Structural, Magnetic and Transport Properties of Some Polar Intermetallics (Stannides and Antimonides) and Silver, copper-Based Quaternary Thio-spinels

by

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(P) Intermetallic Compounds
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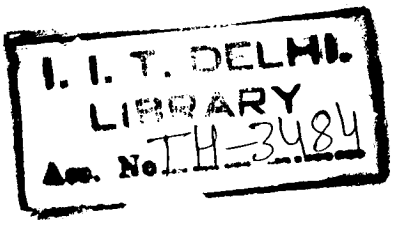

To
my loving parents

CERTIFICATE

This is to certify that the thesis entitled, "**Structural, Magnetic and Transport Properties of Some Polar Intermetallics (Stannides and Antimonides) and Silver, Copper-Based Quaternary Thio-spinels**", being submitted by **Mr. Shalabh Gupta**, to the Indian Institute of Technology Delhi for the award of the degree of **Doctor of Philosophy in Chemistry**, is a record of bonafide research work carried out by him. Mr. Shalabh Gupta has worked under my guidance and supervision, and has fulfilled the requirements for the submission of this thesis, which to my knowledge has reached the requisite standard.

The results contained in this dissertation have not been submitted in part or full, to any other university or institute for award of any degree or diploma.

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ABSTRACT

Significant research activity continues in the broad area of polar intermetallics[1], because interesting and hitherto unknown structure types with novel bonding patterns are quite often encountered. Of special interest to various investigators are the antimonides and stannides as some of them exhibit promising thermoelectric and magnetic properties. Our effort in this work was towards synthesizing novel compounds in the alkali, alkaline-earth antomonide and stannide systems and understanding the role of cations, mainly alkali and alkaline-earth metals in stabilizing or otherwise the structures both with polyanionic substructures and isolated anions. Apart from antimonides and stannides the thesis also deals with new quaternary chalcogenides with the spinel structure. Spinels constitute a large family of materials with the general formula AB_2X_4, where A and B ions may belong to the elements of s-block, main group, transition series or the rare earths. There are approximately 300 known spinels with S and Se alone. Such a vast diversity among this family provides immense possibilities of manipulating the electronic, magnetic and other properties leading to tailor-made materials. There exist a good possibility of varying both the cations and the anions in the spinel structure.

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[1]Part of the research work reported in chapters 2 and 3 was carried out in the facilities of Ames Laoratory, Ames, Iowa, U.S. Department of Energy.

The cation distribution in spinels is guided mainly by the site preference energy and the ionic radii of the cations. Spinels have been studied in the past for their interesting electrical and magnetic properties and is still instigating researchers to synthesize and study new and more complex spinels. They are also envisaged as potential materials for thermopower, colossal magnetoresistance, dilute magnetic semiconductors and more recently, multiferroic applications.

Chapter 1 gives a brief insight into the research activities in the area of polar intermetallics (especially antimonides and stannides) and chalcogenide spinels in last few decades. Various chemical-bonding concepts invoked to explain the structure and bond properties that range from metallic to ionic in character in these polar intermetallics have been discussed. The existence of a very diverse nature of bonding and structure provides researchers with a handle to tailor new materials with desired properties. The novel properties often encountered in these compounds arise from their interesting electronic position between the intermetallics and the true valence compounds. The influence of packing and electronic effects on the stabilities of the ionic cluster salts (polar intermetallic compounds with salt-like behavior are also called Zintl phases) that requires understanding of new concepts like metallic Zintl phases and non-classical bonding has also been discussed in some detail. Cations play an important role in stabilizing the anionic cluster species through appreciable lattice covalency and some examples of this will be presented here. The exploratory nature of the activities involved in this area of research often leads to novel and exquisite structure types and sometimes leads to the completion of the missing links in a known structural family.

The later part of the introduction will dwell on various transition metal based oxide and thio-spinels known in the literature, with emphasis on their structural aspects, electrical and magnetic properties and applications. The effect of cation distribution among available sites and their influence on the transport and magnetic properties, which are of major interest, will be discussed. A brief description of various characterizing tools that have been employed in understanding the structure of these complex systems will be reviewed. Factors such as the effects of ionic charge and radius, crystal and ligand fields, Madelung energy and anion polarization which play an important role in the site preference of cations has been reviewed. A brief overview of current status of research in the area of quaternary thiospinels will also be discussed in this chapter. Synthetic methodologies for obtaining these compounds have also been outlined.

Chapter 2 discusses the synthesis, structure and properties of several new polar antimonides. The alkali and alkaline-earth antimony systems have been of special interest among researchers in the field of polar intermetallics. Among the various families of polar intermetallics, antimonides have been of interest lately due to the possibility of finding interesting magnetic and thermo-electric materials. A new ternary antimonide SrLiSb has been synthesized and characterized using single crystal X-ray studies. It was found to crystallize in the *anti*-$PbCl_2$ structure type (orthorhombic, *Pnma*) with a= 8.0408(8) Å, b= 4.8145(5) Å, c= 8.4517(9) Å) and is isostructural to its calcium analogue (CaLiSb). As in the Ca and Ba analogues, antimony is present as isolated Sb^{3-} ions making SrLiSb electron precise and hence is expected to behave as a classical Zintl

compound. Electrical and magnetic properties of SrLiSb verify the classical Zintl nature of SrLiSb.

Three phases $LiMgCa_{10}Sb_9$, $Mg_2Ca_{10}Sb_9$ and $Li_{1.38(2)}Ca_{10.62}Sb_9$ have been obtained in a novel structure type and characterized by single crystal X-ray diffraction and property measurements. These occur in space group $P4_2/mnm$, $Z = 4$, with a = 11.8658(5), 11.8438(6), 11.9053(7) Å and c = 17.181(2), 17.297(2), 17.152(2) Å, respectively. Li and Mg occupy two distinct crystallographic sites in a Ca–Sb network that contains a 5:2 proportion of Sb^{3-} and Sb_2^{4-} anions and has been described in terms of two slab types stacked along [001]. The three compounds are, respectively, an ideal electron-precise Zintl phase, one e^--rich and 0.40(4) e^--short per formula unit. The $LiMgCa_{10}Sb_9$ compound is correspondingly diamagnetic and presumably a semiconductor.

Two new antimony based intermetallic phases, $Ca_{8.63(5)}Sr_{2.37}Sb_{10}$ and $Ca_{3.66(7)}Sr_{7.34}Sb_{10}$, crystallizing in the $Ho_{11}Ge_{10}$ structure type (tetragonal, *I4/mmm*) have been synthesized and characterized. Although both $Ca_{11}Sb_{10}$ and $Sr_{11}Sb_{10}$ are known to be isostructural and in principal all the sites should be equally accessible to both Ca and Sr, it appears that certain sites are preferentially ordered by Ca in the mixed $(Ca/Sr)_{11}Sb_{10}$ compounds reported here. Simple valence electron count reveals these compounds to be Zintl phases. It is found that the larger Sr or Sr/Ca ions preferentially occupy sites that are closer to the diantimony anions as compared to the smaller Ca ions.

Synthesis and characterization of a new and so far the most metal-rich antimonide, Tm_3Sb is reported. The compound crystallizes in a tetragonal space group $P4_2/n$ with the lattice parameters a =12.2294 Å and c =5.9852 Å with Ti_3P structure type. This compound presents, to the best of our knowledge the first example of a rare-earth

antimonide to crystallize in the Ti_3P structure type and more importantly is the first Tm-rich antimonide known so far.

The ternary polar intermetallic phase $Mg_{5.231(8)}Sm_{0.769(8)}Sb_4$ has been obtained from solid-state reactions at 700–850 °C in sealed Nb containers The compound crystallizes in the trigonal space group $P\bar{3}$ ($Z = 1$) with $a = 4.618(1)$ and $c = 14.902(6)$ Å in a structure that derives from that of Mg_3Sb_2. The result provides the first example of a superstructure of a Mg_3Sb_2-like structure with a doubled c-axis induced by ordering of the larger divalent Sm^{2+} ions and the smaller Mg^{2+} ions separately within alternate layers of octahedral sites.

In **chapter 3** we present our studies on stannides: An interesting structural disorder in some W_5Si_3-type A_5B_3 structures (tertragonal, *I4/mcm*) has been observed because of close approaches of the A1-type atoms on the cell faces at ½, 0, (¼, ¾). This kind of disorder has been found to occur with the larger and more electropositive A and/or in the presence of smaller B atoms. Three new stable ternary derivatives of these have been synthesized via substitution reactions and characterized by single crystal X-ray diffraction means: $Ca_4Sn_{3.223(4)}Mg_{0.777}$, $Ca_4Sn_3Cu_{1.30(4)}$ and $Ca_{4.66(6)}Sn_3Zn_{0.704(4)}$. The problematic A1 sites exhibit diverse modifications in these compounds, whereas the surrounding B2 tetrahedra are largely unaltered.

The compound, $Ca_{2.04}Sr_{0.96}Sn_5$ was synthesized by solid-state reaction and was found to crystallize in the Pu_3Pd_5 structure type (orthorhombic, *Cmcm*) with cell dimensions of a = 10.5179(9) Å, b = 8.4789(8) Å and c = 10.7623(10) Å. The structure consists of isolated Sn_5^{6-} square pyramidal units surrounded by the cations that seem to play a crucial role in stabilizing the Zintl polyanions. The square pyramids contract at low temperature (100 K)

leading to the shortening of the basal intracluster Sn-Sn bond (2.74 Å) while the intercluster bonds become very large, indicating features of bond stretching isomerism. The $(Sr,Ca)_3Sn_5$ compounds show a weakly metallic behavior. Our studies suggest that the 'Sn' polyanions in $Ca_{2.04}Sr_{0.96}Sn_5$ may be described as arachno - Sn_5^{-6} Zintl cluster.

In **chapter 4** we investigate the compositional limits in silver-based quaternary thiospinels: $Ag_2M_{1+x}Sn_{3-x}S_8$ (M= Fe, Mn, and Cr). Various compositions in the series $Ag_2M_{1+x}Sn_{3-x}S_8$ (x= 0.2, 0.4, 0.6, 0.8 and 1.0) have been attempted. Powder X-ray diffraction studies showed that all these thiospinels crystallized in the cubic ($F\,d\bar{3}\,m$) space group. For x=1, in the case of Fe series, SnS was observed as a major phase along with minor apinel phase, whereas in case of Mn no spinel phase was observed. Contrary to the above, in the chromium series, thiospinels with higher purity and better crystallinity could be obtained for higher values of 'x'. Magnetization measurements have been performed on nearly pure phases of $Ag_2M_{1+x}Sn_{3-x}S_8$ (M = Fe or Cr) system. Magnetic studies on the thiospinels obtained in Cr and Fe series clearly indicate the presence of long range magnetic ordering at low temperatures. Resistivity measurements were carried out on $Ag_2Mn_{1+x}Sn_{3-x}S_8$ (nominal composition) and all the samples in this series showed semi-conducting behavior with high values of room temperature resistivity.

Apart for the above, several Sb containing compositions such as $Ag_2MSbSn_2S_8$ (M= Fe, Mn and Cr) were attempted and some of them yielded thiospinel phases in high amounts albeit with small amount of impurities. Compositions of the type $Ag_2M_2Sb_2Sn_3S_{12}$ (M= Fe, Mn and Cr) were also designed based on the charge neutrality conditions and some

success was achieved here as well. Compositions such as $(Ag,Cu)_2MSn_2GeS_8$ (M= Cr, Fe, Ni), where Sn has been substituted by Ge, have been investigated. The structure and properties of these compounds are reported.

Chapter 5 deals with the synthesis, structural, electrical, magnetic and electrochemical properties of novel cation-deficient thiospinels with the general formula $(Cu,Ag)MM'Sn_2S_8$ (M, M'= Cr, Mn, Fe, Co, Ni). Cation-deficient thiospinels have been investigated by researchers for their potential technological applications such as in Li-batteries. However, their practical application has so far been limited by their low specific capacity and a high capacity fading with cycling. Quaternary thiospinels of the type $AgMM'Sn_2S_8$ (M, M'= Cr, Mn, Fe, Co, Ni) have been synthesized by high temperature reactions in vacuum-sealed silica ampoules. X-ray analysis of these samples clearly indicates the formation of cubic spinel phases. These cation-deficient thiospinels lack 50 % of the 8a site cations as compared to the earlier studied quaternary thiospinels of the type $Ag_2MSn_3S_8$. Sn and Fe Mössbauer spectroscopy was carried out to determine the oxidation state and co-ordination environment of these cations. The elemental analysis by energy dispersive x-ray analysis was carried out to determine the composition of the compounds and observed composition corroborated well with the nominal composition. Two-probe resistivity measurements were carried out on sintered disks. All the compounds showed semiconducting behaviour. In continuation to the successful attempts to obtain new cation-deficient Ag based thiospinels, several copper based compositions were also tried. Among these, $CuCrMnSn_2S_8$, $CuMnFeSn_2S_8$, $CuMnCoSn_2S_8$, $CuCrCrSn_2S_8$ and $CuCr_2Sn_2S_8$ could be obtained with high phase purity. Electrochemical studies have been carried out to evaluate these thiospinels for their

possible application in Lithium ion batteries. All the compounds, except $AgMnFeSn_2S_8$, showed redox activity with the appearance of an irreversible peak in their CVs. All give an open circuit voltage expected for a good material for application in lithium batteries.

Abstract

A brief overview of the research activities in the area of polar intermetallic and chalcogenide spinels is presented in this chapter. The chemical-bonding concepts invoked to explain the structure and bond properties that range from metallic to ionic bonding in these polar intermetallics have been discussed. The influence of packing and electronic effects on the stabilities of the ployanionic clusters that requires understanding of new concepts like metallic Zintl phases and non-classical bonding have also been discussed in some details. Cations play an important role in stabilizing the anionic cluster species through appreciable lattice covalency and some examples of this has been presented here. In the later part of the introduction transition metal-based oxide and thio-spinels have been discussed, with emphasis on their structural aspects, electrical and magnetic properties and applications. Some of the recent developments in this area like multiferrocity have been included. The effect of cation distribution and their influence on the transport and magnetic properties will be discussed. Factors such as the effects of ionic charge and radius, crystal and ligand fields, Madelung energy and anion polarization which play an important role in the site preference of cations has been reviewed. In addition a brief overview of current status of research in the area of quaternary thiospinels is also discussed. Synthetic methodologies for obtaining these compounds have also been outlined. Motivation behind carrying out the present work is summarized.

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