QUATERNARY CHALCOGENIDES: SPINEL AND SPHALERITE - RELATED STRUCTURES

by

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To my parents

for all that they

painstakingly endured

for my happiness

CERTIFICATE

This is to certify that the thesis entitled, **"Quaternary Chalcogenides with Spinel and Sphalerite-Related Structures"**, being submitted by **Ms. GUNJAN**, 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 her. Ms. Gunjan 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

This thesis deals with the synthesis and characterization of quaternary chalcogenides related to spinel (AB_2X_4) and sphalerite (ZnS) structures. Spinels show a variety of interesting physical properties like antiferromagnetism, superconductivity, metal-insulator transitions etc. Apart from electrical and magnetic properties, spinels are of great interest for being host materials for Li-ion intercalation. In the recent years many spinels have been developed as active cathode materials for lithium batteries. Due to their unique properties spinels find wide variety of applications in the fields of electronics, telecommunications and other industries. In addition to spinels, quaternary tetrahedral compounds related to ZnS (sphalerite) structure are also known to have immense potential with respect to their semiconducting and non-linear optical properties. In this thesis, attempts have been made to investigate quaternary chalcogenides related to the spinel and sphalerite structures, and to unravel their structural, electrical, magnetic and electrochemical properties.

Chapter I gives a brief overview of the research activity that has taken place in the area of spinels and sphalerites over the years. A review has been presented regarding the structure and properties (electrical, magnetic and electrochemical) of various ternary and quaternary oxide spinels as well as that of thiospinels which are reported in the literature. In addition to spinels, a brief review of the structure and properties of a few tetrahedral quaternary chalcogenides related to zinc sulphide (sphalerite) structure have also been discussed.

In chapter II we discuss copper and tin-based quaternary thiospinels belonging to the formula $Cu_8M_4Sn_{12}S_{32}$ or $Cu_2MSn_3S_8$ (M = Ni, Fe, Mn). Crystal structure analysis of

$Cu_2NiSn_3S_8$ has been carried out by single crystal X-ray diffraction studies which show the presence of cubic symmetry with space group $Fd\bar{3}m$. Copper occupies the 8a tetrahedral sites while 'Ni' and 'Sn' are randomly distributed in the 16d octahedral site and 'S' is cubic close packed in the 32e sites. Powder X-ray diffraction studies on 'Ni', 'Fe' and 'Mn' containing thiospinels show a continuous increase in the lattice parameters from 'Ni' to 'Mn' containing compounds according to the size of the transition metal ions present.

Apart from structural studies, the electrical and magnetic properties of these thiospinels have also been discussed in this chapter. 'Ni' and 'Fe' containing compounds show semiconducting behaviour. An increase in room temperature resistivity from 'Ni' to 'Mn'-containing thiospinel has been observed while the band gap for the 'Ni' containing thiospinel (0.028 eV) was found to be less than that of $Cu_2FeSn_3S_8$ (0.15 eV). From d. c. magnetic susceptibility measurements, $Cu_2NiSn_3S_8$ and $Cu_2MnSn_3S_8$ were found to behave according to the Curie-Weiss equation while in $Cu_2FeSn_3S_8$, possibility of an antiferromagnetic transition at higher temperature (> 300 K) has been observed.

In addition, an attempt to give a possible explanation of the origin of the tetragonal distortion in the reported thiospinels has been given, taking into consideration the mode of filling of the tetrahedral and octahedral cavities of the anionic close packed layers.

In chapter III, we have discussed the structure and properties of silver and tin-based quaternary thiospinels belonging to the formula $Ag_8M_4Sn_{12}S_{32}$ or $Ag_2MSn_3S_8$ (M = Cr, Fe, Mn). $Ag_2MnSn_3S_8$ and $Ag_{1.63}CrSn_3S_8$ have been structurally characterized by carrying out Rietveld refinement on powder X-ray diffraction data. A significant amount of 'Ag'-deficiency in 8a tetrahedral site has been observed in case of 'Cr' containing thiospinel which leads to the composition, $Ag_{1.63}CrSn_3S_8$ and crystallizes in cubic ($Fd\bar{3}m$) space group. This is the first report on cation-deficient silver-based thiospinel. However, refinement studies on 'Mn'-containing thisospinel show full site occupancy by silver in 8a sites.

Apart from structural studies, the electrical, magnetic and electrochemical properties of these thiospinels have also been discussed in this chapter. From four-probe resistivity studies, room temperature resistivities of 'Mn' and 'Fe' containing thiospinels were found to be greater than their copper analogues, $Cu_2MnSn_3S_8$ and $Cu_2FeSn_3S_8$, which is in accordance to the size of Ag^+ and Cu^+. $Ag_{1.63}CrSn_3S_8$ shows exceptionally low value of room temperature resistivity (0.3 Ω-cm) in comparison to the other silver-based thiospinels. This may be due to the presence of Cr^{II} and Cr^{III} in the octahedral sites, due to which migration of holes is feasible. Magnetic studies on 'Mn' and 'Cr' containing thiospinels show paramagnetic behaviour in the temperature range (5 – 300 K) while the 'Fe' containing compound, $Ag_2FeSn_3S_8$, shows possibility of antiferromagnetic transition at higher temperatures (above 300K). Electrochemical studies on the above thiospinels show high capacity for $Ag_2FeSn_3S_8$ as compared to $Ag_2MnSn_3S_8$ and $Ag_{1.63}CrSn_3S_8$. The cell with $Ag_2MnSn_3S_8$ as cathode was found to have stable performance with cycling.

Chapter IV discusses the study of four new cation-deficient quaternary thiospinels, $Cu_{5.5}Si\square_{1.5}Fe_4Sn_{12}S_{32}$, $Cu_{5.47}Fe_{2.9}Sn_{13.1}S_{32}$, $Cu_{7.07}Ni_4Sn_{12}S_{32}$ and $Cu_{7.38}Mn_4Sn_{12}S_{32}$. For the first time detailed structural analysis for any of cation-deficient thiospinel has been reported by single crystal X-ray diffraction studies. All these compounds were found to crystallize in cubic symmetry space group ($Fd\bar{3}m$). In case of

$Cu_{5.5}Si\square_{1.5}Fe_4Sn_{12}S_{32}$, additional vacancies in the copper site are compensated by the higher valence of the Si^{IV} ion and the presence of Sn^{II}/ Sn^{IV} as well as Fe^{II}/ Fe^{III} species has been proved by Mössbauer studies. The above compound was found to be a semiconductor in the temperature range 100 – 300 K with a low band gap of 0.107 eV. Possibility of a magnetic transition at higher temperature (> 300 K) has been observed for $Cu_{5.5}Si\square_{1.5}Fe_4Sn_{12}S_{32}$ from magnetic measurements while in the low temperature range (below 200 K) it behaves according to the Curie-Weiss equation. A broad magnetic transition has been observed in a. c. magnetization data around 50 – 90 K.

We could also obtain a cation-deficient thiospinel, $Cu_{5.47}Fe_{2.9}Sn_{13.1}S_{32}$, without doping any higher valent ion. We find a significant amount of nonstoichiometry existing between the Fe / Sn sites. All the earlier studies on quaternary spinels have M^{+2}/ Sn^{+4} in the ratio 1:3. The refined composition exactly fulfills the conditions of electroneutrality of the compound. Our Mössbauer data is also in accordance with the single crystal X-ray studies.

In addition to the above two thiospinels, we could obtain two more cation-deficient thiospinels, $Cu_{7.07}Ni_4Sn_{12}S_{32}$ and $Cu_{7.38}Mn_4Sn_{12}S_{32}$. The structure for both these compounds were solved by single crystal X-ray studies which show the presence of cubic symmetry with space group $Fd\bar{3}m$. We have carried out electrochemical studies on $Cu_{5.5}Si\square_{1.5}Fe_4Sn_{12}S_{32}$ and $Cu_{7.38}Mn_4Sn_{12}S_{32}$.

We have also discussed the probable reason for the cubic ($Fd\bar{3}m$) space group for cation-deficient 'Fe' containing thiospinels, $Cu_{5.5}Si\square_{1.5}Fe_4Sn_{12}S_{32}$ and $Cu_{5.47}Fe_{2.9}Sn_{13.1}S_{32}$, while pure 'Fe' containing thiospinel $Cu_2FeSn_3S_8$ has been reported in the tetragonal space group ($I4_1/a$).

Chapter V deals with the quaternary tetrahedral compounds having structure related to sphalerite (ZnS). We have attempted to synthesize quaternary compounds belonging to four different classes (I_2 II IV VI_4, I II_2 III VI_4, I III IV_2 V_4, II III_2 IV V_4) which may stabilize in the tetrahedral structure. We have tried to synthesize copper and silver-based selenides, as well as tellurides belonging to the formula I II_2 III VI_4 (I = Cu, Ag, II = Cr, Mn, Fe, Co, Zn, Cd, III = Al, In, VI = Se, Te). Single phase could be obtained for $CuZn_2InTe_4$ which crystallizes in the cubic space group $F\bar{4}3m$. Transition metal ions like 'Mn', 'Fe', 'Co' did not lead to the formation of quaternary phases. In case of selenium containing compositions like $AgZn_2AlSe_4$ and $AgZn_2InSe_4$, the binary ZnSe or ternary phases like $AgIn_5Se_8$ and $ZnIn_2Se_4$ could be observed. Four-probe resistivity studies on $CuZn_2InTe_4$ show metal to semiconductor transition around 270 K. The room temperature resistivity is around 6×10^{-3} ohm-m and the activation energy calculated was 0.037 eV. This compound was found to be diamagnetic from magnetic susceptibility measurements.

Silver-based sulphides and selenides belonging to the formula I II_2 IV VI_4 (I = Ag, II = Mn, Fe, Co, Zn, IV = Si, Sn, Pb, VI = S, Se) have also been investigated. Single phase could be obtained for Ag-Fe-Si-S system (Ag_2FeSiS_4). Electron diffraction studies confirm the results obtained from powder X-ray diffraction studies. The compound has an orthorhombic cell with lattice parameters **a** = 7.28 (1), **b** = 7.473 (6) and **c** = 10.59 (1) Å. We have also obtained a single phase for the 'Ni' contaning composition (Ag_2NiSiS_4) while for 'Mn' and 'Co' containing compositions (Ag_2MnSiS_4 and Ag_2CoSiS_4), orthorhombic phase could be obtained along with some impurity phases. In addition to sulphides, we have obtained quaternary phase in the selenium containing composition ($Ag_2FeSiSe_4$) along with the impurity phases, Se and FeSe.

Apart from chalcogenides (group 16), we have attempted to obtain quaternary compounds with group 15 elements belonging to the formula I III IV_2 V_4 (I = Ag, III = Al, In, IV = Si, Sn, Ge, V = P, Sb, Bi) and II III_2 IV V_4 (II = Cr, Mn, Ni, Zn, Cd, III = Al, In, IV = Si, Sn, V = P). However, we were unable to obtain the target compounds.

ABBREVIATIONS AND SYMBOLS

Å	Angstrom
°C	Centigrade
T	Tesla
min	Minutes
h	Hours
d	Days
XRD	X-ray diffraction
PXRD	Powder X-ray diffraction
Ω	Ohm
ρ	Resistivity
μ	Magnetic moment
χ_M	Molar magnetic susceptibility
M'	Magnetization (real part)
M"	Magnetization (imaginary part)
H	Magnetic field
Oe	Oersted
F	Faraday
Z'	Impedance (real part)
Z"	Impedance (imaginary part)

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