesized by the Slow Heating Method

The synthesized MnSb nanoparticle sample was subjected to the magnetic measurements as a powder sample, and the resultant magnetic properties reflect both the MnSb core and the MnO$_2$ shell. Careful band structure calculations (utilizing the generalized gradient approximation) indicate that the NiAs structure of MnSb strongly favors the magnetic alignment leading to high magnetic moments of MnSb and fairly high density of states asymmetry of the majority and minority spin sub-bands. Although the magnetic properties of MnSb are largely associated with the Mn d- states, the exchange interaction is reduced by the effects of p-d hybridization related to Sb anions. Note that the magnitude of the magnetic moment for small and light anions in a series of MnAs, MnSb, and MnP is gradually reduced, due to the changes in the Mn-Mn bond length and the degree of p-d hybridization.$^{134-135}$

Fig. 3.11 shows the temperature (T) dependence of the molar magnetization (normalized to Mn moles) (M) recorded upon warming after Zero-Field-Cooling (ZFC) and Field-Cooling
(FC) the MnSb nanoparticles (synthesized by slow heating with optimized reaction conditions) under an external magnetic field of 100 Oe.

![Graph](image)

**Figure 3.11:** Temperature dependence of the DC molar magnetization (M) (normalized to Mn moles) recorded under Zero-Field-Cooled (ZFC) and Field-Cooled (FC) conditions (collected at 100 Oe) for MnSb nanoparticles synthesized by the slow heating method at 280 °C for 5 h.

The FC plot shows a gradual increase of molar magnetization with decrease of temperature from 320 K which then saturates at temperatures roughly below 50 K. In the ZFC curve, the sample shows a broad maximum in the range of 245-255 K, near the intersection of FC with the ZFC. Collectively, the above behavior suggests superparamagnetic behavior. Under FC conditions, the magnetic moments of the particles are frozen along the direction of applied magnetic field upon cooling, producing saturation at low-temperature. In contrast, for ZFC samples, the moments are frozen in random orientation at low temperature, and start to align in the field upon heating, reaching a maximum at the blocking temperature, $T_B$, above which superparamagnetic behavior is exhibited, resulting in a drop in magnetization again. The $T_B$ depends on the volume of the nanoparticle, the presence of anisotropy (shape or magnetocrystalline), as well as the time-scale of the measurement ($\sim 10^{-9}$ s for DC
magnetometry). In the present case the peak corresponding to $T_B$ is relatively broad suggesting a distribution of values reflecting the polydispersity of the sample.\textsuperscript{136} We attribute the irregularity in both FC and ZFC plots around 43 K to a small leak of oxygen into the sample chamber that makes a condensed film of oxygen, resulting a para-antiferromagnetic transition of oxygen around 43 K.\textsuperscript{40}

**Fig. 3.12** shows the molar magnetization ($M$) vs applied magnetic field ($H$) data obtained at 300 K and 50 K for the same sample.

![Graph](image1.png)

**Figure 3.12**: Field dependence of the DC molar magnetization ($M$) (normalized to Mn moles) recorded at different magnetic fields ($H$) at (a) 300 K and (b) 50 K for MnSb nanoparticles synthesized by the slow heating method at 280 °C for 5 h. The inset shows an enlarged image of the loop of the hysteresis curve obtained at 50 K.

At 300 K, the hysteresis loop is essentially closed, consistent with superparamagnetism as expected above $T_B \sim 250$ K; however, at 50 K (i.e., below $T_B$) the broadening of the hysteresis loop suggests a small degree of coercivity, approximately 150 Oe. Although the presence of the $\text{MnO}_2$ antiferromagnetic shell, revealed by HAADF-STEM imaging, might be expected to result in exchange bias effects (a shift of the hysteresis loop along the x-axis), this is not observed in the 50 K data, possibly due to the relatively low Neel temperature for $\text{MnO}_2$ (*ca* 90 K) coupled
with the thin nature of the shell giving rise to an antiferromagnetic blocking temperature that is less than 50 K.\textsuperscript{137} However, as disclosed by the inset in Fig. 3.12(b), there is a small asymmetry in the hysteresis, a thinning of the loop close to zero applied field, suggesting some degree of metamagnetism in the MnSb nanoparticles that is not reported in bulk phases, and which could be a consequence of spin-fluctuations at the antiferromagnetic/ferromagnetic interface.\textsuperscript{138} When measured at the saturated level, the ferromagnetic moment of these nanoparticles is approximately 0.04 BM/MnSb, two orders of magnitude smaller than that realized in bulk (3.6 BM/Mn).\textsuperscript{139} Thus, the observed magnetic moment in our case is a fraction of what is expected based on experimental data on bulk samples and theory.

\textbf{Figure 3.13:} Field dependence of the DC molar magnetization (M) (normalized to Mn moles) recorded at different magnetic fields (H) at 50 K for MnSb nanoparticles synthesized by the slow heating method at 280 °C.

The significant decrease in the moment is attributed in part to the manganese oxide shell around the magnetic component of the nanoparticle.\textsuperscript{, In order to further confirm this hypothesis we repeated M-H measurement on the same sample mentioned above after about 6 months during which the sample was exposed to the ambient, under the same experimental conditions.}
The saturation magnetization further decreased approximately by 25%, confirming the surface oxidation of the nanoparticles.

![Magnetic properties of MnSb nanoparticles synthesized by the cannulation method](image)

**Figure 3.14**: Magnetic properties of MnSb nanoparticles synthesized by the cannulation method. (a) Temperature dependence of the DC molar magnetization (M) (normalized to Mn moles) recorded under Zero-Field-Cooled (ZFC) and Field-Cooled (FC) conditions (collected at 100 Oe). Field dependence of the DC molar magnetization (M) (normalized to Mn moles) recorded at different magnetic fields (H) recorded at (b) 300 K and (c) 50 K.

The strong tendency of MnSb to form surface oxides is well-established, with oxide thicknesses of 7 nm observed in thick films (ca. 250 nm). Although the amorphous shell appears to be relatively thin compared to the MnSb core in our particles (Fig. 3.8 (e)),
considering the small diameter of our particles (14 nm), it is feasible that a significant portion of the volume is oxidized in the magnetic samples. A rough calculation suggests a \textit{ca} 2 nm diameter core of MnSb within a 14 nm particle.

Given such a small volume, it is surprising that the $T_B$ is as high as it is; epitaxial nanodisks with volumes 10x greater than our materials are reported to have $T_B$ of 150K. The magnetic behavior corresponding to the MnSb nanoparticles synthesized by the cannulation method, recorded under the same conditions as the slow heating method, shows the same behavior (Fig. 3.14), suggesting that this behavior is intrinsic to colloidal MnSb.

### 3.4 Conclusions

Solution-phase synthetic methods were developed to synthesize discrete MnSb nanoparticles (\textit{ca.} 14 nm in diameter) with a high degree of reproducibility and low polydispersity. In order to prevent formation of Sb as a byproduct, excess Mn precursor is required and synthetic temperatures much lower than those successfully applied for MnAs and MnP must be used. The presence of excess moles of Mn$_2$(CO)$_{10}$ ensures the reaction mixture contains enough Mn$_2$(CO)$_{10}$ to compensate for the loss of Mn$_2$(CO)$_{10}$ as manganese oxide (as both byproduct and amorphous shell) by an adventitious oxygen source. However, the oxide shell significantly reduces the magnetic moment of the MnSb nanoparticles. It has been reported that a layer of surface antimony can act to prevent oxidation in thin films,\textsuperscript{140} an approach we are currently investigating, along with variation of size. Moreover, building on our previous synthetic route for MnAs, we will also turn our attention to the formation of ternary phases MnAs$_{1-x}$Sb$_x$ as a means to tune the magnetocaloric response for near room-temperature magnetic refrigeration. We expect that this new synthetic approach for MnSb will be amenable to other
transition metals, and that metals less oxophilic than Mn (e.g. Fe, Co, Ni, etc.), will be more easily prepared and less subject to surface oxidation.
CHAPTER 4 - ANISOTROPIC MANGANESE ANTIMONIDE NANOPARTICLE FORMATION BY SOLUTION-SOLID-SOLID GROWTH MECHANISM: CONSEQUENCE OF SODIUM BOROHYDRIDE ADDITION TOWARDS REDUCED SURFACE OXIDATION AND ENHANCED MAGNETIC MOMENT

** The content of this chapter is accepted by Nanoscale for publication

4.1 Introduction

Bulk MnSb, and related ternary phases, have long been studied due to the strong coupling between the ferromagnetic properties and caloric, optical (Kerr effect) and/or structural changes, achievable near room temperature. Therefore, these phases are of interest as potential magnetic refrigerant materials,¹ and components in data storage/processing devices² and magneto-optical readouts.³ Nano-structures of MnSb have also been investigated, as epitaxial dots grown on supporting substrates including Si⁴ and GaAs³, and as thin films on Ge/Si⁵. MnSb nanoparticles on Si (111) with lateral diameter ≥ 15 nm are ferromagnetic at room temperature.⁴ For GaAs, the cluster coalescence of MnSb nano dots (nominal thickness 0.35-1.05 nm) leads to an increased saturation magnetization compared to thin films of MnSb (thickness 5 nm), and polar magnetic dichroism, an indication of the active magneto-optical properties of these MnSb dots.³ Finally, in the case of molecular beam epitaxial growth of 70 nm thickness MnSb (0001) films on Ge (111)/Si (111) by reduced pressure vapour deposition, a saturation magnetization value of 3.3 BM/Mn⁵, approaching the experimentally recorded moment for bulk MnSb (3.5 BM/Mn)⁶ is achieved. The Brock group has pioneered the synthesis of MnSb nanoparticles by solution phase routes.⁷ Growing nanocrystals in the solution phase evades strain induced in the nanoparticles due to epitaxial supports, enabling the study of intrinsic size and shape-dependent properties. As described in CHAPTER 3, in this method of synthesizing MnSb nanoparticles, the driving factor for the successful preparation of MnSb with no evident precipitation of elemental antimony (Sb) as a secondary phase, was to use a large excess of manganese (Mn) precursor, manganese
carbonyl [Mn$_2$(CO)$_{10}$] (ca. 160% mole Mn excess). We rationalized the need for excess Mn$_2$(CO)$_{10}$ as a function of the high volatility of Mn$_2$(CO)$_{10}$ in the reaction at elevated temperatures. In addition, the observed manganese oxide (MnO$_x$) shell around the MnSb nanoparticle core, which we suspected formed because of an adventitious oxygen source. This MnO$_x$ shell formation not only consumes a portion of the Mn$_2$(CO)$_{10}$, resulting in Mn precursor deficiency relative to triphenyl antimony (Ph$_3$Sb), but also reduces the magnetic moment of the material when calculated with respect to the Mn moles in the final product (0.04 BM/MnSb vs. 3.3 BM/MnSb for bulk). We presume that when excess Mn$_2$(CO)$_{10}$ is present, it acts as a sacrificial agent to react with adventitious oxygen producing free MnO$_x$ that washes away in the purification process, in addition to forming an amorphous shell around the MnSb core. Further, we hypothesized that a reducing agent would be a stronger sacrificial agent (better oxygen-getter) than Mn$_2$(CO)$_{10}$ and could react quickly with adventitious oxygen before it reacts with Mn$_2$(CO)$_{10}$, thus reducing or eliminating the excess Mn$_2$(CO)$_{10}$ for the reaction and the extent of oxidation. **CHAPTER 4** studies are based on this hypothesis, in which we employed a mild reducing agent, sodium borohydride (NaBH$_4$), in the synthesis, and in so doing revealed a new mechanism for MnSb formation based on the Solution-Solid-Solid (SSS) mechanism. SSS growth has become a prominent synthetic strategy for synthesizing one dimensional (1-D) semiconductor nanorods and nanowires in solution, such as ZnSe$^{8-10}$ and CdSe$^{8,11-13}$ In SSS, a solid particle acts as an active catalyst, facilitating the formation of tail growth by breaking down precursor components in the solution phase. This mechanism is distinguished from the more common Solution-Liquid-Solid (SLS) growth mechanism by the use of nucleating particles with bulk melting points several hundred degrees above the reaction temperature.$^{141-149}$ In general, nucleating nanoparticles are superionic in character, and the growth is vacancy driven. However,
Buhro and co-workers have observed the same growth pattern for CdTe when Bi nanoparticles are employed, with \( \text{Bi}_2\text{Te}_3 \) identified as the “active catalyst”. SSS has also proven to be a model method to synthesize complex ternary and quaternary nanowires and nanoribbons such as \( \text{CuInS}_2 \), \( \text{CuGaS}_x\text{Se}_{2-x} \), and \( \text{AgInZn}_7\text{S}_9 \) which are challenging to prepare by conventional reaction approaches. To the best of our knowledge, the use of antimonides as catalysts for SSS has not been reported.

4.2 Experimental

All the materials used in the synthesis of anisotropic MnSb nanoparticles are given in CHAPTER 2.

4.2.1 Synthesis of MnSb nanoparticles in the presence of NaBH\(_4\)

The synthetic method for production of solution-phase MnSb nanoparticles in the presence of NaBH\(_4\) was developed by modification of our previously reported MnSb nanoparticle synthesis method (CHAPTER 3).\(^7\) TOPO (4.0 g), Ph\(_3\)Sb (1 mmol), Mn\(_2\)(CO)\(_{10}\) (0.6-1.5 mmol), NaBH\(_4\) (0.53-2.64 mmol), and 1-ODE (20.0 mL) were combined together in a Schlenk flask in the glove box and moved to a Schlenk line in a fume hood. The Schlenk flask was evacuated for about 20 min at 60 °C followed by purging with argon (Ar) to degas the mixture. The flask was heated using a heating mantle controlled by a programmable temperature controller with a thermocouple placed directly in the solution. The contents were slowly heated (20 °C/10 min) up to 180 °C under Ar to avoid volatilization of Mn\(_2\)(CO)\(_{10}\), and then the temperature was rapidly increased up to 250 °C and maintained for 3-8 h. Upon heating, the initial light yellow color solution gradually turned into orange, red, dark red and black. The final black product was allowed to cool naturally to room temperature. The product was dispersed in
chloroform and precipitated with ethanol, followed by centrifugation. This process was repeated several times, and then the product was dried under vacuum to obtain a free-flowing powder.

4.2.2 Study of Morphological Transformation

Near-stoichiometric amounts of $\text{Mn}_2(\text{CO})_{10}$ (0.6 mmol), $\text{Ph}_3\text{Sb}$ (1 mmol), along with TOPO (4.0 g), 1-ODE (20.0 mL) and $\text{NaBH}_4$ (0.92 mmol) were initially employed, and the contents of the flask were slowly heated under Ar following the procedure described above for the synthesis of MnSb nanoparticles. After allowing the reaction to run for 3 h at 250 ℃, a fraction (0.2 mL) was taken out and quenched in cold chloroform for PXRD and TEM analyses. Immediately after taking out the fraction, $\text{Mn}_2(\text{CO})_{10}$ (0.9 mmol) heated and dissolved in 1-ODE (<10.0 mL) was cannulated into the initial reactant mixture at 250 ℃ under inert conditions. The contents were further heated for 3-8 h at 250 ℃. The resultant black solution was then purified and isolated using the method described above. PXRD and TEM analysis were carried out to determine any phase or morphology differences, respectively.

4.2.3 Characterization

The synthesized MnSb nanoparticles were characterized by Powder X-Ray Diffraction (PXRD), Transmission Electron Microscopy (TEM), Inductively Coupled Plasma – Mass Spectrometry (ICP-MS), High Angle Annular Dark Field- Scanning Transmission Electron Microscopy (HAADF-STEM), and magnetometry. The basic principles and the function of the above instruments are described in CHAPTER 2.
4.3 Results and Discussion

4.3.1 Effect of NaBH₄ Addition on MnSb Nanoparticle Synthesis with Near-Stoichiometric Mn₂(CO)₁₀

In order to test our hypothesis, i.e., the introduction of a reducing agent eliminates the need for excess Mn₂(CO)₁₀ to avoid co-precipitation of Sb, discrete MnSb nanoparticles were synthesized in the presence of NaBH₄ (0.53 mmol) by heating at 250°C using a slight excess of Mn₂(CO)₁₀ (1.2 mmol Mn: 1.0 mmol Sb) in TOPO and 1-ODE for a dwell time of 3 h. Fig. 4.1 shows the difference between the two MnSb nanoparticle syntheses carried out using near-stoichiometric Mn₂(CO)₁₀ in the absence and presence of NaBH₄.

![Figure 4.1: PXRD data of the product of MnSb synthesis carried out in the absence and in the presence of NaBH₄ (0.53 mmol). The corresponding peaks for Sb, (012) at 2θ=28.7 and (110) at 2θ=42, are marked with asterisks for comparison. (MnSb-PDF # 03-065-0388, Sb-PDF # 00-035-0732).](image-url)

The addition of NaBH₄ clearly results in less elemental Sb formation and also, based on diffraction peak broadening, smaller MnSb nanoparticles. Assuming that the remaining Sb precipitate could be avoided by an increase of the amount of NaBH₄, we increased the amount of
reductant incrementally from 0.53 to 2.64 mmol, keeping the concentrations of Mn and Sb unchanged.

According to Fig. 4.2 (a, b), the increase of NaBH₄ up to 0.79 mmol continues to decrease Sb precipitation (qualitatively determined by the intensity ratio of (012) and (110) [marked with asterisks] of the Sb phase to (101) and (110) peaks [as labelled] of the MnSb phase). However, complete elimination of Sb is not observed. The quantity remains small but constant up through 1.06 mmol (Fig. 4.2 c, d) whereas for higher NaBH₄ concentrations (1.59 – 2.64 mmol) the amount of Sb is again increased (Fig. 4.2 e, f)

Scherrer size calculations of the crystallite size of the MnSb nanoparticles for different NaBH₄ amounts (0.53, 0.79, 0.92, 1.06, 1.59, 2.64 mmol), when measured from either MnSb (101) peak, or the MnSb (110) (when significant peak overlap of MnSb (101) with Sb (012) occurs), are presented in Table 4.1 and compared to values for the Sb impurity phase.

![Figure 4.2: PXRD data of the product of MnSb synthesis (1 mmol Sb and 1.2 mmol Mn) as a function of added NaBH₄. The asterix denotes the position of elemental Sb; the principal peaks of MnSb are labeled. (MnSb-PDF # 03-065-0388, Sb-PDF # 00-035-0732).](image-url)
Table 4.1: The crystallite size of MnSb and Sb nanoparticles, synthesized using different NaBH$_4$ amounts, calculated by Scherrer equation.$^{152}$

<table>
<thead>
<tr>
<th>NaBH$_4$ amount (mmol)</th>
<th>Crystallite size of MnSb from the (101) peak (nm)</th>
<th>Crystallite size of MnSb from the (110) peak (nm)</th>
<th>Crystallite size of Sb from the Sb (110) peak (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.53</td>
<td>*</td>
<td>16</td>
<td>66</td>
</tr>
<tr>
<td>0.79</td>
<td>*</td>
<td>40</td>
<td>**</td>
</tr>
<tr>
<td>0.92</td>
<td>22</td>
<td>23</td>
<td>**</td>
</tr>
<tr>
<td>1.06</td>
<td>43</td>
<td>36</td>
<td>37</td>
</tr>
<tr>
<td>1.59</td>
<td>34</td>
<td>35</td>
<td>54</td>
</tr>
<tr>
<td>2.64</td>
<td>*</td>
<td>25</td>
<td>39</td>
</tr>
</tbody>
</table>

*Crystallite size cannot be calculated due to peak overlap

** Crystallite size cannot be calculated due to the low intensity of the peak

In cases where the (101) peak can be resolved, the crystallite sizes are similar to values obtained from the MnSb (110) peak. However, there is no clear trend observed in crystallite size for MnSb and/or Sb vs NaBH$_4$ amount.

The challenges in computing crystallite size based on Scherrer equation become evident upon evaluation of TEM data. Fig. 4.3 and 4.4 shows the TEM images of the MnSb samples corresponding to the PXRD patterns displayed in Fig. 4.2. Clearly, the introduction of NaBH$_4$ has had a profound effect on the morphology, resulting in tadpole-shaped particles, and rendering the Scherrer calculation for spherical nanoparticles inappropriate. According to Fig. 4.3 and 4.4 all the nanoparticles synthesized by the addition of NaBH$_4$ possess a head-tail morphology rather than the spherical morphology characteristic of MnSb when no NaBH$_4$ is included.$^{101}$
However, except in the case of 2.64 mmol of NaBH$_4$, the size of the head is relatively constant (ca. 14-19 nm) in diameter as is the tail width (ca. 8-10 nm) throughout the different NaBH$_4$ values used. In contrast, the tail part lengthens gradually with the addition of NaBH$_4$, from 30 to 100 nm, resulting in elongated head-tail nanoparticles. When the NaBH$_4$ amount is 2.64 mmol the former spherical-shaped head becomes oval in shape, ca. 35 nm, (head diameter measured along the direction of the tail), the diameter swells to 13 nm and the length extends to 165 nm.

**Figure 4.3:** TEM images of MnSb syntheses in the presence of different amounts of NaBH$_4$ (0.53-0.92 mmol) and associated histograms corresponding to the head diameter, tail length, and tail width.
In order to probe the compositional heterogeneity, the elemental mapping of individual head-tail particles was obtained from HAADF-STEM imaging combined with elemental analysis (EDS) as shown in Fig. 4.5. Fig. 4.5 a-c reveals the presence of Mn and Sb elements throughout the particle, from head to tail. However, when considering the distribution of Mn and Sb in the line scan (Fig. 4.5 g), Sb is slightly rich in the head region, while both Mn and Sb are co-localized in the tail region. Elemental mapping of individual particles was also done for O, P and B to check for incorporation of these elements (Fig. 4.5 d, e) and Fig 4.6). According to the
HAADF-STEM data, oxygen is present throughout the particle, which we presume is due to surface oxidation or a shell of MnO$_x$. However, the MnO$_x$ shell appears thinner (< 1 nm) than in the nanoparticles synthesized in the absence of NaBH$_4$ (ca. 2 nm). The mapping data do not indicate co-localization of B despite its small atomic size (Fig 4.6), but P is evident throughout the head-tail morphology (Fig. 4.5 g). Based on these data, we conclude that the nanoparticles are composed of an Sb-rich MnSb head and a MnSb tail, with a small amount of P throughout the structure.

**Figure 4.5:** (a) HAADF-STEM of MnSb nanoparticles synthesized in the presence of NaBH$_4$ (2.64 mmol) and EDS mapping of (b) Sb and (c) Mn (d) O and (e) P; (f) Bottom mount image of a portion of the tail part of a MnSb nanoparticle showing lattice fringes; (g) line scan elemental analysis of a single head-tail MnSb nanoparticle: Sb (green), Mn (red), O (blue), and P (cyan).
According to the ICP-MS analysis, the P content is 0.2% of the total atomic composition, consistent with minimal uptake. This P may correspond to either the presence of surface bound TOPO, the stabilizing agent that protects the particles from aggregation, or incorporation of P into the nanoparticle lattice during the synthesis. According to previous studies of MnAs nanoparticles reported by our group, unintentional incorporation of P into nanoparticles of as high as a few percent can occur when TOPO is used. This incorporation takes place during the nucleation step, and then P is lost due to a self-purification process. We surmise a similar process is going on in the MnSb synthesis. From ICP-MS data analysis, the Mn:Sb ratio of the overall particle was 1:1.08. This excess Sb presence can be either attributed to MnSb + Sb, MnSb$_{1+\delta}$ or as a concentration gradient of Mn and Sb, as is observed in CdS$_{1-x}$Se$_x$ nanorods. However, the presence of peaks corresponding to elemental Sb in the PXRD (Fig. 4.2) suggests MnSb + Sb is the more likely scenario. Note that Scherrer size calculations for Sb-grain sizes (ca 40-70 nm, Table 4.1) are not reflected in the TEM, likely due to sampling errors. Keeping in mind that a few larger crystallites will dominate the PXRD pattern, but may correspond to a small volume fraction, this is either not-captured during “snap-shots” acquired on the TEM grid,
or the larger grains do not make it onto the grid at all (they settle out after sonication, and before application of solution to the grid).

Furthermore, some head-tail particles with ‘swollen areas’ in the tail were observed, particularly when the NaBH₄ amount becomes ≥1.59 mmol, reminiscent of peas in a pod (Fig. 4.7).

![Figure 4.7: TEM image of MnSb nanoparticles reminiscent of peas in a pod synthesized in the presence of 2.64 mmol NaBH₄.](image)

In order to analyze these ‘pea pods’, we took line scans along the horizontal and vertical axes of these tails, across the ‘swollen areas’. According to Fig. 4.8, the ‘swollen areas’ or ‘peas’ are richer in Sb relative to Mn and P, while in the non-swollen areas, both Mn and Sb have similar concentrations. Moreover, according to Fig. 4.8 b, the core is rich in Sb. Thus the ‘swollen areas’ are similar to the heads, representing Sb rich areas.

### 4.3.3 Mechanism of Formation and Transformation

We posit that the anisotropic growth of nanoparticles arises from an SSS growth mechanism. Aliquots taken as a function of time reveal that at short times, ca. 30 min, the samples are heterogeneous, comprising short rods and spheres (Fig. 4.9, 30 min). By 60 min the nanoparticle morphology mostly consists of tadpoles, and there is no significant morphology change at longer times (Fig. 4.9, 60 - 180 min).
Figure 4.8: HAADF-STEM of a MnSb nanoparticle with a ‘swollen tail’ synthesized in the presence of 2.64 mmol of NaBH$_4$ and line scan elemental analysis (a) axial (b) vertical scan across the tail: Sb (green) Mn (red) and P (cyan).

At the same time, the PXRD data for all the samples (Fig. 4.9 (b)) are very similar, with all patterns indicative of MnSb formation, but peak asymmetry in the (101) reflection suggests elemental Sb is also present. It has been reported in the literature that colloidal Sb nanocrystals can be rapidly (< 1 min) obtained by hot injection methods at modest (150-200 °C) temperatures,$^{154}$ and these act as precursors for alloy$^{155}$ and composite$^{156-157}$ formation. Moreover, it is known that superlattices of Mn and Sb spontaneously form epitaxial MnSb at the interface, (with lattices oriented along the <110> or <001> direction)$^{158}$; the latter is consistent with our observation of ~3 Å lattice spacing ((002) lattice plane) along the growth direction. Fig. 4.5f. Accordingly, a simple hypothesis would be that Mn solution species react with Sb nuclei
generating MnSb nanorods oriented epitaxially along $c$ with growth occurring at the head-tail interface: the SSS mechanism. However, the actual mechanism is likely more complex, as diffusion of Mn into the Sb nuclei forms a MnSb shell (see Fig. 4.8) from which the “tail” emerges at one end. Note that the SSS mechanism is chosen over Solution-Liquid-Solid (SLS) based on the high melting point (mp) of bulk Sb (mp: 630.6 °C) and MnSb (mp: 840 °C) relative to the synthesis temperature.

**Figure 4.9:** (a) TEM images (b) PXRD patterns of the fractions obtained at different time intervals (30, 60, 90, 120, 180 min) and quenched in cold chloroform from the reaction using near-stoichiometric Mn$_2$(CO)$_{10}$ and 0.92 mmol NaBH$_4$.

We think it likely that the reductant also results in a higher concentration of reactive Mn in solution, which promotes tail growth. If reactive Mn is the limiting reactant, then the more reductant added, the longer the rods should be (assuming a constant number of nuclei), which is
exactly what we see. So, Sb nucleates, reacts with Mn to form MnSb, which grows as a rod because of the epitaxial relationship and the high precursor concentration. Note that head diameter and tail width does not change much with increasing NaBH$_4$ concentration (ca 18 nm head diameter and 9 nm tail) until the concentration gets quite large. At this point the head diameter doubles, tail width increases by 50 % and length doubles. This is also where swollen Sb-rich features become apparent along the length of the particle. We surmise that MnSb is not stable to disproportionation to the elements for high reductant concentrations and that liberated antimony condenses to form nuclei within the structure (i.e., the swollen features). The fate of Mn is unclear, but it may be reconstituted as a reactive precursor. Thus, the ‘tail’ grows longer because the reactive Mn precursor concentration is higher, but this is superposed over a thickening of the ‘head’ and ‘tail’ to accommodate Sb nanoparticle nucleation and growth.

In an attempt to better understand how Mn and NaBH$_4$ concentrations dictate the formation mechanism and to probe whether the morphologies can be interconverted and excess Sb eliminated, a set of reactions was carried out in the presence of NaBH$_4$ (0.79 mmol), with the addition of 0.7, 0.9, and 1.5 mmol of Mn$_2$(CO)$_{10}$ (i.e. 40, 80, 200% excess of moles, respectively). Note that 0.9 mmol is the Mn$_2$(CO)$_{10}$ amount used in the successful synthesis of MnSb nanoparticles in the absence of a reducing agent.$^{101}$ Fig. 4.10 shows the corresponding TEM images. Interestingly, the morphology of the MnSb nanoparticles has evolved from the elongated head–tail (no excess Mn$_2$(CO)$_{10}$) to contracted head-tail (0.7 mmol excess Mn$_2$(CO)$_{10}$) and then spherical-shaped nanoparticles (≥0.9 mmol excess Mn$_2$(CO)$_{10}$). Therefore, even in the presence of NaBH$_4$, when there is a large excess of Mn$_2$(CO)$_{10}$ the MnSb nanoparticles obtained are spherical in shape as is the case for MnSb nanoparticles reported previously. As shown in Fig. 4.11 the PXRD pattern of the synthesis with 0.7 mmol of Mn$_2$(CO)$_{10}$ is indicative of the
MnSb phase; however, no conclusion can be drawn as to the presence or absence of a small amount of Sb phase due to the breadth of the peak. Indeed, the asymmetry of the peak (unusually broad at the base) may suggest an amorphous component. In addition, the presence of crystalline MnO₂ peaks was noted. The PXRD patterns of 0.9 mmol and 1.5 mmol of Mn₂(CO)₁₀ do not have apparent oxide peaks (Fig. 4.11) and if Sb is present, it is a minor product in relation to MnSb. Thus, spherical particles appear to form when Mn is present in excess and formation of elemental Sb is minimized.

Figure 4.10 (a-c): TEM images of MnSb nanoparticles synthesized in the presence of NaBH₄ (0.79 mmol), using 0.7, 0.9, 1.5 mmol (40, 80, 200% mole excess) of Mn₂(CO)₁₀ (particle diameter refers to the head diameter).

4.3.4 Alternations between Two Morphologies

After seeing that there exist two different morphologies that correlate to the amount of Mn₂(CO)₁₀ amounts (near-stoichiometric and excess), we sought to evaluate whether these two morphologies can be interchanged as a function of the Mn₂(CO)₁₀ amount. In order to do so, MnSb nanoparticles were synthesized by using near-stoichiometric reactant amounts in the presence of 0.79 mmol of NaBH₄, and then excess Mn₂(CO)₁₀ (0.9 mmol) in 1-ODE was introduced to the same reaction mixture and the morphology evolution probed as a function of time. Fig. 4.12 shows how the elongated head-tail morphologies that arise under the near-
stoichiometric reactant conditions progressively transform into spherical nanoparticles, when heated for different reaction times (3-5 h) at 250 °C.

**Figure 4.11**: PXRD patterns of MnSb nanoparticles synthesized in the presence of NaBH$_4$ (0.79 mmol), using (a) 0.7 (b) 0.9 (c) 1.5 mmol (40, 80, 200% mole excess) of Mn$_2$(CO)$_{10}$. MnO$_2$ peaks are marked with asterisks (PDF #-00-42-1169).

According to **Fig. 4.12**, the initial head-tail nanoparticles having the head diameter *ca.* 16 nm and tail width *ca.* 9 nm formed in the presence of a slight excess of Mn$_2$(CO)$_{10}$ relative to Ph$_3$Sb 1.59 mmol of NaBH$_4$ (**Fig. 4.12 a, b**) turn into mixed spheres (diameter *ca.* 18 nm) and rods (width *ca.* 9 nm) 3 h after introduction of excess Mn$_2$(CO)$_{10}$ (0.9 mmol). After 5 h reaction time almost all these mixed morphologies have converted to spherical-shaped nanoparticles with a diameter *ca.* 8 nm. As shown in **Fig. 4.13** a minor amount of elemental Sb appears along with the majority MnSb phase in the presence of a near-stoichiometric Mn$_2$(CO)$_{10}$ amount. However, this minor phase disappears upon the introduction of more Mn$_2$(CO)$_{10}$ to the mixture and heating for an additional 3-8 h. A control experiment was carried out to determine whether this morphological transformation was actually an effect of additional Mn$_2$(CO)$_{10}$ or an effect of extended reaction time.
**Figure 4.12:** Low and high magnification TEM images showing the transformation of initial elongated head-tail nanorods, [(a) (low mag), (b) (high mag)] into mixed head-tail nanorod and spherical nanoparticles 3h after adding 0.9 mmol of Mn$_2$(CO)$_{10}$ [(c) (low mag), (d) (high mag)] and into spherical nanoparticles after 5 h total [(e) (low mag), (f) (high mag)].

An initial reaction mixture having near-stoichiometric Mn$_2$(CO)$_{10}$ (0.6 mmol) was heated for 8 h at 250 °C. **Fig. 4.14** shows the TEM images (low mag and high mag) and PXRD pattern of the reaction product. According to these TEM images, after an extended reaction time (8 h), the sample was still dominated by elongated head-tail nanoparticles or nanorods, with only a minute amount of spherical nanoparticles. The PXRD pattern indicates the presence of Sb (minor phase) and MnSb (major phase). This suggests that the main driver for the morphology is the Mn$_2$(CO)$_{10}$ concentration relative to Ph$_3$Sb and NaBH$_4$. 
Figure 4.13: PXRD patterns of near-stoichiometric \( \text{Mn}_2(\text{CO})_{10} \) containing reaction mixture and upon the introduction of excess \( \text{Mn}_2(\text{CO})_{10} \) to the near-stoichiometric \( \text{Mn}_2(\text{CO})_{10} \) containing the reaction mixture after 3 and 5 h carried out in the presence of 1.59 mmol \( \text{NaBH}_4 \).

Figure 4.14: (a) Low magnification and (b) high magnification TEM images (c) PXRD pattern of the \( \text{MnSb} \) nanoparticles synthesized under near stoichiometric \( \text{Mn}_2(\text{CO})_{10} \) amount with \( \text{NaBH}_4 \) (1.59 mmol) after heating for a total of 8 h.
Based on the above observations, we surmise that in the presence of excess Mn$_2$(CO)$_{10}$, elongated MnSb nanoparticles transform into spherical nanoparticles. While the mechanism is not clear, we hypothesize that the narrow areas between two swollen Sb-rich islands, as shown in Fig. 4.8 (a) and 4.12 (c), are likely vulnerable to particle etching. Hence, the excess Mn$_2$(CO)$_{10}$ in the solution can attach to the open facets and “pinch-off” a particle. Alternatively (or in addition) the shape may be related to surface energetics for manganese oxide shells, with thick shells dictating spherical geometry.

4.3.5 Magnetic Properties of the Elongated Head-Tail vs Spherical MnSb Nanoparticles

Our prior studies established that MnSb nanoparticles prepared with excess Mn and without NaBH$_4$ are ferromagnetic, as expected, with Tc> 340K (operating limit of our instrument; bulk MnSb has a Tc of 572K) with superparamagnetic blocking temperature ($T_B$, obtained from zero-field and field-cooled data) in the range 245-255 K, but very small per-Mn moments (0.04 BM$^{101}$ vs. ca 3.5 BM$^{159}$ reported for bulk MnSb). The small moments were attributed to a large volume fraction of amorphous manganese oxide, motivating our study of the use of a reducing agent to limit oxide formation. Accordingly, the elongated MnSb head-tail nanoparticles synthesized under near-stoichiometric Mn$_2$(CO)$_{10}$ and in the presence of 0.79 mmol NaBH$_4$ were evaluated for comparison. Fig. 4.15 (a) shows the magnetization per mole of Mn (M) vs applied magnetic field (H) data obtained at 50 K. Additionally, M vs. H data were acquired on nanoparticles prepared with excess Mn$_2$(CO)$_{10}$, respectively, also in the presence of 0.79 mmol NaBH$_4$, and are shown in Fig. 4.15 (b). It is evident from comparison of Fig. 4.15 (a, b) that the sample prepared with near-stoichiometric Mn has a larger moment (saturation magnetization) than the one with excess Mn. Additionally, there is also a significant paramagnetic component when excess Mn is present, as indicated by the linearity in the M vs H at higher field in Fig. 4.15
(b). Subtracting this component yields the M vs H curve shown in the lower inset of Fig. 4.15 (b) from which an estimated ferromagnetic moment of 0.04 BM/mol Mn is obtained for the ca 8 nm spherical particles, the same as obtained in our prior study.

![Figure 4.15](image-url)

**Figure 4.15:** Field dependence of the DC molar magnetization (M) (normalized to Mn moles) recorded at different magnetic fields (H) at 50 K for MnSb nanoparticles synthesized (a) with near-stoichiometric Mn$_2$(CO)$_{10}$ amount (0.6 mmol) and (b) with excess Mn$_2$(CO)$_{10}$ (1.5 mmol) in the presence of 1.0 mmol of Ph$_3$Sb and 0.79 mmol NaBH$_4$ (250 °C for 3 h). The top insets show an enlarged image of the loops of the hysteresis curve obtained at 50 K; the bottom inset in Fig 4.15 (b) shows that curve after subtraction of paramagnetic background component.

Thus, regardless of the inclusion of NaBH$_4$ in the reaction, in all cases where Mn is present in excess, a significant reduction in ferromagnetic MnSb occurs. In contrast, when Mn concentration is limited and NaBH$_4$ is present, a moment of 0.8 BM/mol Mn is obtained, consistent with our original hypothesis. Using this value as representative of “nanoscale MnSb”, we can compute the relative moment of the ferromagnetic (presumably MnSb, 0.8 BM) to paramagnetic portion of the sample in Fig. 4.15 (b). These data suggest that >75% by mass of MnSb samples prepared with excess Mn is attributable to a paramagnetic phase, most likely an amorphous oxide. Applying this formulation, in our ca ~8 nm particles, the ferromagnetic MnSb core would be ~5 nm in diameter.
In addition, there is also evidence for a second magnetic phase in samples prepared with excess Mn. Note that in the case of the near-stoichiometric Mn$_2$(CO)$_{10}$ amount, the hysteresis loop reflects a coercivity of \textit{ca.} 150 Oe. In contrast, for the sample prepared with excess Mn$_2$(CO)$_{10}$ the hysteresis loop is much narrower, indicative of a coercivity of \textit{ca.} 67 Oe. Moreover, with excess Mn, the hysteresis loop demonstrates a small asymmetry, a thinning of the loop (\textit{goose-neck} effect) close to zero applied field. We attributed this previously to metamagnetism;\textsuperscript{101} however, in the absence of evidence for metamagnetism in bulk MnSb, it is more likely that the asymmetry is indicative of a second magnetic phase.\textsuperscript{160-161}

As the samples in \textbf{Fig. 4.15 (a, b)} were prepared under different conditions, we cannot discern whether the differences in magnetic response are a function of morphology or just reflect the relative volumes of crystalline MnSb. However, we can say that while the morphology of the samples prepared in the presence of NaBH$_4$ with near-stoichiometric Mn is complex, the magnetism is fairly simple and indicative of MnSb as the only magnetic phase (albeit with 25\% of the expected moment). In contrast, with excess Mn where well-formed spherical particles are produced, there appear to be two ferromagnetic contributors (both minor), and the major product is paramagnetic.

\textbf{4.4 Conclusion}

The addition of NaBH$_4$ into the previously reported MnSb nanoparticle system eliminates the necessity of adding an excess amount of Mn$_2$(CO)$_{10}$ that can compensate for the adventitious oxygen source that leads to MnO$_x$. This approach changes the particle morphology into elongated head-tail structures, in which the heads are slightly rich in Sb, and the tail composed of more or less equal amounts of Mn and Sb. The formation of these head-tail morphologies can be explained by the Solution-Solid-Solid (SSS) growth mechanism, in which Sb-rich Mn-Sb
clusters serve as solid catalysts that trigger the formation of the MnSb tail along the <001> direction. We also show that there is a morphological transformation between the elongated head-tail nanoparticles and spherical shape nanoparticles upon introduction of more Mn$_2$(CO)$_{10}$ into the previously prepared head-tail nanoparticles. The saturation magnetic moment of these head-tail nanoparticles is about twenty times higher (0.8 BM/MnSb) compared to the saturation magnetic moment of previously reported spherical shape MnSb nanoparticles (CHAPTER 3), or the ones reported herein prepared with excess Mn.
CHAPTER 5 -SYNTHESIS OF TERNARY PHASE MnAsxSbx-1x NANOPARTICLES:
CONSEQUENCES OF COMPOSITIONAL INHOMOGENEITY, AND MAGNETIC
PROPERTIES

5.1 Introduction

Introduction of cation and anions to bulk MnAs paves a way to tune the FOPT
temperature, producing a range of materials with FOPT’s spanning the temperature of interest.51-52, 62-63 In the bulk phase, the MnSbxAs1-x ternary phase forms solid solutions over all x.60-61 The Curie temperature of bulk MnSbxAs1-x is highly compositional dependent, wherein the composition of MnSb0.1As0.9 possesses a Tc of ca. 280 K. The Tc decreases until the composition MnSb0.3As0.7, which has the minimum Tc of the series at ca. 200 K. Then the Tc start rising up to ca. 587 K giving the maximum Tc for MnSb0.9As0.1.

There is no structural transformation from the NiAs-type for MnSbxAs1-x observed for x ≥0.1. However, for the concentration range of x=0 to 0.1 the transition from the FM hexagonal phase to the PM orthorhombic phase is first-order. Further, it is also reported that for the compositions of x=0.1 and x=0.05 no thermal hysteresis behavior is observed in a magnetic field of 1 T.52 The magnetic transition becomes second order in the range of x=0.1 to 0.9, and there is no accompanying structural change. However, the x>0.1 phases exhibit high ∆SM, hence high MCE at their Tc.52 Nanostructuring of MnSbxAs1-x is expected to lead to improved functionality for magnetic refrigeration because reducing the size of the material down to the nano scale is expected to reduce the thermal hysteresis,62 forming a graded nano structures that enable a range of Tc’s to be accessed.

In this chapter we describe the synthesis of a series of MnAsxSbx-1x (x=0.1-0.9) nanoparticles by employing the knowledge developed by the Brock group for the synthesis of discrete MnAs nanoparticles90-92 and MnSb nanoparticles (CHAPTER 3 and 4).101 Further, the
compositional distribution within a nanoparticle and the magnetic properties with respect to the target composition MnAs$_{0.5}$Sb$_{0.5}$, are discussed in detail.

5.2 Experimental

5.2.1 Synthesis of MnAs$_x$Sb$_{1-x}$ Nanoparticles: slow heating-one pot synthesis

Mn$_2$(CO)$_{10}$ (0.5-1.2 mmol), Ph$_3$Sb (0.1-0.9 mmol), Ph$_3$AsO (0.1-0.9 mmol) were mixed along with 1-ODE (20-30 mL) and TOPO (4.0 g) in a single Schlenk flask in a glove box filled with argon (Ar). The sealed Schlenk flask was then removed from the glove box, to a Schlenk line in a fume hood. The contents in the flask were then evacuated for 20 min followed by Ar purging for about another 20 min at 60 °C. The contents were then slowly heated (20°C/10 min) up to 180°C under Ar to avoid any volatilization of Mn$_2$(CO)$_{10}$. Then, the temperature was rapidly increased up to 250-300 °C and maintained for 1-6 h. The final black product was allowed to cool naturally to room temperature. The product was dispersed in chloroform and precipitated with ethanol followed by centrifugation. This process was repeated several times and then the product was dried under vacuum.

5.2.2 Characterization

The synthesized ternary phase MnAs$_x$Sb$_{1-x}$ (x=0.1-0.9) nanoparticles were characterized by Powder X-ray Diffraction (PXRD), Transmission Electron Microscopy (TEM), X-Ray Fluorescence Spectrometry (XRF), High Angle Annular Dark Field-Scanning Transmission Electron Microscopy (HAADF-STEM), Inductively Coupled Plasma – Mass Spectrometry (ICP-MS), and magnetometry. The basic principles and function of above instruments are described in CHAPTER 2.
5.3 Results and Discussion

The synthesis methodology of discrete MnAs$_x$Sb$_{1-x}$ nanoparticles was based on the synthetic route of MnSb nanoparticles reported by the Brock group with some modifications. In this synthetic protocol, the reactant precursors of Mn$_2$(CO)$_{10}$, Ph$_3$Sb, and Ph$_3$AsO were mixed together along with the stabilizing ligand, TOPO, and the solvent, 1-ODE. The contents in the flask were then heated to 250-300 °C for 1-6 h. As per the knowledge gained by the previous synthesis we sought to begin with a slight molar excess of Mn (1.1 mmol) with respect to Ph$_3$Sb and Ph$_3$AsO (totaling 1 mmol).

In the initial attempts of synthesizing MnAs$_x$Sb$_{1-x}$ nanoparticles, the reaction time and the reaction temperature were maintained at 3 h and 250 °C, respectively, based on the synthetic protocol previously reported for MnSb nanoparticle synthesis. Fig. 5.1 shows the PXRD pattern obtained for the synthesis (initial attempt 0.5 mmol As:0.5 mmol Sb: 1.1 mmol Mn) carried out at 250°C for 3 h. According to Fig. 5.1, the PXRD pattern is consistent with the MnSb phase (hexagonal) with a shift to higher 2Θ values along with a significant amount of elemental Sb, similar to our experiences with MnSb nanoparticle synthesis. With the knowledge in hand regarding the synthesis of one of the end products of the MnAs$_x$Sb$_{1-x}$ series, i.e. MnSb nanoparticles, we hypothesized that the Sb formation could be a consequence of reaction time, reaction temperature or a deficiency of Mn$_2$(CO)$_{10}$ precursor.
5.3.1 Effect of Reaction Time and Reaction Temperature

In order to check the effect of reaction time we sought to heat the reactants for shorter (1 h) and longer (6 h) reaction times (Fig. 5.2). However, the peaks for elemental Sb are prominent in both samples suggesting time is not a critical parameter (Fig. 5.2).

Therefore, we sought to keep the reaction time at 3 h, and tried to optimize the reaction by increasing the temperature from the ideal value for MnSb towards the higher temperature required by MnAs (330 °C). However, as evident in the intensities of the peaks corresponding to elemental Sb, this impurity actually increases upon the rise of the temperature from 265 to 300 °C.

**Figure 5.1:** PXRD pattern of initial synthesis of MnAs$_{0.5}$Sb$_{0.5}$ nanoparticles (target composition) using 1.1 mmol of Mn and heating the reaction mixture at 250 °C for 3 h (MnSb-PDF#-03-065-0388, Sb-PDF#-00-035-0732).

**Figure 5.2:** PXRD patterns of the syntheses showing the effect of reaction time when heated at 250 °C in the presence of 1.1 mmol of Mn. (MnSb-PDF#-03-065-0388, Sb-PDF#-00-035-0732)
°C (Fig. 5.3). Therefore, we kept the temperature at 250 °C as reported for MnSb nanoparticle synthesis.

![PXRD patterns of the syntheses showing the effect of reaction temperature towards the MnAs<sub>0.5</sub>Sb<sub>0.5</sub> nanoparticles (target composition) synthesis in the presence of 1.1 mmol of Mn and heated for 3 h (MnSb-PDF#-03-065-0388, Sb-PDF#-00-035-0732)](image)

**Figure 5.3:** PXRD patterns of the syntheses showing the effect of reaction temperature towards the MnAs<sub>0.5</sub>Sb<sub>0.5</sub> nanoparticles (target composition) synthesis in the presence of 1.1 mmol of Mn and heated for 3 h (MnSb-PDF#-03-065-0388, Sb-PDF#-00-035-0732)

As clearly evident by the two PXRD patterns at 280 °C and 300 °C, the peaks for MnSb phase appear asymmetric. This may be due to the presence of multiple phases in the target MnAs<sub>x</sub>Sb<sub>1-x</sub> phase. In order to avoid the segregation of elemental Sb, we sought to add a mild reducing agent, NaBH<sub>4</sub>, as described in **CHAPTER 4** for MnSb nanoparticle synthesis. However, all the attempts failed, resulting in phase segregation into MnSb and MnAs (Fig. 5.4).

![Effect of NaBH<sub>4</sub> addition towards the MnAs<sub>x</sub>Sb<sub>1-x</sub> nanoparticle synthesis (MnSb-PDF#-03-065-0388, MnAs-PDF#-00-028-0644)](image)

**Figure 5.4:** Effect of NaBH<sub>4</sub> addition towards the MnAs<sub>x</sub>Sb<sub>1-x</sub> nanoparticle synthesis (MnSb-PDF#-03-065-0388, MnAs-PDF#-00-028-0644).
5.3.2 Effect of Excess Mn\(_2\)(CO)\(_{10}\) Addition

We then hypothesized that the elemental Sb deposition is due to the absence of excess Mn\(_2\)(CO)\(_{10}\), assuming inevitable losses due to oxidized by-products. Therefore, the Mn amount was gradually increased from 1.1 mmol to 1.5 mmol, maintaining the reaction conditions of 250\(^\circ\)C for 3 h. Fig. 5.4 shows the PXRD patterns relative to the amount of Mn\(_2\)(CO)\(_{10}\) addition.

![PXRD patterns](image)

**Figure 5.5**: PXRD patterns of MnAs\(_{0.5}\)Sb\(_{0.5}\) (target composition) synthesized using different amounts of Mn (MnSb-PDF#-03-065-0388, Sb-PDF#-00-035-0732).

According to Fig. 5.5, the elemental Sb peak appears at ca. 28 degrees (2\(\theta\)) when the Mn amount is 1.1 mmol (Fig. 5.5 (a)), diminishes when the Mn amount is 1.2 mmol (Fig. 5.5 (b)), and disappears when the Mn amount is 1.5 mmol (Fig. 5.5 (c)). However, in the cases of 1.1 and 1.2 mmol of Mn addition, the peaks for MnAs\(_x\)Sb\(_{1-x}\) phase appear broad. However, when the Mn is capable of getting rid of all Sb, the corresponding peaks for the possible ternary system become narrower, albeit remaining asymmetric, perhaps suggesting some degree of homogenation as the Mn content is increased. Collectively taken, the excess Mn is likely reacting with elemental Sb in the reaction mixture. As previously described in CHAPTER 3 and 4, the
The necessity of excess $\text{Mn}_2(\text{CO})_{10}$ in the reaction mixture could be due to the high volatility of $\text{Mn}_2(\text{CO})_{10}$ and/or ‘in-situ’ oxidation by an adventitious oxygen source. This phenomenon will be further discussed later in this section. After optimizing the reaction conditions for the 50:50 composition, a series of compositions was synthesized targeting $x=0.1$ to 0.9. The Powder X-ray Diffraction (PXRD) and Transmission Electron Microscopy (TEM) images of individual nanoparticles of $\text{MnAs}_{x}\text{Sb}_{1-x}$ ($x=0.1-0.8$) are shown in Fig. 5.6 (a) and (b).

The PXRD patterns were normalized with respect to an internal Si standard (peaks are indicated as asterisks marks near 28 and 47 degrees ($2\Theta$)). PXRD patterns of materials with composition $x=0.1-0.8$ were closely related to the hexagonal NiAs type MnSb structure (PDF#: 03-065-0388) with a slight shift to higher $2\Theta$ values with increasing As. Owing to the small atomic size relative to Sb, incorporation of As into the MnSb lattice is expected to decrease/compress the MnSb lattice dimensions, causing the PXRD pattern to shift towards higher $2\Theta$ values (Fig. 5.6 (a)).

![Figure 5.6 (a): PXRD pattern of $\text{MnAs}_{x}\text{Sb}_{1-x}$ ($x=0.1-0.8$) nanoparticles normalized with respect to Si standard. Peaks for Si are shown with asterisks marks (MnSb-PDF#-03-065-0388).](image)
The nanoparticle samples have low polydispersity, with particles that are spherical in shape with an average diameter of *ca.* 10-13 nm.

As expected, the PXRD pattern of the composition MnAs$_{0.9}$Sb$_{0.1}$ was closely related to the orthorhombic MnAs phase (PDF #01-071-0923), exhibiting a shift towards lower 2\(\Theta\), suggesting increase in unit cell size, consistent with Sb incorporation. The nanoparticles appear spherical in shape with the average diameter of *ca.* 13 nm (*Fig. 5.7 (a) and (b)*).
5.3.3 Elemental Composition and Lattice Refinement

In order to check the actual elemental compositions of these nanoparticles relative to the target elemental compositions, solid powder samples of these compositions were analyzed by XRF. Table 5.1 shows the differences between the target compositions and the actual compositions determined by XRF.

Table 5.1: Differences between the target and the actual compositions of MnAs$_x$Sb$_{1-x}$ nanoparticles determined by XRF

<table>
<thead>
<tr>
<th>Target composition</th>
<th>Actual composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnAs$<em>{0.1}$Sb$</em>{0.9}$</td>
<td>MnAs$<em>{0.03}$Sb$</em>{0.95}$</td>
</tr>
<tr>
<td>MnAs$<em>{0.2}$Sb$</em>{0.8}$</td>
<td>MnAs$<em>{0.06}$Sb$</em>{0.92}$</td>
</tr>
<tr>
<td>MnAs$<em>{0.3}$Sb$</em>{0.7}$</td>
<td>MnAs$<em>{0.13}$Sb$</em>{0.87}$</td>
</tr>
<tr>
<td>MnAs$<em>{0.4}$Sb$</em>{0.6}$</td>
<td>MnAs$<em>{0.14}$Sb$</em>{0.86}$</td>
</tr>
<tr>
<td>MnAs$<em>{0.5}$Sb$</em>{0.5}$</td>
<td>MnAs$<em>{0.31}$Sb$</em>{0.69}$</td>
</tr>
<tr>
<td>MnAs$<em>{0.6}$Sb$</em>{0.4}$</td>
<td>MnAs$<em>{0.46}$Sb$</em>{0.60}$</td>
</tr>
<tr>
<td>MnAs$<em>{0.7}$Sb$</em>{0.3}$</td>
<td>MnAs$<em>{0.52}$Sb$</em>{0.48}$</td>
</tr>
<tr>
<td>MnAs$<em>{0.8}$Sb$</em>{0.2}$</td>
<td>MnAs$<em>{0.57}$Sb$</em>{0.43}$</td>
</tr>
<tr>
<td>MnAs$<em>{0.9}$Sb$</em>{0.1}$</td>
<td>MnAs$<em>{0.85}$Sb$</em>{0.15}$</td>
</tr>
</tbody>
</table>

Figure 5.8 Graphical representation of target composition vs actual composition (the solid red line indicates expected trend in compositions, the dotted lines provide a guidance to the eyes).

According to Table 5.1, the actual compositions deviate from the target compositions, mostly by giving low As content. The cell parameters of the compounds (MnAs$_{0.1}$Sb$_{0.9}$ to MnAs$_{0.8}$Sb$_{0.2}$) were refined by CELREF version 3, using high intensity peaks in the PXRD [(011), (012), and (110)], calibrated by Si as an internal standard. The refined lattice parameters $a$, $c$, and the cell volume of the hexagonal crystal structures are given in Table 5.2. The graphical representations are shown in Fig. 5.9.
Table 5.2: Refined lattice parameters of hexagonal crystal structures of MnAs$_{0.1}$Sb$_{0.9}$ to MnAs$_{0.8}$Sb$_{0.2}$

<table>
<thead>
<tr>
<th>Target composition</th>
<th>$a$ [Å]</th>
<th>$c$ [Å]</th>
<th>$V$ [Å$^3$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnAs$<em>{0.1}$Sb$</em>{0.9}$</td>
<td>4.1300(62)</td>
<td>5.7897(56)</td>
<td>85.52(15)</td>
</tr>
<tr>
<td>MnAs$<em>{0.2}$Sb$</em>{0.8}$</td>
<td>4.1228(36)</td>
<td>5.8048(33)</td>
<td>85.45(09)</td>
</tr>
<tr>
<td>MnAs$<em>{0.3}$Sb$</em>{0.7}$</td>
<td>4.1073(41)</td>
<td>5.7829(38)</td>
<td>84.49(10)</td>
</tr>
<tr>
<td>MnAs$<em>{0.4}$Sb$</em>{0.6}$</td>
<td>4.1095(32)</td>
<td>5.7860(30)</td>
<td>84.62(08)</td>
</tr>
<tr>
<td>MnAs$<em>{0.5}$Sb$</em>{0.5}$</td>
<td>4.1049(10)</td>
<td>5.7886(09)</td>
<td>84.47(03)</td>
</tr>
<tr>
<td>MnAs$<em>{0.6}$Sb$</em>{0.4}$</td>
<td>4.0919(17)</td>
<td>5.7825(15)</td>
<td>83.85(04)</td>
</tr>
<tr>
<td>MnAs$<em>{0.7}$Sb$</em>{0.3}$</td>
<td>4.0874(02)</td>
<td>5.8008(02)</td>
<td>83.93(01)</td>
</tr>
<tr>
<td>MnAs$<em>{0.8}$Sb$</em>{0.2}$</td>
<td>4.0898(51)</td>
<td>5.7891(48)</td>
<td>83.86(13)</td>
</tr>
</tbody>
</table>

Figure 5.9: The refined lattice parameters of target compositions MnAs$_x$Sb$_{1-x}$ (x=0.1-0.8) (a) $a$ axis (b) $c$ axis (c) cell volume.
The lattice refined data show a decrease in lattice parameter $a$, upon the increase of As amount. The cell volume also follows the similar trend upon the increase of As amount. However, the lattice parameter $c$, remains scattered around a minute $c$ value change. Overall, the change in $a$ value is larger than the $c$ value. A similar trend has been reported for bulk phases having $a$ decreasing systematically with As composition, while changes in $c$ are minimal.\textsuperscript{162} Taking into account the two parent structures, i.e. MnAs and MnSb, the difference in the $a$ axis between these two are 13\%, while the variation of $c$ axis is around 1\%.\textsuperscript{162}

The elemental distribution of these nanoparticles was probed, and the elemental mapping data are shown in \textbf{Fig. 5.10} for a nanoparticle with the representative composition of MnAs\textsubscript{0.5}Sb\textsubscript{0.5} (target composition). According to the HAADF-STEM image of a single particle, the MnAs\textsubscript{0.5}Sb\textsubscript{0.5} nanoparticle is composed of a high contrast crystalline core and an amorphous shell (\textbf{Fig. 5.10 (a)}). As revealed by elemental mapping, Mn and O are more concentrated in the shell area while As is essentially concentrated in the core. Even though a considerable amount of Sb is loaded into the core, it is also distributed throughout the entire particle (\textbf{Fig. 5.10 (a-h)}). A line scan obtained for the same composition nanoparticle (MnAs\textsubscript{0.5}Sb\textsubscript{0.5}) is shown in \textbf{Fig. 5.10 (k)}. According to the line scan, we see two regions of inhomogeneity. The shell is composed largely of Sb whereas As is largely segregated to the core. Oxygen is evident in high intensity in the shell area suggestive of surface oxidation. The Mn concentration decreases in the core relative to the shell, just as the As signal grows in, and the Sb signal intensifies suggesting a significant deficiency of Mn in the core. Modeling as a sphere of $ca$ 16 nm, the core is likely an Sb-As alloy (4 nm) with an 8 nm thick shell of MnSb on the surface.
According to the literature, the lattice matching of MnSb with Sb is fairly good. In both MnSb and Sb lattices, Sb triangular lattice planes are stacked along the c axis, making in-plane lattice mismatch of a axis. Therefore, As-Sb alloy core can impart an epitaxial strain (ca. 1.7%) on the MnSb shell by altering the lattice parameters of the MnSb.

5.3.4 Magnetic Properties of MnAs_xSb_{1-x} nanoparticles

In order to evaluate the magnetic properties of these compositions with respect to the compositional inhomogeneity, temperature (T) dependence of the molar magnetization (M)
(normalized to Mn moles) under Zero-Field-Cooled (ZFC) and Field-Cooled (FC) conditions over the temperature range 10-320 K and under an external magnetic field of 100 Oe) were determined for the target composition MnAs$_{0.5}$Sb$_{0.5}$. Additionally, the magnetic field dependence (H) of the molar magnetization (M) (at 50 and 300 K) were acquired (Fig. 5.11).

Figure 5.11: (a) Temperature dependence of the DC molar magnetization (M) (normalized to Mn moles) recorded under Zero-Field-Cooled (ZFC) and Field-Cooled (FC) conditions (collected at 100 Oe) (b) Field dependence of the DC molar magnetization (M) (normalized to Mn moles) recorded at different magnetic fields (H) at 300 K and 50 K for the target nanoparticle composition of MnAs$_{0.5}$Sb$_{0.5}$. The inset shows an enlarged image of the loop of the hysteresis curves obtained at 300 K and 50 K.

According to Fig. 5.11 (a), The FC plot shows a monotonous increase of molar magnetization with decrease of temperature from 320 K. In the corresponding ZFC curve the sample shows a broad maximum in the range of 50-100 K. It seems that the intersection of FC with the ZFC curve takes place close to 320 K. Collectively taken, the above behavior closely represents the behavior of superparamagnetic nanoparticles. The Blocking temperature ($T_B$), in which the peak maximum of ZFC curve is attained in the range of 50-100 K. In general, $T_B$ depends on the size and the anisotropy (magnetic and shape) of a nanoparticle. The broad distribution of $T_B$ is an indication of sample polydispersity. However, according to Fig. 2(b) the
particle size distribution has low polydispersity (13.0±1.5 nm). Moreover, the magnetization of the FC curve monotonically increases upon the decrease of the temperature, without being saturated. These behaviors can be attributed to the sample inhomogeneity,\textsuperscript{163} i.e. the presence of more than one phase within a nanoparticle as revealed by line scan and the elemental mapping data (Fig. 5.10).

**Fig. 5.11 (b)** shows the field dependence of DC molar magnetization (M) recorded at different magnetic fields (H) measured at 50 K and 300 K for the nanoparticle sample of MnAs\textsubscript{0.5}Sb\textsubscript{0.5} (target composition). According to the M-H curve, magnetic hysteresis is present both at 50 K and 300 K. However, the hysteresis loop is narrower at 300 K, compared to the 50 K, indicative of lower hysteresis at 300 K. The corresponding coercivities are *ca.* 200 Oe and 400 Oe at 300 K and 50 K, respectively.

When comparing the above magnetic data with that of the nanoparticles of the two end products, i.e. MnAs and MnSb, the behavior of ZFC and FC curves mostly resembles that of the MnSb nanoparticles, in appearance.\textsuperscript{101} However, the T\textsubscript{B} value is much smaller in the MnAs\textsubscript{0.5}Sb\textsubscript{0.5} nanoparticles compared to that of MnSb nanoparticles (*ca.* 50-100 K vs 245-255 K) previously reported.\textsuperscript{101} This is attributed to the smaller volume of MnSb nanoparticles. The T\textsubscript{c} of bulk MnAs\textsubscript{0.5}Sb\textsubscript{0.5} appears at *ca.* 250 K.\textsuperscript{162} The β-MnAs nanoparticles of *ca.* 12 nm size exhibit coercivity value of 216 Oe (at 20 K), while MnSb nanoparticles of *ca.* 13 nm possess 150 Oe (at 50 K) coercivity.

### 5.4 Conclusions

The compositions of MnAs\textsubscript{x}Sb\textsubscript{1-x} (x=0.1-0.9) were synthesized by employing the MnAs and MnSb synthetic protocols with slight modifications. The PXRD patterns appear phase-pure, however, the corresponding peaks appear asymmetric indicating the presence of multiple peaks.
There is also evidence of compositional inhomogeneity by line scan and the elemental mapping data, and compositions are all As-poor relative to the target compositions. According to line scan and the elemental mapping data obtained for MnAs$_{0.5}$Sb$_{0.5}$ nanoparticles (target composition), As and Sb have concentrated in the core of the nanoparticles forming a crystalline core. Mn, Sb and O are more abundant in the shell structure. The presence of an MnSb shell on the As-Sb core imparts an epitaxial strain on the MnSb crystal structure. The asymmetry of the peaks of the PXRD pattern could be an effect of non-uniform strain and/or the presence of a overlapping peak due to crystalline As-Sb core. The magnetic behavior of the corresponding sample represents the inhomogeneity of the sample having broad $T_B$ and monotonous increase of the FC curve. Comparatively, the target composition of MnAs$_{0.5}$Sb$_{0.5}$ nanoparticles possess lower $T_B$ and higher coercivity values compared to the MnAs and MnSb nanoparticles.

Note that $M$ vs $H$ and $M$ vs $T$ (ZFC and FC) results on other MnAs$_x$Sb$_{1-x}$ ($x=0.1,0.2,0.7,0.9$) nanoparticle compositions were also collected and are presented in Appendix A.
6.1 Introduction

Nanoparticle assemblies of porous three-dimensional (3-D) architectures are expected to provide coupled magnetic properties when compared to the discrete nanoparticles. These assembled nanostructures may be more favorable for functional MR in terms of high surface area of contact with the heat transfer fluid,\textsuperscript{71} mechanical stability during the refrigeration cycling,\textsuperscript{72} and lower magnetic hysteresis owing to the small size of the nanoparticles.\textsuperscript{73}

Discrete nanoparticles can be assembled into the 3-D architectures by employing different methods. The Brock group has pioneered the sol-gel assembly of metal chalcogenide\textsuperscript{78-83} and phosphide\textsuperscript{84-85} nanoparticles by surface oxidation, metal assisted bridging and covalent-metal (Sn\textsuperscript{4+}) assisted crosslinking. The studies in CHAPTER 6 are focused on assembling Fe\textsubscript{2-x}Ni\textsubscript{x}P nanoparticles into a 3-D network and evaluating the magnetic properties of the composite. Discrete nanoparticle systems of Fe\textsubscript{2-x}Ni\textsubscript{x}P are well-established and compositions over all values of x are reported. Nanoparticles of Fe\textsubscript{2-x}Ni\textsubscript{x}P systems where x= 0.2 (Fe\textsubscript{1.8}Ni\textsubscript{0.2}P) and x=0.6 (Fe\textsubscript{1.4}Ni\textsubscript{0.6}P), are reported to have T\textsubscript{c}’s close to room temperature (250 and 265 K, respectively). However, we elected to probe Fe\textsubscript{1.2}Ni\textsubscript{0.8}P, owing to the fact that the T\textsubscript{c} value of Fe\textsubscript{1.2}Ni\textsubscript{0.8}P nanoparticle composition is well below room temperature (125 K for nano and 140 K for bulk), therefore, easy to probe with a conventional magnetometer, and the particle morphology is elongated\textsuperscript{164} leading uniaxial magnetic anisotropy along c and forming more robust gels.\textsuperscript{165} In addition to enabling MR, we hypothesized that interconnecting these nanoparticles into three-dimensional (3-D) architectures would enhance the magnetic properties, and perhaps result in magneto-compliant porous solids. By this study we expect to understand how porous
nanocomposites behave relative to discrete nanoparticles with regard to their magnetic properties.

6.2 Experimental

6.2.1 Synthesis of Fe\textsubscript{1.2}Ni\textsubscript{0.8}P Nanoparticles

Nanoparticles of composition Fe\textsubscript{1.2}Ni\textsubscript{0.8}P were synthesized using the methods developed by the Brock group\textsuperscript{166}. Briefly, a mixture of Ni(acac)\textsubscript{2}, oleylamine, octylether, and TOP was degassed and heated to 230 °C to yield a black solution, comprising amorphous Ni-P particles. Fe(CO)\textsubscript{5} was then added (in a 1.2 Fe:0.8 Ni ratio) and the content was heated further at 230 °C for another 30 min to yield Ni-Fe-P amorphous particles, and then heated to 350 °C for 10 h to induce crystallization.

6.2.2 Thiolate Exchange of Ternary phosphide Nanoparticles

The surface ligand exchange of the above nanoparticles was carried out using 11-MUA or 1-DDT, in 1:4 metal to ligand ratio. The amount of ligand required was estimated by the formula weight of the corresponding nanoparticles, assuming no contribution by the surface ligands (oleylamine or TOP) towards the mass of the product. The surface ligand exchanges with 11-MUA or 1-DDT were carried out following the reported procedures for InP\textsuperscript{84} and Ni\textsubscript{2}P\textsuperscript{85} nanoparticles, respectively.

6.2.3 Wet Gel and Aerogel Formation

The ligand exchanged nanoparticles were then subjected to oxidative-induced gelation using 3% H\textsubscript{2}O\textsubscript{2}. The thiolate capped nanoparticles were dispersed in absolute ethanol (3-5 mL) in a polyethylene vial. An aqueous solution of 3% H\textsubscript{2}O\textsubscript{2} (65-100 µL) was added into this dispersion, and the vial was briefly agitated. The gelation starts in 11-MUA exchanged nanoparticles in approximately 30 min, while the gelation of 1-DDT capped nanoparticles can be
observed after about 12 h. The vials were then kept aging for about 14 days. The resultant wet
gels were then supercritically dried using a critical point dryer as described in CHAPTER 2 of
this dissertation.

6.2.4 Characterization

The synthesized Fe$_{1.2}$Ni$_{0.8}$P nanoparticles, and their corresponding aerogels were
characterized by Powder X-Ray Diffraction (PXRD), Transmission Electron Microscopy (TEM),
Energy Dispersive Spectroscopy (EDS), Nitrogen adsorption/desorption, Thermo Gravimetric
Analysis (TGA) and magnetometry. The basic principles and function of the above instruments
are described in CHAPTER 2.

6.3 Results and Discussion

Three-dimensional assembly of discrete nanoparticles of Fe$_{1.2}$Ni$_{0.8}$P was based on the
methodologies developed by the Brock group for InP$^{84}$ and Ni$_2$P$^{85}$ nanoparticle assemblies, with
minor modifications. The Fe$_{1.2}$Ni$_{0.8}$P nanoparticles were thiolate exchanged using 11-MUA or 1-
DDT, and these thiolate-exchanged nanoparticles were then assembled using 3% H$_2$O$_2$ as an
oxidant. The wet gels were then aged for about 14 days, and supercritically dried to obtain
Fe$_{1.2}$Ni$_{0.8}$P aerogels.

6.3.1 Gelation of Discrete Fe$_{1.2}$Ni$_{0.8}$P Nanoparticles with Different Aspect Ratios, and
Different Functionalized Ligands

The size and the shape of Fe$_{2.4}$Ni$_x$P (0<x<2) nanoparticles are highly composition
dependent, and these nanoparticles tend to form rods when x≤0.8. At the same time, it is
reported that the aspect ratio of these nanoparticles, even in the same composition, can be altered
by using different TOP amounts. Fig. 6.1 (a-c) shows the nanoparticles synthesized by
changing volumes of TOP in the synthesis and the resultant assemblies of Fe$_{1.2}$Ni$_{0.8}$P. We were
further capable of altering the length (L) and the width (W) of the nanoparticles by using different amounts of oleylamine, as well. As reported by the Brock group, the short rods (L: 19.98±2.21 nm, W:10.76±1.59 nm and aspect ratio 1.7) of Fe$_{1.2}$Ni$_{0.8}$P nanoparticles were synthesized using 3.0 mL of TOP and 2.0 mL of oleylamine.

Increasing the TOP to 5 mL while using the same amount of oleylamine increased the length of the nanorod by about four times (89.16 ±5.81 nm) and width by about two times (20.07 ±3.62 nm) (aspect ratio 4.7) (Fig. 6.1 (b)). Furthermore, decreasing the oleylamine amount to 1.0 mL
and keeping the TOP amount unchanged at 5.0 mL, resulted in nanoparticles of length 22.53±1.69 nm and width 6.02±0.91 nm (aspect ratio 2.7) (Fig. 6.1 (c)).

These different nanoparticles were then assembled into 3-D architectures by the oxidation-induced sol-gel method. Briefly, the nanoparticles were thiolate exchanged overnight with 11-MUA in a 1:4 metal to thiol ratio, and then 3%(v/v) H₂O₂ was added as the oxidant into the purified nanoparticle dispersion in ethanol to induce gelation. After supercritically drying, a solid black monolith was obtained in each case (insets: Fig. 6.1 (d-f)). These monoliths comprise an interconnected network morphology with an extensive network of pores across a range of sizes (Fig 6.1 (d-f)).

**Figure 6.2:** The PXRD images corresponding to the aerogels in Fig. 6.1 (e-f) of the Fe₁.₂Ni₀.₈P composition synthesized by using (a) 2.0 mL of oleylamine and 3.0 mL of TOP (b) 2.0 mL of oleylamine and 5.0 mL of TOP (c) 1.0 mL of oleylamine and 5.0 mL of TOP, and thiolate exchanged using 11-MUA (Fe₂P-PDF #-00-051-0943)
The crystallite sizes of the nanoparticles obtained from the Scherrer size calculation PXRD data for samples in Fig. 6.1 (a-c) is shown in Fig. 6.2.

As shown in Fig. 6.2, the PXRD patterns of original nanoparticles and the aerogel are closely related to the PDF pattern of Fe$_2$P, with a slight shift to higher 2$\Theta$ values, indicative of Ni incorporation into the Fe$_2$P structure. According to Fig. 6.2, it seems that there is no change in the crystal structure, even after assembling the nanoparticles into a 3-D network. When calculated by the Scherrer equation,$^{152}$ the crystallite sizes of the original nanoparticles, and the

![Graphs showing nitrogen adsorption/desorption isotherms](image)

**Figure 6.3:** Nitrogen adsorption/desorption isotherms of aerogels relevant to Fig. 6.2 (d-f). Insets indicate pore size distribution
aerogel are ca. 13 nm and ca. 12 nm, respectively. The surface areas of these 3-D assemblies were determined by nitrogen adsorption/desorption by the application of Brunauer-Emmett-Teller (BET) model. The surface areas of the aerogels in Fig. 6.2 (d-f) were 89, 86, 107 m²/g, respectively. The adsorption-desorption isotherms of all three assemblies are similar in shape and represent a type IV curve, characteristic of a mesoporous (2-50 nm pore diameter) material (Fig. 6.3). Note that the pore size distribution related to the aerogel in Fig 6.2 (f) has limited to the small pore diameters, compared to that of Fig 6.2 (d) and (e).

After functionalizing the Fe₁.₂Ni₀.₈P nanoparticles using 11-MUA, we sought to functionalize the same compositional nanoparticles (synthesized using 2.0 mL oleylamine and 5.0 mL TOP) with a different ligand, 1-DDT, following the same procedure described in 6.2.2 and 6.2.3. Unlike 11-MUA, 1-DDT is a short chain ligand with no pendant carboxylate group as in 11-MUA. After supercritically drying the wet gel, a solid black monolith was obtained. The TEM image of this aerogel is shown in Fig. 6.3 (a). The PXRD patterns of the Fe₁.₂Ni₀.₈P aerogel, functionalized by 1-DDT is shown in Fig. 6.4 (b).

![Figure 6.4: (a) TEM image (b) PXRD pattern of the Fe₁.₂Ni₀.₈P nanoparticles, thiolate exchanged with 1-DDT, after 3-D assembly. The inset on Fig. 6.4 (a) shows a high magnification image of the corresponding aerogel sample.](image-url)
As revealed by the TEM, the monolith is composed of an interconnected network of nanoparticles. It is clearly observed that the initial elongated particle morphology is retained even after the aerogel formation. The Scherrer size calculation of the crystallite size of the original nanoparticles and the aerogel appears at \( ca. 13 \) nm. However, when compared to the gelation of \( \text{Fe}_{1.2}\text{Ni}_{0.8}\text{P} +11\)-MUA nanoparticles, gelation of \( \text{Fe}_{1.2}\text{Ni}_{0.8}\text{P} +1\)-DDT nanoparticles takes a much longer time to give evidence of gel formation (approximately 1 h vs. 12 h), provided that all the other conditions are identical. Moreover, the resultant monolith with \( \text{Fe}_{1.2}\text{Ni}_{0.8}\text{P} +1\)-DDT nanoparticles is more fragile compared to that of \( \text{Fe}_{1.2}\text{Ni}_{0.8}\text{P} +11\)-MUA nanoparticles. Attempts to conduct surface area measurement of this sample failed due to excessive of degassing.

As described by **CHAPTER 1** of this dissertation, it is clear that there appears two distinct mechanisms for 11- MUA capped and 1-DDT capped \( \text{Ni}_2\text{P} \) nanoparticles leading to the gelation.\(^{85}\) While both 11-MUA and 1-DDT ligands binding to the nanoparticles leads to gelation upon introduction of oxidant, the nature of the interparticle linkages is distinct. The pendent group in 11-MUA is capable of bridging metal ions, which leach out upon oxidative removal of surface thiolates, leading to metal-assisted gelation (**CHAPTER 1-Fig. 1.24**). In order to confirm this fact we sought to use EDTA as reported previously.\(^{88-89}\) EDTA is a chelating agent that can complex with transition metal ions and main group ions. Therefore, addition of EDTA is expected to remove the bridging metal ions in the aerogel, dispersing the nanoparticles and destroying the gel network. In order to test this hypothesis, an EDTA solution with concentration equal to the total metal ion concentration in the samples was prepared, and the pH was adjusted to pH 12. The EDTA solution was then added drop-wise to the aerogels (\( \text{Fe}_{1.2}\text{Ni}_{0.8}\text{P} +11\)-MUA and \( \text{Fe}_{1.2}\text{Ni}_{0.8}\text{P} +1\)-DDT) with brief agitation. After the addition of EDTA, within less than 1
min, the Fe$_{1.2}$Ni$_{0.8}$P +11-MUA gel started dispersing (Fig. 6.5 (a)). After about 5 min of EDTA addition, the residue settled down at the bottom, leaving a wine-red color supernatant (Fig. 6.5 (b)). The change in the initial colorless solution of EDTA into a wine-red color is indicative of metal binding with EDTA complex. In contrast, the addition of EDTA into the Fe$_{1.2}$Ni$_{0.8}$P +1-DDT aerogel does not disperse the gel, and imparts no change in the original color of EDTA (Fig. 6.5 (c)).

Analogous to our results obtained with Ni$_2$P, we presume that 1-DDT, which does not have a pendent carboxylate capable of metal-crosslinking results in phosphate linkages from oxidation of phosphides.

**Figure 6.5:** (a) About 1 min after EDTA addition into Fe$_{1.2}$Ni$_{0.8}$P +11-MUA aerogel (b) supernatant of Fig. 6.5 (b) (c) EDTA addition into Fe$_{1.2}$Ni$_{0.8}$P +1-DDT aerogel

### 6.3.2 Effect of heat treatment towards the Fe$_{1.2}$Ni$_{0.8}$P Aerogels

As the next move, we sought to post-heat treat the above aerogels under reducing (5% $\text{H}_2$) and neutral (Ar) conditions. We presume that the post-heat treatment imparts alternations in the bonding of these aerogels, such as phosphate to phosphide conversion and decomposition of surface bound ligands. Accordingly, we sought to assess the stability of these aerogels under different temperatures and/or reducing/neutral environments.
Aerogels were heat treated under different conditions as described below. For the initial studies, the Fe$_{1.2}$Ni$_{0.8}$P nanoparticle composition, which was synthesized using 2.0 mL oleylamine, and 3.0 mL of TOP (ca. 20 x 11 nm short rods), and thiolate exchanged with 11-MUA, was used. The aerogel was roughly divided into four equal weights and heat treated as described below,

(1) 250 °C under Ar for 1 h

(2) 250 °C under reducing conditions (5% H$_2$) for 1 h

(3) 400 °C under Ar for 1 h

(4) 400 °C under reducing conditions (5% H$_2$) for 1 h

After the heat treatments, the aerogels were then compared to the original gel, for any changes in their crystal structure and the morphology. **Fig. 6.6** shows the comparison of PXRD patterns of the aerogels treated as mentioned above, to the original.

**Figure 6.6:** PXRD patterns of the Fe$_{1.2}$Ni$_{0.8}$P aerogels (thiolate exchanged with 11-MUA) heat treated under different conditions.
When analyzing the PXRD patterns, we see there is no significant change in the crystal structure compared to the gel that is not heat treated. This is evidence that the Fe$_{1.2}$Ni$_{0.8}$P aerogels are robust under heat treatment in reducing and neutral atmospheres. This can be further confirmed by the TEM images shown in Fig. 6.7. The high magnification insets show the retention of the initial morphology even after different heat treatments.

![TEM images](image)

**Figure 6.7:** TEM images of Fe$_{1.2}$Ni$_{0.8}$P aerogels (thiolate exchanged with 11-MUA) treated under different conditions: (a) heated at 250 °C under Ar for 1 h; (b) heated at 250 °C under H$_2$ (5%) for 1 h (c) heated at 400 °C under Ar for 1 h (d) heated at 400 °C under H$_2$ (5%) for 1 h

The elemental composition analysis of these gels by EDS confirms the retention of the elemental composition of the original gel for all the above mentioned conditions, except the gel heated under H$_2$ (5%) at 400 °C (Table 6.1) where a deficient of P was noted. This is attributed to the
loss of P, in the form of PH\textsubscript{3} under reducing conditions, and loss of ligands on the nanoparticle surface. Note that for all the compositions Ni is deficient compared to the target composition.

Table 6.1: The elemental composition analysis of post-heat treated Fe\textsubscript{1.2}Ni\textsubscript{0.8}P aerogels by EDS

<table>
<thead>
<tr>
<th>Condition</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>original gel</td>
<td>Fe\textsubscript{1.20}Ni\textsubscript{0.25}P\textsubscript{0.99}</td>
</tr>
<tr>
<td>250 °C/Ar</td>
<td>Fe\textsubscript{1.20}Ni\textsubscript{0.25}P\textsubscript{0.99}</td>
</tr>
<tr>
<td>250 °C/H\textsubscript{2}</td>
<td>Fe\textsubscript{1.20}Ni\textsubscript{0.25}P\textsubscript{0.86}</td>
</tr>
<tr>
<td>400 °C/H\textsubscript{2}</td>
<td>Fe\textsubscript{1.20}Ni\textsubscript{0.23}P\textsubscript{0.68}</td>
</tr>
<tr>
<td>400°C/Ar</td>
<td>Fe\textsubscript{1.20}Ni\textsubscript{0.23}P\textsubscript{0.92}</td>
</tr>
</tbody>
</table>

Thermogravimetric analysis carried out under reducing conditions (5% H\textsubscript{2}) also revealed of a weight loss, \textit{ca.} 7.2%, starting from around 300 °C, and leveling off by 450 °C (Fig. 6.8) in addition to the loss at 100 °C (likely adsorbed water).

Figure 6.8: TGA analysis of Fe\textsubscript{1.2}Ni\textsubscript{0.8}P aerogel

Additionally, when the original gel (of sample ca. 23 x 6 nm) is heat treated under 5% H\textsubscript{2} for 1 h at 400 °C, the surface area is reduced. Fig. 6.9 shows the BET isotherms obtained for original Fe\textsubscript{1.2}Ni\textsubscript{0.8}P aerogel (thiolate exchanged with 11-MUA), and for the same aerogel heated at 400 °C under H\textsubscript{2} (5%) for 1 h.
Figure 6.9: Nitrogen adsorption/desorption isotherms obtained for the Fe$_{1.2}$Ni$_{0.8}$P original aerogel thiolate exchanged with 11-MUA (red), and the same aerogel heated at 400 °C under H$_2$ (5%) for 1 h (black). The inset shows the pore size distribution.

The original aerogel in Fig. 6.9 possesses a BET surface area of 93 m$^2$/g, while the heat treated aerogel at 400 °C for 1 h under reducing conditions has a surface area of 49 m$^2$/g. The latter isotherm exhibits an open loop likely due to out-gassing. It seems that upon heat treatment there is no apparent change in pore diameter distribution (Fig. 6.9 inset), however, the total pore volume reduces upon the heat treatment suggesting pores are eliminated in the heating process.

The same heat-treatment protocol was applied to the Fe$_{1.2}$Ni$_{0.8}$P nanoparticle aerogels, prepared from 1-DDT capped nanoparticles. These gels were post-heat treated for 1 h under 5% H$_2$ at 400 °C only. Fig. 6.10 shows the TEM image and PXRD relevant to the original gel and the aerogel heat treated under reducing conditions.
Figure 6.10: (a) TEM image and (b) PXRD relevant to the original gel and the aerogel heat treated under reducing conditions (5% H$_2$) at 400 °C for 1 h.

According to Fig. 6.10 (b), the crystal structure and the crystallite size are unchanged upon the heat treatment at 400 °C under reducing conditions. However, according to Fig. 6.10 (a), the TEM image indicates significant fragmentation of the extended network into ca. 100-400 nm aggregates and free individual nanoparticles. These individual nanoparticles are more common in the grid areas analyzed by TEM than aggregates.

Based on the previous studies on phosphide nanoparticles assembly, we posit that the discrete nanoparticles functionalized by 1-DDT can undergo sol-gel assembly by oxidation of phosphide to phosphite or phosphate followed by condensation. However, at elevated temperatures under reducing conditions the connecting P-O-P linkages can break up as phosphate or phosphite species are reduced back to phosphide leading to the separation of nanoparticles from their assemblies.
6.3.4 Magnetic Measurements of 3-D Assembled Aerogels

For comparison, we have synthesized two identical Fe$_{1.2}$Ni$_{0.8}$P nanoparticles samples of 20 x 11 nm short rods, employing 2 mL of oleylamine and 3 mL of TOP. The synthesized nanoparticle samples were then thiolate exchanged separately by 11-MUA and 1-DDT. The resultant aerogel monoliths were subjected to ZFC and FC measurements as described in CHAPTER 2. The resultant M vs T plots were compared with respect to those of discrete nanoparticles (Fig. 6.11).

Figure 6.11: ZFC and FC curves of (a) discrete nanoparticles of Fe$_{1.2}$Ni$_{0.8}$P (as-prepared, capped with oleylamine and TOP (b) aerogels prepared from nanoparticles thiolate-capped with 11-MUA, before and after heat treatment at 400 °C under 5% H$_2$ (c) aerogels prepared from nanoparticles thiolate-capped with 1-DDT, before and after heat treatment at 400 °C under 5% H$_2$. All data were acquired under a field of H=100 Oe
According to Fig. 6.11, the blocking temperatures ($T_B$) of discrete nanoparticles, 11-MUA capped aerogel, and the 1-DDT capped aerogel are 140 K, *ca.* 50-150 K, and 125 K, respectively. It seems that the aerogels composed from 11-MUA capped nanoparticles exhibit different magnetic properties from the initial nanoparticle, while the aerogels made from 1-DDT capped nanoparticles demonstrate similar magnetic properties. Further, it seems that heat treatment at 400 °C under 5% H$_2$ has little effect on aerogels prepared from 1-DDT capped nanoparticles whereas discrete but subtle changes are observed in aerogels prepared from 11-MUA capped nanoparticles. The lower $T_B$ of Fe$_{1.2}$Ni$_{0.8}$P +11-MUA aerogels suggests that the interparticle interactions may facilitate spin re-orientation. However, $T_B$ of Fe$_{1.2}$Ni$_{0.8}$P +1-DDT aerogels remain close to the original value suggesting little or no cooperative behavior. The fact that the separated nanoparticles after heat treatment are similar to aerogels, both of which are similar to describe starting nanoparticles, suggests phosphate interfaces limit interparticle magnetic interactions. It appears that the $T_c$ in both cases appear after 250 K, while the reported value for bulk Fe$_{1.2}$Ni$_{0.8}$P appears at 140 K$^{167}$ and 125 K$^{166}$ for Fe$_{1.2}$Ni$_{0.8}$P nanoparticles.

### 6.4 Conclusions

Nanoparticle assembly methods employed for binary InP and Ni$_2$P nanoparticles, are effective for assembling ternary phase Fe$_{1.2}$Ni$_{0.8}$P nanoparticles into 3-D gel networks with no significant change of their original phase, crystallinity and particle morphology by using an oxidation induced sol-gel pathway. The nature of the interparticle interactions depends on the ligand, since in the presence of a pendent carboxylate (11-MUA), the gelation can take place via metal bridging, in addition to formation of P-O-P linkages, which is the only option in the presence of non-pendent 1-DDT ligand. Any alternations of these interparticle interactions, imparted by post-heat treatment under reducing and neutral conditions, may affect the magnetic
properties of 3-D assemblies. It is also evident that the heat treatment does not impart a significant crystalline or morphology change to the aerogels. However, the aerogel of Fe_{1.2}Ni_{0.8}P nanoparticles functionalized by 1-DDT, separated back to individual nanoparticles upon heating at 400 °C under reducing conditions, suggestive of limited interparticle interactions possibly due to the phosphite interfaces. Evaluation of the interparticle interactions of these gels in terms of advantageous magnetic properties towards effective magnetic refrigeration material(s) will be carried out in future work.

Note that preliminary results on assembly of CoFeP nanoparticles were also collected and are presented in Appendix B.
CHAPTER 7-CONCLUSIONS AND PROSPECTUS

7.1 Conclusions

The increasing demand for energy-efficient and environmentally friendly refrigeration motivates exploration of magnetic refrigeration (MR) technologies. Materials with MR technologies are predicted on having a large magneto-caloric effect (MCE), minimal thermal and magnetic hysteresis, a broad working temperature range around room temperature, low cost, and high abundance. Transition metal based compounds have distinct advantages over traditional MR materials of gadolinium and its associated intermetallic compounds because of their low cost, high abundance, and large MCE. Bulk MnAs exhibits a magnetic entropy change ($\Delta S_M$) of 30 J kg$^{-1}$ K$^{-1}$ in the presence of 5 T magnetic field, at the $T_c$ of 318 K. However, the significant thermal hysteresis of about 7 K disqualifies bulk MnAs as a practical MR material. It is reported that nanostructuring can minimize the thermal hysteresis, while the cation and anion doping could fine-tune the $T_c$ to be workable in a broad temperature range. Moreover, reducing the materials’ dimensions to the nanoscale has the potential to enable formation of three-dimensional architectures thereby expanding the temperature window.

Therefore, in this dissertation study our first goal was to synthesize a solid-solution of MnAs$_x$Sb$_{1-x}$ over all x, as discrete nanoparticles. To lay the ground work, we first focused on MnSb nanoparticle synthesis, and the associated magnetic properties, since there was no reported literature about phase-pure and low polydispersity discrete MnSb nanoparticle syntheses. In CHAPTER 3, we reported the solution-phase synthesis of discrete MnSb nanoparticles of ca. 14 nm in diameter, with low polydispersity. In order to avoid the deposition of elemental Sb as a by-product, a large excess of Mn precursor, which is Mn$_2$(CO)$_{10}$, was used. As a consequence, a shell of MnO$_x$ was formed around the MnSb core, which in turn reduced the saturation magnetic
moment of MnSb nanoparticles far below the magnetic moment reported for bulk MnSb (3.5 BM). This lowering of saturated magnetic moment led to the study in CHAPTER 4.

In CHAPTER 4, we added a mild reducing agent, NaBH₄, to the MnSb reaction mixture employed in CHAPTER 3. In CHAPTER 3, we concluded that an adventitious oxygen source, which is capable of reacting ‘in-situ’ with oxophilic Mn₂(CO)₁₀ was responsible for the shell formation around the MnSb core. Therefore, we hypothesized that the addition of a mild reducing agent, such as NaBH₄, will act as a getter for adventitious oxygen precluding oxidation of Mn₂(CO)₁₀. Therefore, we further assumed that in the presence of NaBH₄, the necessity of large excess amount of Mn₂(CO)₁₀ for MnSb nanoparticle synthesis is lessened. To test this premise, two MnSb nanoparticle syntheses were carried out in the presence and absence of NaBH₄, employing a slight excess of Mn₂(CO)₁₀ (20% mole excess of Mn₂(CO)₁₀ compared to 80% mole excess of Mn₂(CO)₁₀ in CHAPTER 3). In agreement with our hypothesis, MnSb nanoparticle synthesis carried out in the presence of NaBH₄, still yielded elemental Sb peaks, but the peak intensities are low compared to the synthesis carried out in the absence of NaBH₄. Suprisingly, the addition of NaBH₄ had altered the particle morphology into elongated head-tail nanoparticles with the head region slightly rich in Sb, while the tail region was composed of equimolar amounts of Mn and Sb. It was observed that the elongated head-tail morphology can be transformed into spherical shape nanoparticles upon addition of excess Mn₂(CO)₁₀. Most importantly, the saturation magnetization moment was increased by twenty times in these elongated head-tail nanoparticles.

The previous knowledge gained from the Brock group on MnAs nanoparticles synthesis was combined with the knowledge gained from CHAPTER 3 and 4 of MnSb nanoparticle syntheses, to synthesize ternary phase MnAsₓSb₁₋ₓ nanoparticles targeting x=0.1 to 0.9, as
described in CHAPTER 5. All the target compositions appeared phase-pure by PXRD, and the particles exhibited low polydispersity (ca. 12-13 nm in diameter). The target compositions of x=0.1-0.8 resembled hexagonal MnSb phase, while the target composition of x=0.9 adapted orthorhombic MnAs phase. Almost all the compositions exhibited low As incorporation into the particles, and the As had concentrated into the core of the nanoparticle, making an inhomogeneous elemental distribution. According to line scan and elemental mapping data, there is clearly two regions of inhomogeneity in the particle, a Sb-As alloy core and MnSb shell. Because of this alloy core the outer layer of MnSb susceptible to in a strain.

The second goal of this dissertation was to assemble the discrete magnetic nanoparticles into three-dimensional porous architectures enabling facile heat transfer through high surface area, providing possible mechanical stability during the refrigeration cycling, and reducing magnetic hysteresis owing to the small size of the primary particles. Initially we selected discrete Fe$_{1.2}$Ni$_{0.8}$P and CoFeP nanoparticles for this study, since the Fe$_{2-x}$Ni$_x$P nanoparticle system is well established, and its T$_c$ well below room temperature, making it easy to probe with a conventional magnetometer. CHAPTER 6 studies focused on oxidation-induced three-dimensional assembly of discrete Fe$_{1.2}$Ni$_{0.8}$P nanoparticles, thiolate exchanged by 11-MUA or 1-DDT. The composition was capable of forming solid, black monoliths after drying the wet gels supercritically to form aerogels. There was no significant change in initial nanoparticle phase, crystallite size, and the particle morphology, upon the assembly. Both 11-MUA and 1-DDT can undergo surface P-O-P bond formation in the presence of an oxygen transferring species. In addition, due to the presence of a carboxylate functionality, 11-MUA can participate in metal cross-linking via its pendent group. Therefore, upon the addition of EDTA, the bridging metals can be extracted, re-dispersing the nanoparticles into a solution. EDTA has no effect on the gels
made from 1-DDT. The aerogels were further heat treated at 250 and 400 °C under reducing (5% H₂) and neutral (Ar) conditions. However, the aerogel of Fe₁.₂Ni₀.₈P nanoparticles functionalized by 1-DDT, separated back to individual nanoparticles and gel fragments upon heating at 400 °C under reducing conditions, suggestive of minimum or low interactions between the particles due to the phosphate interfaces. It seems that the magnetic properties are highly dependent on the interparticle interaction of the aerogels. Aerogels made with 11-MUA exhibited lower T_B and broad ZFC curve compared to those of as-prepared nanoparticles and aerogels made with 1-DDT.

7.2 Prospectus

7.2.1 Formation of New Antimonides for Magnetic Refrigeration

The need for of new MR materials that impart high MCE is one of the main challenges facing exploitation of MR technology. Theoretical studies have identified ternary phases such as MnNiSb, MnPdSb, MnGa₂Sb₂ phases as potential MR materials. It is likely that such materials will benefit from nano-structuring, for which we will need to develop synthetic pathways. The developed synthetic protocols for MnSb nanoparticles, slow heating and through the SSS growth mechanism, were capable of producing ca. 13 nm nanoparticles with narrow polydispersity. Therefore, we expect that these new synthetic approaches for MnSb will be amenable to other transition metals, can be used to synthesize those phases.

Moreover, during the studies described in CHAPTER 3 and 4 we saw that Mn-based compounds are prone to oxidation due to their oxophilicity. As a consequence, these compounds possess low saturation magnetization discouraging its potential as a MR material. Therefore, it is a good idea to focus on metals that are less oxophilic than Mn (e.g. Fe, Co, Ni, etc.), as these will be more easily prepared and less subject to surface oxidation.
7.2.2 MnAs$_x$Sb$_{1-x}$ Solid Solutions

Since we saw low As incorporation into the nanoparticles, and compositional inhomogeneity, a study of this composition as a function of annealing is recommended since the post-heat treatment may allow more As incorporation and an increase in the homogeneity of the sample. Even though, in CHAPTER 6 we have evaluated the phase segregation of MnAs$_{0.5}$Sb$_{0.5}$, it is important to evaluate the target series from $x=0.1$ to 0.9, in terms of compositional distribution and magnetic properties in order to understand whether the phase segregation occurs throughout. Furthermore, evaluating the magnetic entropy and $T_c$ of these compositions and relating those parameters to compositional inhomogeneity will contribute to our understanding of MnAs$_x$Sb$_{1-x}$ solid solutions. Finally, PDF analysis can help us to determine the contribution of amorphous component.

7.2.3 Magnetic Composites

We assume that evaluating the magnetic properties of the composites with different interparticle bonding is important to access the stability of the aerogels under different conditions, such as different temperatures and reducing vs neutral environments. In order to achieve this, the aerogels will be subjected to post-heat treatment under reducing and the non-reducing conditions, and these composites will be analyzed by IR spectroscopy. Depending on the progress given by the IR data, further analysis by XPS can be carried out to understand the oxidation states associated with the alternations. In such a way, the evaluation of inter-particle interaction towards the magnetic properties can be assessed.

In addition, compositions of Fe$_{2-x}$Ni$_x$P systems where $x=0.2$ (Fe$_{1.8}$Ni$_{0.2}$P) and $x=0.6$ (Fe$_{1.4}$Ni$_{0.6}$P), are also reported to have $T_c$’s close to room temperature, 250 and 265 K, respectively, and compositions Co$_{0.7}$Fe$_{1.3}$P and CoFeP with $T_c>340$ K are superparamagnetic at
room temperature. These materials provide new systems in which to study cooperative magnetic properties. Magnetic compliance studies such as magnetic entropy/ MCE of these materials would be helpful to determine the suitability of these materials in practical magnetic refrigeration.
APPENDIX A- MAGNETIC PROPERTIES OF MnAs_xSb_{1-x} NANOPARTICLES

The Magnetization vs Temperature (ZFC and FC) data and Magnetization (M) vs Applied Magnetic Field (H) for the target compounds MnAs_{0.1}Sb_{0.9}, MnAs_{0.2}Sb_{0.8}, MnAs_{0.7}Sb_{0.3}, MnAs_{0.5}Sb_{0.1} are as follows.

**Figure A1:** Magnetization vs Applied magnetic field (M-H) and M Magnetization vs Temperature profiles of target compositions MnAs_{0.1}Sb_{0.9} and MnAs_{0.2}Sb_{0.8}
**Figure A2:** Magnetization vs Applied magnetic field (M-H) and Magnetization vs Temperature (M vs T) profiles of target compositions MnAs$_{0.7}$Sb$_{0.3}$ and MnAs$_{0.9}$Sb$_{0.1}$

**Fig. A3** summerizes the blocking temperatures and coercivity at T=50 K for the above target compounds and the target compound MnAs$_{0.95}$Sb$_{0.05}$ described in CHAPTER 5.
Figure A3: Blocking temperatures and coercivity values distribution of the target compositions MnAs$_{0.1}$Sb$_{0.9}$, MnAs$_{0.2}$Sb$_{0.8}$, MnAs$_{0.5}$Sb$_{0.5}$, MnAs$_{0.7}$Sb$_{0.3}$, and MnAs$_{0.9}$Sb$_{0.1}$ (the dotted lines are guidance to eyes)

According to Fig. A3, minimum $T_B$ and coercivity are reported for the target composition MnAs$_{0.7}$Sb$_{0.3}$. 
APPENDIX B - ASSEMBLY OF CoFeP NANOPARTICLES

In addition to assembling of Fe$_{1.2}$Ni$_{0.8}$P nanoparticles as described in CHAPTER 6, preliminary studies on assembly of CoFeP were also performed. Early studies on bulk cobalt phosphide revealed that the magnetic properties can be altered from paramagnetic to ferromagnetic upon the introduction of iron into the Co$_2$P crystal structure. Some compositions of bulk and nano Co$_{2-y}$Fe$_y$P (0≤x≤2) are reported in literature. The Curie Temperatures (T$_c$) of these compositions are highly composition dependent. Compositions of Co$_{0.7}$Fe$_{1.3}$P and CoFeP nanoparticles have T$_c$>340 K are superparamagnetic at room temperature.

A similar approach described in CHAPTER 6 was taken to assemble CoFeP, after thiolate exchanging with 11-MUA or 1-DDT. CoFeP nanoparticles were synthesized following a procedure reported by the Brock group. Briefly, a solution of Co$_2$(CO)$_8$ and Fe(CO)$_5$ in 1-ODE was injected to a mixture of 1-ODE and oleylamine under inert (Ar) atmosphere in a Schlenk flask at 200 °C. The resultant black solution was then aged for 20 min at 200 °C, and TOP was introduced to the solution. The mixture was then heated to 330°C for 1.5 h. CoFeP nanoparticles form hollow spherical shape particles of ca. 14 nm (Fig. B1 (a)). These particles were thiolate exchanged and 3-D assembled as described for Fe$_{1.2}$Ni$_{0.8}$P nanoparticles in section 6.2.2 and 6.2.3. Fig. B1 shows the TEM images of CoFeP assemblies carried out using 11-MUA (Fig. B1 (b)) and 1-DDT (Fig. B1 (c)). The insets in Fig. B1 (b) and Fig. B1 (c) show the black solid monoliths obtained after supercritically drying the wet gel. TEM images of aerogels prepared from 11-MUA and 1-DDT terminated particles reveal an extended network structure, in which the original hollow spherical shape of the particles was retained.
Figure B1: (a) initial, and 3-D assembled CoFeP nanoparticles functionalized with (b) 11-MUA, (c) 1-DDT. The insets show the corresponding monolithes obtained after supercritical drying of the wet gels (top right), and for (c) a high magnification image of the gel (lower right).

The PXRD patterns of the original nanoparticles and the 3-D assemblies are shown in Fig. B2 and B3. The crystallite size of the initial nanoparticles, which was ca. 13 nm, remained unchanged after the assembly. However, in the case of 11-MUA, we observed an additional peak at ca. 35 degrees (2θ), indicative of cobalt oxide (Fig. B2).
**Figure B2:** The PXRD images of original CoFeP nanoparticles, and the aerogel made from 11-MUA capped nanoparticles (Co$_2$P-PDF #00-32-0306)

**Figure B3:** The PXRD images of original CoFeP nanoparticles, and the aerogel made from 1-DDT capped nanoparticles (Co$_2$P-PDF #00-32-0306)

We assume that this oxide formation is due to the moderate to strong oxophilic nature of cobalt and its compounds.$^{173}$ The surface area of the 3-D assembly of CoFeP nanoparticles, thiolate exchanged with 11-MUA, when measured by BET, was 184 m$^2$/g, and exhibits the behavior of a type IV mesoporous material. However, the BET surface area of the 3-D assembly of CoFeP nanoparticles, thiolate exchanged with 1-DDT, was only 16 m$^2$/g.
Figure B4: Nitrogen adsorption/desorption isotherms obtained for the Fe$_{1.2}$Ni$_{0.8}$P aerogels made from 11-MUA capped nanoparticles

Fig. B5 shows the CoFeP aerogels prepared by 1-DDT before and after the heat treatment at 400 °C under 5% H$_2$.

Figure B5: TEM images of CoFeP aerogels prepared by 1-DDT (a) before (b) after heat treatment at 400 °C under 5% H$_2$

According to Fig. B5, it is clearly observed that for CoFeP aerogels prepared by 1-DDT, the aerogel became fragmented separating individual nanoparticles. We surmise this is attributed to low interparticle interactions as described more fully in CHAPTER 6, section 6.3.
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ABSTRACT

BINARY AND TERNARY TRANSITION METAL PNICTIDES NANOPARTICLES AND THEIR THREE DIMENSIONAL ASSEMBLIES: TOWARDS PROMISING MAGNETIC REFRIGERATION MATERIALS

by

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Bulk MnAs has been recognized as a potential MR material with large MCE. However, the magnetic transition of bulk MnAs suffers from a large thermal hysteresis of 6 K precluding efficient MR cycling, and the magnetic entropy change associated with the phase transition is limited to a narrow temperature range, making the temperature control window very small. Solid solutions of MnAs, synthesized by both cation and anion doping, are reported to reduce the hysteresis, enabling tuning of the optimal temperature range. Reducing the materials’ dimensions to the nano scale has the potential to enable formation of nano 3-dimensional graded macrostructures thereby greatly expanding the temperature window.

This dissertation research focused on: (1) synthesis, characterization, and magnetic property evaluation of MnAs$_{x}$Sb$_{1-x}$ ($x$=0.1-0.9) nanoparticles, and (2) three-dimensional assembly of discrete nanoparticles of a well-established system Fe$_{1.2}$Ni$_{0.8}$P. As a sub-goal of objective (1), MnSb nanoparticle synthesis was carried out in the solution-phase, employing two strategies.
The slow heating approach yielded phase-pure, spherically shaped MnSb nanoparticles of ca. 13 nm in diameter with an amorphous manganese oxide shell around the MnSb core, which suppresses the saturation magnetization (0.04 BM/mol Mn). The NaBH$_4$ addition method produced elongated head-tail MnSb nanoparticles with saturation magnetization that was twenty times higher than the former case.

MnAs$_x$Sb$_{1-x}$ nanoparticles over all x were synthesized by slight modification of the protocol developed for MnSb nanoparticle synthesis. The target compositions of x=0.1-0.9 appeared phase-pure in PXRD, but almost all the compositions were As deficient as revealed by elemental compositional analysis by XRF. The particles appeared to comprise a Sb-As alloy core with an MnSb shell, suggesting solid solutions were not formed.

In order to achieve objective (2), Fe$_{1.2}$Ni$_{0.8}$P discrete nanoparticles were selected. These nanoparticles were assembled into three-dimensional networks by oxidation-induced gelation, after functionalization by 11-MUA or 1-DDT. Discrete nanoparticle compositions of Fe$_{1.2}$Ni$_{0.8}$P were capable of forming solid, black monoliths after supercritical drying. All the assembled compositions maintained their initial crystallinity and morphology, even after gelation, and importantly, most of these composites exhibit no significant alternation in the crystallinity and the morphology after post-heat treatment in reducing or neutral conditions. Magnetic properties of these composites were evaluated as a function of different heating conditions.
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PUBLICATIONS


• Hettiarachchi M.A., Abdelhamid, E., Nadgorny, B., Brock, S.L. *Synthesis of Ternary Phase MnAs$_{x}$Sb$_{1-x}$ Nanoparticles and the Compositional Dependent Magnetic Properties – manuscript in preparation*

• Hettiarachchi M.A., Abdelhamid, E., Nadgorny, B., Brock, S.L. – *Anisotropic Manganese Antimonide Nanoparticle Formation by Solution-Solid Growth Mechanism : Consequence of Sodium Borohydride Addition Towards Reduced Surface Oxidation and Enhanced Magnetic Moment manuscript accepted by Nanoscale*


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