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# Crystal structure, magnetic and electrochemical properties of a quaternary thiospinel: $\text{Ag}_2\text{MnSn}_3\text{S}_8$

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## Abstract

A monophasic sample of  $\text{Ag}_2\text{MnSn}_3\text{S}_8$  has been prepared by heating stoichiometric amounts of the constituent metals and sulfur in evacuated silica tubes at 670°C. Structural analysis of  $\text{Ag}_2\text{MnSn}_3\text{S}_8$  using Rietveld refinement of powder X-ray diffraction data shows that it crystallizes in the  $Fd\bar{3}m$  space group with  $a = 10.6984(2)$  Å. Magnetization measurements in the temperature range 5–300 K indicate paramagnetic behavior with a  $\mu_{\text{eff}}$  of  $5.80 \mu_{\text{B}}$ , consistent with the divalent nature of manganese. Electrochemical studies show a coulombic capacity of  $\sim 50 \text{ Ah kg}^{-1}$  for the cell constructed with  $\text{Ag}_2\text{MnSn}_3\text{S}_8$  as the positive electrode.

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## 1. Introduction

Thiospinels show a variety of interesting physical properties including superconductivity [1], metal–insulator and magnetic transition [2], colossal magnetoresistance [3] and are of great interest as host materials for Li-ion intercalation [4]. Copper-based quaternary thiospinels with the formula  $\text{Cu}_8M_4\text{Sn}_{12}\text{S}_{32}$  or  $\text{Cu}_2M\text{Sn}_3\text{S}_8$  ( $M = \text{Ni}, \text{Fe}, \text{Co}, \text{Mn}$ ) have been reported in the literature [5]. These thiospinels crystallize in the  $Fd\bar{3}m$  space group, analogous to the well-known oxide spinels [6]. Recently, we reported the crystal structure and electrical properties of  $\text{Cu}_8\text{Ni}_4\text{Sn}_{12}\text{S}_{32}$  [7]. In addition, single-crystal X-ray structures of copper-based cation-deficient quaternary thiospinels,  $\text{Cu}_{7.07}\text{Ni}_4\text{Sn}_{12}\text{S}_{32}$  [8],  $\text{Cu}_{7.38}\text{Mn}_4\text{Sn}_{12}\text{S}_{32}$  [8],  $\text{Cu}_{5.5}\square_{1.5}\text{SiFe}_4\text{Sn}_{12}\text{S}_{32}$  [9] and  $\text{Cu}_{5.47}\text{Fe}_{2.9}\text{Sn}_{13.1}\text{S}_{32}$  [10] have also been reported.

Compared to copper-based thiospinels, there are relatively limited studies reported on the silver-based analogs. The ternary thiospinel  $\text{Ag}_{0.5}\text{In}_{2.5}\text{S}_4$  has been previously studied as a host lattice for lithium insertion

by both chemical and electrochemical methods [11]. The structure of only one silver-based quaternary thiospinel ( $\text{Ag}_2\text{FeSn}_3\text{S}_8$ ) has been reported in the literature [12]. It crystallizes in the tetragonal space group ( $I4_1/a$ ) similar to the copper analog,  $\text{Cu}_2\text{FeSn}_3\text{S}_8$  [13]. However, to our knowledge, there are very sparse reports on the electrical, magnetic and electrochemical properties of silver-based thiospinels.

Here we report the synthesis, structure and physical properties of the silver-based quaternary thiospinel,  $\text{Ag}_2\text{MnSn}_3\text{S}_8$ . The compound was structurally characterized by Rietveld refinement of the powder X-ray diffraction data. We also report here the magnetic and electrochemical properties of this compound.

## 2. Experimental

Stoichiometric amounts of Ag (Aldrich, 99.9%), Mn (Aldrich, 99.9%), Sn (Acros organics, Belgium, 99.9%) and S (CDH, India, 98%) were mixed in a  $\text{N}_2$ -filled glove box and sealed in silica ampoules under vacuum ( $10^{-5}$  Torr). The ampoules were heated in a programmable furnace at 680°C for 8 days and then furnace

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cooled to room temperature. This led to the formation of a single-phase  $\text{Ag}_2\text{MnSn}_3\text{S}_8$  in the form of black cuboidal crystals.

The diffraction data were collected with a Scintag X3 diffractometer equipped with a Peltier cooled Li-drifted germanium detector. Samples were finely ground and were placed on a glass slide with petroleum jelly. Data were collected over a  $2\theta$  range of  $5\text{--}120^\circ$  with a step size of  $0.015^\circ$  and a residence time of 10 s at each step. Rietveld refinement was carried out using Topas [14] software using Fundamental Parameters approach for the modeling of peak shape. The instrument parameters have been refined with a corundum standard.

Magnetic data were collected with a Quantum Design, Physical Property Measuring System (PPMS) in the temperature range  $5\text{--}300\text{ K}$  at applied fields between 1 and 3 T. The magnetic susceptibility was corrected for diamagnetic contribution of the constituent ions [15].

For the electrochemical measurements, the thiospinel electrodes were prepared by mixing 80% of thiospinel, 15% of graphite and 5% teflon binder, which was then pasted onto a stainless steel grid. These cathode electrodes were coupled with a large area 'Li' metal anode using 0.1 M  $\text{LiClO}_4$  in THF as an electrolyte to fabricate 'Li' cells. Charge–discharge measurements were carried out in this cell for a few initial cycles with a constant current density, controlled with the help of a computerized data-acquisition system. All the procedures of handling and fabricating the cell were performed in an argon-filled glove box. Cyclic voltammetry was carried out with an Autolab model PGSTAT 30 Potentiostat/Galvanostat connected to a three-electrode cell comprised of an  $\text{Ag}_2\text{MnSn}_3\text{S}_8$ -coated Pt electrode, a Pt-flag counter electrode and an Ag/AgCl reference electrode. Potential cycling between  $-1$  and  $+0.5\text{ V}$  was carried out in 1.0 M aqueous  $\text{LiClO}_4$  solution at different scan rates.

### 3. Results and discussion

The reaction of stoichiometric amount of metals with sulfur in evacuated silica ampoules led to the formation of black shiny crystals of the title compound. These crystals were too small for single-crystal structural studies. However, they could be ground easily to make a homogenous mixture for powder diffraction measurements. X-ray diffraction studies on the powdered sample showed a single-phase cubic compound. All the reflections could be indexed based on a cubic unit cell with  $a = 10.6984(2)\text{ \AA}$ . The lattice parameter of  $\text{Ag}_2\text{MnSn}_3\text{S}_8$  is larger than that reported for the copper analog [7]. This is expected because the size of  $\text{Ag}^+$  ( $1.0\text{ \AA}$ ) is greater than that of  $\text{Cu}^+$  ( $0.60\text{ \AA}$ ) [16].

No evidence of symmetry lowering (peak split or anomalous broadening) has been found. Profile

matching (Le Bail) in the cubic  $Fd\bar{3}m$  and tetragonal  $I4_1/a$  (corresponding to the rhodostannite,  $\text{Cu}_2\text{FeSn}_3\text{S}_8$  structure [13]) models yielded identical values of  $R$ -factors, and refined  $c/(a\sqrt{2})$  ratio for the tetragonal model is unity within the error bar. Rietveld refinement in the tetragonal model also did not yield any improvement of the fit or decrease of the thermal factors. Therefore, the higher symmetry cubic  $Fd\bar{3}m$  model has been adopted. The refinement yielded reasonable reliability factors ( $R_p = 5.20$ ,  $R_{wp} = 6.66$ ,  $\text{GOF} = 1.558$ ). Anomalously high values of the thermal factors were observed (Table 1). This can originate from the sample transparency effect due to the relatively small amount of sample used for data collection [17], combined with possible incomplete Ag site occupancy. The experimental, calculated and difference patterns are presented in Fig. 1. Selected interatomic distances are summarized in Table 1.

The dc magnetic susceptibility (measured at 1 T) of the powdered sample is shown in Fig. 2. The susceptibility data could be fit to the Curie–Weiss equation,  $\chi_M = C/(T - \theta)$ , where  $\chi_M$  is the molar magnetic susceptibility,  $C$  is Curie constant,  $\theta$  is the Weiss constant and  $T$  is the absolute temperature. The experimentally observed effective magnetic moment ( $\mu_{\text{eff}} = 5.80\text{ \mu}_B$ ) is similar to the value reported by

Table 1  
Positional and thermal parameters of atoms and bond distances for  $\text{Ag}_2\text{MnSn}_3\text{S}_8$

Atom	Wyckoff symbol	$x$	$y$	$z$	$B_{\text{iso}} (\text{\AA}^2)$
Ag	8a	0	0	0	3.3(1)
Mn/Sn	16d	1/2	1/2	1/2	1.8(1)
S	32e	0.7410(3)	$=x$	$=x$	1.9(1)
Bond distances: Ag–S, 2.484(5) \AA; Mn/Sn–S, 2.582(3) \AA					

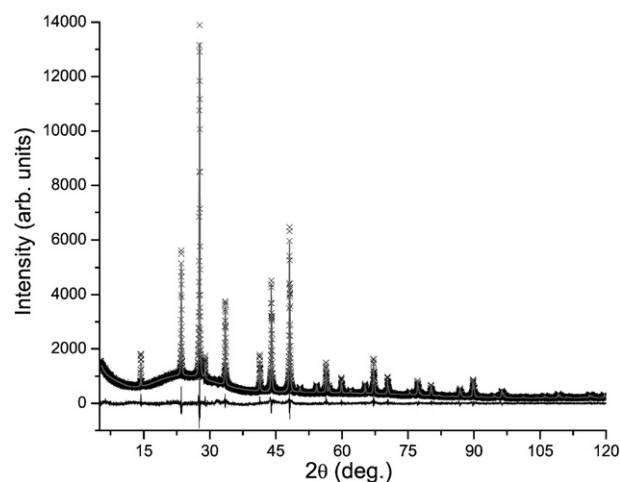


Fig. 1. Final Rietveld plot showing the observed, calculated and difference pattern for  $\text{Ag}_2\text{MnSn}_3\text{S}_8$ .

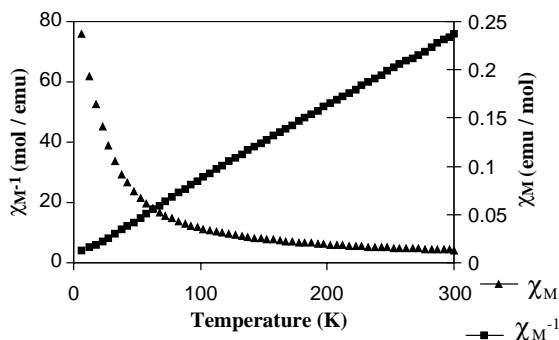


Fig. 2. Plot of  $\chi_M$  and  $\chi_{M^{-1}}$  versus temperature for  $\text{Ag}_2\text{MnSn}_3\text{S}_8$ .

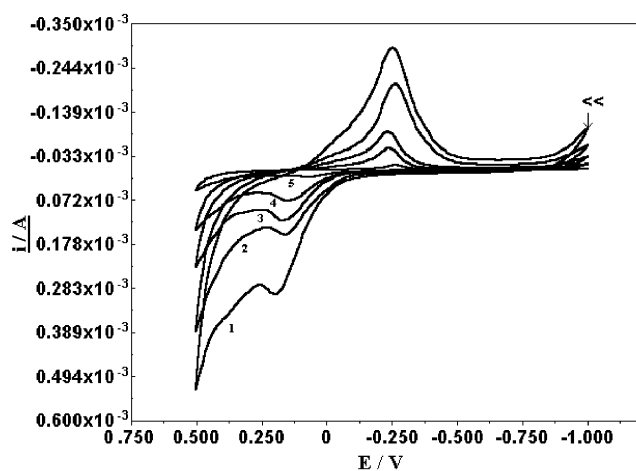


Fig. 3. Cyclic voltammograms of  $\text{Ag}_2\text{MnSn}_3\text{S}_8$  on platinum disc as working electrode, Ag/AgCl reference electrode in a 1 M  $\text{LiClO}_4$  aqueous solution at different scan rates: (1)  $500 \text{ mV s}^{-1}$ , (2)  $300 \text{ mV s}^{-1}$ , (3)  $200 \text{ mV s}^{-1}$ , (4)  $100 \text{ mV s}^{-1}$  and (5)  $50 \text{ mV s}^{-1}$ .

Padiou et al. [5], and agrees well with the expected value ( $5.92 \mu_B$ ) for high-spin  $\text{Mn}^{2+}$  ( $S = 5/2$ ). The estimated Weiss Constant ( $\theta$ ) of  $-10 \text{ K}$  indicates that the precursor exchange correlations are anti-ferromagnetic in nature, although no long-range order was evident down to the lowest temperature of measurement ( $5 \text{ K}$ ).

Cyclic voltammetry was carried out with the sample as working electrode in  $1.0 \text{ M}$  aqueous  $\text{LiClO}_4$ , a Pt flag counter electrode, and Ag/AgCl as the reference electrode. Fig. 3 shows a quasi-reversible voltammogram as a function of the scan rate. Both oxidation and reduction peaks are evident and more significantly, electron transfer process becomes more facile at larger scan rates ( $500 \text{ mV s}^{-1}$ ). The reduction peaks are more distinct compared to the oxidation peaks and this could be attributed to the presence of a large amount of  $\text{Mn}^{2+}$  in the sample. The half-wave potential measured by the average of the anodic and cathodic peak potentials is in good agreement with the presence of  $\text{Mn}^{2+}$  in the initial compound.

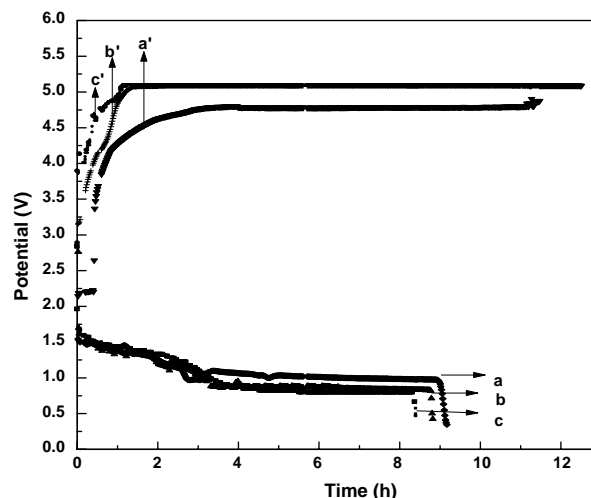


Fig. 4. Variation of electrode potential of  $\text{Ag}_2\text{MnSn}_3\text{S}_8$  during charge–discharge studies (*a*, *b*, *c* are discharging curves and *a'*, *b'*, *c'* are charging curves for different cycles).

The usefulness of these silver-based thiospinels as the positive electrode for rechargeable batteries was investigated with electrochemical charge–discharge measurements. Fig. 4 shows such a charge–discharge profile for a typical cell fabricated with  $\text{Ag}_2\text{MnSn}_3\text{S}_8$  as the positive electrode (area  $1 \text{ cm}^2$ ) and Li foil as anode at a current density of  $0.125 \text{ mA cm}^{-2}$  at room temperature ( $30^\circ\text{C}$ ). The open circuit voltage of the freshly prepared cell in the range of  $2.8\text{--}2.9 \text{ V}$  was found to be stable for several weeks. During the discharge, the voltage drops quickly to  $1.5 \text{ V}$  and a second voltage plateau obtained at ca.  $0.5 \text{ V}$  suggests that Li intercalation occurs in two stages. The capacity obtained for the first cycle is ca.  $51.5 \text{ Ah kg}^{-1}$ , while the second and third cycles show a small decrease in capacity,  $50.06$  and  $47.6 \text{ Ah kg}^{-1}$ , respectively.  $\text{Ag}_2\text{MnSn}_3\text{S}_8$  as a positive electrode shows stable performance upon further cycling at the same rate, which suggests that  $\text{Li}^+$  ions intercalate reversibly in the host lattice.

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## References

- [1] T. Bitoh, T. Hagino, Y. Seki, S. Chikazawa, S. Nagata, J. Phys. Soc. Jpn. 61 (8) (1992) 3011.

- [2] S. Nagata, T. Hagino, Y. Seki, T. Bitoh, *Physica B* 194–196 (1994) 1077–1078.
- [3] A.P. Ramirez, R.J. Cava, J. Krajewski, *Nature* 38 (1997) 156–159.
- [4] R. Schöllhorn, A. Payer, *Angew. Chem. Intl. Ed. Engl.* 24 (1985) 67.
- [5] J. Padiou, J.C. Jumas, M. Ribes, *Rev. Chim. Miner.* 18 (1981) 33.
- [6] M.M. Thackeray, W.I.F. David, J.B. Goodenough, *Mater. Res. Bull.* 17 (1982) 785.
- [7] G. Garg, S. Bobev, A.K. Ganguli, *J. Alloys Compd.* 327 (2001) 113.
- [8] G. Garg, S. Bobev, A.K. Ganguli, *Solid State Ion.* 146 (2002) 195.
- [9] G. Garg, S. Bobev, A. Roy, J. Ghose, D. Das, A.K. Ganguli, *J. Solid State Chem.* 161 (2001) 327.
- [10] G. Garg, S. Bobev, A. Roy, J. Ghose, D. Das, A.K. Ganguli, *Mater. Res. Bull.* 36 (2001) 2429.
- [11] C. Bousquet, A. Kramer, C.P. Vicente, J.L. Tirado, J. Olivier-Fourcade, J.C. Jumas, *J. Solid State Chem.* 134 (1997) 238.
- [12] J. Yajima, E. Ohta, Y. Kanazawa, *J. Mineral* 15 (1991) 222.
- [13] J.C. Jumas, E. Philippot, M. Maurin, *Acta Crystallogr. Sect. B* B35 (1979) 2195.
- [14] R.W. Cheary, A.A. Coelho, *J. Appl. Crystallogr.* 25 (1992) 109.
- [15] P. Selwood, *Magnetochemistry*, Interscience, New York, 1956.
- [16] R.D. Shannon, *Acta Crystallogr. Sect. A* 32 (1976) 751.
- [17] L.B. McCusker, R.B. Von Dreele, D.E. Cox, D. Louer, P. Scardi, *J. Appl. Crystallogr.* 32 (1999) 36.