

Eva M. Heppke, Shamini Mahadevan, Martin Lerch

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Document type Journal article | Published version (i. e. publisher-created published version, that has been (peer-) reviewed and copyedited; also known as: Version of Record (VOR), Final Published Version)

This version is available at https://doi.org/10.14279/depositonce-12527

Citation details Heppke, E. M., Mahadevan, S., & Lerch, M. (2020). New compounds of the Li2 MSn3S8 type. In Zeitschrift für Naturforschung B (Vol. 75, Issues 6–7, pp. 625–631). Walter de Gruyter GmbH. https://doi.org/10.1515/znb-2020-0050

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Eva M. Heppke, Shamini Mahadevan and Martin Lerch* New compounds of the Li₂MSn₃S₈ type

https://doi.org/10.1515/znb-2020-0050

Received April 16, 2020; accepted April 27, 2020; published online July 6, 2020

Abstract: The substitution of Cu/Ag by lithium in complex thiospinels with the general formula $A_2^1B^{II}C^{V_3}X^{VI_8}$ was achieved by ball milling and a subsequent annealing step in an atmosphere of H₂S. Four hitherto unknown compounds Li₂*M*Sn₃S₈ with *M* = Mg, Mn, Fe, Ni were obtained without side phases and have been structurally investigated. From X-ray powder diffraction experiments, space group $Fd\overline{3}m$ and a spinel-type structure are suggested. In these so-called normal spinels, lithium occupies one eighth of the tetrahedral voids (Wyckoff position 8*a*) of the cubic closest packing of the sulfide ions whereas *M* and Sn can be found on one half of the octahedral voids (Wyckoff position 16*d*).

Keywords: band gap determination; lithium; mechanochemical synthesis; Rietveld refinement; thiospinels.

1 Introduction

Quaternary thiospinels of the type $A_{2}^{I}B^{II}C^{IV}{}_{3}X^{VI}{}_{8}$ with copper or silver as monovalent cations have been described in the literature [1-11]. The largest group among this class of materials are Sn-containing compounds. However, also a few thiospinels containing titanium [6, 10] or zirconium [11] have been synthesized. Most of the reported compounds crystallize in space group $Fd\overline{3}m$ while a few examples such as Cu₂CdSn₃S₈ exhibit space groups with lower symmetry, for example $I4_1/a$ [1, 5]. Due to the similar atomic arrangements in the crystal structures with the space groups $Fd\overline{3}m$ and $I4_1/a$ it can be difficult to distinguish between these groups unambiguously using conventional X-ray powder techniques. For some $A_{2}^{I}B^{II}C^{IV}{}_{3}X^{VI}{}_{8}$ compounds, Li⁺ intercalation experiments were carried out [3, 4, 8, 12]. These materials may be promising cathode materials for lithium batteries. In this contribution we present the results

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of our work concerning Cu/Ag substitution by lithium in $A_2^1 B^{II} C^{IV}_3 X^{VI}_8$ thiospinels, which has afforded five compounds Li₂*M*Sn₃S₈ with *M* = Mg, Mn, Fe, Co, Ni. We used a mechanochemical route followed by an annealing step under flowing H₂S gas.

2 Results and discussion

Four new thiospinels $Li_2MSn_3S_8$ with M = Mg, Mn, Fe, Ni have been prepared without side phase by mechanochemical synthesis. Samples of the corresponding Co compound always contained CoS_2 and are not presented here in detail. The crystallinity of the obtained powders was increased by a subsequent annealing procedure. The cation contents of the $Li_2MSn_3S_8$ phases were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis and are in accordance with the molar ratio derived from the chemical formulas (Table 1). No loss of Li_2S was observed after annealing up to T = 550 °C.

Rietveld refinements were performed for space groups $Fd\overline{3}m$ and $I4_1/a$. Convergence problems occurred during the refinements in the tetragonal space group concerning the positions of the sulfur atoms, while successful refinements were achieved in cubic space group $Fd\overline{3}m$. Figures 1–4 show the powder diffraction patterns with the results of the Rietveld refinements. Details are summarized in Table 2. Tables 3-6 list the atomic and structural parameters for each compound. The diffraction patterns point to phase purity for $Li_2MSn_3S_8$ with M = Mg, Mn, Fe, Ni. The total occupancies of cations on the Wyckoff positions 8a/16d were fixed to the ideal cation value which was proofed by ICP-OES analysis. The Debye Waller factors of Li and S were also set and kept fixed during the refinements. As described in the literature, monovalent cations in this structure type [5] or related chalcogenide phases [13] show high Debye-Waller factors. Therefore, the Debye–Waller factor for Li on position 8a was set to a value of 2, keeping in mind that lithium is a poor X-ray scatterer. Mg/Mn/Fe/Ni, and Sn are located on Wyckoff position 16d in a molar ratio of 1:3. Li₂MgSn₃S₈ and $Li_2FeSn_3S_8$ are not stable in air; therefore, capton foils were used for the X-ray powder diffraction experiments with these two compounds resulting in a "hill" in the range of 2θ = 15-30° of the diffraction patterns.

One computational study on the investigation of the probable crystal structure of $Li_2ZnSn_3S_8$ is mentioned in literature [14]. Unfortunately, attempts to synthesize this

^{*}Corresponding author: Martin Lerch, Institut für Chemie, Technische Universität Berlin, Straße des 17. Juni 135, 10623 Berlin, Germany, E-mail: martin.lerch@tu-berlin.de

Technische Universität Berlin, Straße des 17. Juni 135, 10623 Berlin, Germany

Table 1: Cation contents of $Li_2MSn_3S_8$ phases with M = Mg, Mn, Fe, Ni calculated from ICP-OES analyses together with the calculated ideal compositions.

		Li ₂ MgSn ₃ S ₈			Li ₂ MnSn ₃ S ₈
	Ideal (wt%)	Measured (wt%)		Ideal (wt%)	Measured (wt%)
Li	2.1	2.2	Li	2.0	2.1
Mg	3.7	3.8	Mn	8.0	7.7
Sn	54.7	55.2	Sn	52.3	51.5
		Li ₂ FeSn ₃ S ₈			Li ₂ NiSn ₃ S ₈
	Ideal (wt%)	Measured (wt%)		Ideal (wt%)	Measured (wt%)
Li	2.0	2.0	Li	2.0	2.1
Fe	8.2	8.0	Ni	8.6	8.9
Sn	52.2	51.2	Sn	52.0	54.6



Figure 1: X-ray diffraction pattern of $Li_2MgSn_3S_8$ with the results of the Rietveld refinement.



Figure 2: X-ray diffraction pattern of $Li_2MnSn_3S_8$ with the results of the Rietveld refinement.



Figure 3: X-ray diffraction pattern of Li_2FeSn_3S₈ with the results of the Rietveld refinement.



compound by mechanochemical synthesis have not been successful yet.

Li₂*M*Sn₃S₈ phases with *M* = Mg, Mn, Fe, Ni crystallize in the normal spinel-type structure (space group $Fd\overline{3}m$). This structure type can be described as a cubic closest packing of the sulfide ions where one eighth of the tetrahedral voids is occupied by lithium and one half of the octahedral voids by *M* and Sn. Interatomic lithium–sulfur distances range from 2.4048(11) Å for Li₂MgSn₃S₈, 2.4114(16) Å for Li₂MnSn₃S₈, 2.4051(19) Å for Li₂FeSn₃S₈ to 2.3917(16) Å for Li₂NiSn₃S₈ and are in agreement with those found for other tetrahedrally coordinated Li-bearing chalcogenides such as NaLiS (Li–S: 2.456(5) Å) [15] or Li₂(Pb/Eu)GeS₄ (Li–S: 2.4534(9) Å/2.4581(4) Å) [16]. Bond lengths for *M*/Sn–S vary from 2.5669(11) Å for Li₂MgSn₃S₈, 2.5677(16) Å for Li₂MnSn₃S₈, 2.5461(19) Å for Li₂FeSn₃S₈ to 2.5305(16) Å for Li₂NiSn₃S₈ and correlate well with those reported for other complex thiospinels which exhibit a statistical distribution of octahedrally surrounded *M* and Sn with *M* = Mg, Mn, Fe, Ni (Figure 5) [17–19]. Bond angles are depicted in Table 7. Sulfur is coordinated by 1 Li and 3 (*M*/Sn), the tetrahedra being slightly distorted. As the ionic radii of Mg²⁺/Mn²⁺/Fe²⁺/Ni²⁺ and Sn⁴⁺ are close to each other, a statistical distribution of these ions on position 16*d* is quite plausible (C.N. = 6: Mg²⁺: 0.90 Å; Mn²⁺: 0.915 Å high spin; Fe²⁺: 0.825 Å high spin; Ni²⁺: no value given, Sn⁴⁺: 0.86 Å) [20]. It should be mentioned that the refined bond lengths fit well with the values from ionic radii calculations.

Empirical formula	Li ₂ MgSn ₃ S ₈	Li ₂ MnSn ₃ S ₈	Li ₂ FeSn ₃ S ₈	Li ₂ NiSn ₃ S ₈	
Color	Orange	Black-brown	Black	Black-brown	
Structure type	Spinel				
Space group	Fd3m				
Crystal system	Cubic				
Ζ	4				
<i>a</i> , Å	10.5422(3)	10.5543(3)	10.4862(4)	10.4241(3)	
V, Å ³	1171.63(5)	1175.67(6)	1153.08(7)	1132.69(5)	
Calc. density, g cm ⁻³	3.69	3.85	3.93	4.02	
Diffractometer	PANalytical X'Pert M	DP Pro			
Radiation	CuKα radiation				
Wavelength, Å	$\lambda_1 = 1.54056, \lambda_2 = 1$	1.54439			
R _p	0.0162	0.0197	0.0167	0.0181	
R _{wp}	0.0227	0.0268	0.0244	0.0246	
R _{exp}	0.0193	0.0206	0.0209	0.0173	
R _{Bragg}	0.0176	0.0284	0.0309	0.0201	
S	1.18	1.30	1.17	1.42	

Table 2: Results of the Rietveld refinements for $Li_2MSn_3S_8$ with M = Mg, Mn, Fe, Ni (standard deviations in parenthesis).

2.1 UV-Vis spectroscopy

For the determination of the optical band gaps, UV–Vis measurements were performed and the Tauc plot method [21, 22] was applied. As an example, the Tauc plot of the absorbance spectra for the direct optical band gap of $Li_2MgSn_3S_8$ is depicted in Figure 6. The results for all four

investigated Li₂*M*Sn₃S₈ phases with *M* = Mg, Mn, Fe, Ni are presented in Table 8. For Li₂FeSn₃S₈, the optical band gap could not be determined because the measuring range of the instrument is limited to λ = 900 nm. As the determined value of *E*_g = 2.36 eV for Li₂MgSn₃S₈ correlates well with its orange color, the direct optical band gap seems to be the most reliable value; this applies also to the other Li₂*M*Sn₃S₈ phases.

Table 3: Refined atomic parameters for $Li_2MgSn_3S_8$ (standard deviations in parenthesis).

Table 5: Refined atomic parameters for $Li_2FeSn_3S_8$ (standard deviations in parenthesis).

Atom	Wyckoff position	x	У	z	s.o.f	B _{iso} (Ų)
Li	8a	1/8	1/8	1/8	1	2
Mg	16 <i>d</i>	1/2	1/2	1/2	0.25	0.87(2)
Sn	16 <i>d</i>	1/2	1/2	1/2	0.75	0.87(2)
S	32e	0.25670(9)	x	x	1	1

Atom	Wyckoff position	X	у	Z	s.o.f	B _{iso} (Ų)
Li	8 <i>a</i>	1/8	1/8	1/8	1	2
Fe	16 <i>d</i>	1/2	1/2	1/2	0.25	1.44(4)
Sn	16 <i>d</i>	1/2	1/2	1/2	0.75	1.44(4)
S	32e	0.25742(19)	x	x	1	1

Table 4: Refined atomic parameters for $Li_2MnSn_3S_8$ (standard deviations in parenthesis).

Atom	Wyckoff position	X	у	Z	s.o.f	B _{iso} (Ų)
Li	8a	1/8	1/8	1/8	1	2
Mn	16 <i>d</i>	1/2	1/2	1/2	0.25	0.56(3)
Sn	16 <i>d</i>	1/2	1/2	1/2	0.75	0.56(3)
S	32 <i>e</i>	0.25691(14)	x	x	1	1

Table 6: Refined atomic parameters for $Li_2NiSn_3S_8$ (standard deviations in parenthess).

Atom	Wyckoff position	x	y	Z	s.o.f	B _{iso} (Ų)
Li	8a	1/8	1/8	1/8	1	2
Ni	16 <i>d</i>	1/2	1/2	1/2	0.25	0.95(4)
Sn	16 <i>d</i>	1/2	1/2	1/2	0.75	0.95(4)
S	32 <i>e</i>	0.25747(15)	x	x	1	1



Figure 5: M/Sn octahedra in $Li_2MSn_3S_8$ phases (M = Mg, Mn, Fe, Ni) with determined bond lengths (Å) and description of the different sulfur atoms for selected angles in Table 7.

Table 7: Selected bond angles (deg) for $Li_2MSn_3S_8$ phases with M = Mg, Mn, Fe, Ni (standard deviations in parentheses).

	$Li_2MgSn_3S_8$	Li ₂ MnSn ₃ S ₈	$Li_2FeSn_3S_8$	Li ₂ NiSn ₃ S ₈
S–Li–S	109.47(7)	109.47(10)	109.47(12)	109.47(10)
aS-M-bS	93.20(7)	93.30(10)	93.55(6)	93.58(10)
aS–M–cS	179.98(7)	180.00(12)	180.00(14)	180.00(12)
aS-M-dS	86.80(5)	86.70(10)	86.45(10)	86.42(10)
Li-S-M	123.03(4)	122.96(6)	122.79(6)	122.77(6)
M-S-M	93.11(4)	93.21(6)	93.45(6)	93.47(6)

Table 8: Optical band gaps (eV) of $Li_2MSn_3S_8$ phases with M = Mg, Mn, Fe, Ni.

	$Li_2MgSn_3S_8$	Li ₂ MnSn ₃ S ₈	Li ₂ FeSn ₃ S ₈	Li ₂ NiSn ₃ S ₈
Direct band gap	2.36	1.74	/	1.60
Indirect band gap	2.03	1.30	1	1.12



Figure 6: UV–Vis spectra of $Li_2MgSn_3S_8$ with Tauc plot determination of the direct optical band gap (orange).

3 Conclusion

The substitution of Cu/Ag by lithium in complex thiospinels with the general formula $A_2^{I}B^{II}C^{IV}_{3}X^{VI}_{8}$ led to the formation of four hitherto unknown compounds: Li₂*M*Sn₃S₈ with *M* = Mg, Mn, Fe, Ni. A mechanochemical method was used for the preparation. Its success again shows the great potential of this kind of synthetic approach for the preparation of multinary sulfides.

4 Experimental section

4.1 Synthesis

 $Li_2MSn_3S_8$ phases with M = Mg, Mn, Fe, Co, Ni have been synthesized by ball milling of the corresponding binary sulfides Li₂S (Sigma-Aldrich, 99.9%), MgS, MnS (Alfa Aesar, 99.9%), FeS₂ (Sigma-Aldrich, 99.8%), CoS₂ (Sigma-Aldrich, 99.98%), NiS, SnS, and sulfur (Fluka, 99.99%) in a high energy planetary mill (Pulverisette 7, Fritsch, Idar-Oberstein, Germany) at a rotational speed of 450 rpm for 4 h in a 45 mL zirconia grinding breaker with six zirconia balls with a diameter of 15 mm. To increase the crystallinity, the milled products were annealed in a tube furnace at 550 °C for 2-3 h in H₂S atmosphere. MgS was synthesized by annealing of amorphous MgO at 750 °C for 3 h under flowing H₂S gas. Amorphous MgO was prepared using the modified Pechini method [23] with a calcination temperature of 450 °C. A hot and weakly acidic 0.1 M NiSO₄·6H₂O solution and H₂S (Air Liquide, 99.5%) were used for the precipitation of NiS. For the preparation of SnS a solid state reaction of the elements

Sn (Merck, 99.9%) and S (Fluka, 99.99%) in an evacuated and sealed silica ampoule was applied.

4.2 Structural and chemical characterization

Powder diffraction data was collected using a Panalytical X'Pert Pro diffractometer with Cu*K* α radiation (Bragg–Brentano geometry). Rietveld refinements [24] were performed with the program FULLPROF [25] by applying a pseudo-Voigt function. For chemical characterization, ICP-OES was used (715 ES spectrometer, Varian Inc., Palo Alto, USA). For these analyses about 1 mg of the annealed powder was dissolved in small volumes of aqua regia and the solution obtained diluted with purified water up to 15 mL.

Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: +49 7247 808 666; E-mail: crysdata@fiz-karlsruhe.de, https://www. fiz-informationsdienste.de/en/DB/icsd/depot_anforderung. html) on quoting the deposition numbers CSD-1999952–CSD-1999955.

4.3 UV–Vis spectroscopy

The optical properties of the prepared thiospinel phases were measured in diffuse reflectance mode using a Cary 300 UV–Vis spectrometer (Varian Inc., Palo Alto, USA). The obtained spectra were converted into absorption spectra with the Kubelka–Munk function. The standard deviation for E_g was estimated close to 0.05 eV.

Acknowledgment: The authors would like to thank Astrid Müller-Klauke for performing the ICP-OES analysis and Leo Sagurna for his support and provision of the UV–Vis spectrometer (both TU Berlin).

Author contribution: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

Research funding: This project was partially supported by the German Science Foundation (DFG, LE 781/19-1).

Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

References

1. Jumas J. C., Philippot E., Maurin M. Structure du rhodostannite synthétique. *Acta Crystallogr*. 1979, *B35*, 2195–2197.

- Yajima J., Ohta E., Kanazawa Y. Toyohaite Ag₂FeSn₃S₈ a new mineral. *Mineral. J.* 1991, *15*, 222–232.
- Lavela P., Tirado J. L., Morales J., Olivier-Fourcade J., Jumas J. C. Lithium intercalation and copper extraction in spinel sulfides of general formula Cu₂MSn₃S₈ M-Mn-Fe-Co-Ni. *J. Mater. Chem.* 1996, *6*, 41–47.
- Cochez M. A., Jumas J. C., Lavela P., Morales J., Olivier-Fourcade J., Tirado J. L. New tin-containing spinel sulfide electrodes for ambient temperature rocking chair cells. *J. Power Sources* 1996, *62*, 101–105.
- Chykhrij S. I., Sysa L. V., Parasyuk O. V., Piskach L. V. Crystal structure of the Cu₂CdSn₃S₈ compound. *J. Alloys Compd.* 2000, 307, 124–126.
- Branci C., Womes M., Lippens P. E., Olivier-Fourcade J., Jumas J. C. Use of X-ray absorption spectra as a "fingerprint" of the local environment in complex chalcogenides. *J. Solid State Chem.* 2000, *150*, 363–370.
- Garg G., Bobev S., Ganguli A. K. Single Crystal structure and electrical properties of Cu₈Ni₄Sn₁₂S₃₂. J. Alloys Compd. 2001, 327, 113–115.
- Garg G., Ramanujachary K. V., Lofland S. E., Lobanov M. V., Greenblatt M., Maddanimath T., Vijayamohanan K., Ganguli A. K. Crystal structure, magnetic and electrochemical properties of a quaternary thiospinel: Ag₂MnSn₃S₈. J. Solid State Chem. 2003, 174, 229–232.
- Parasyuk O. V., Olekseyuk I. D., Piskach L. V., Volkov S. V., Pekhnyo V. I. Phase relations in the Ag₂S–CdS–SnS₂ system and the crystal structure of the compounds. *J. Alloys Compd.* 2005, *399*, 173–177.
- Sachanyuk V. P., Fedorchuk A. O., Olekseyuk I. D., Parasyuk O. V. New compounds Cu₂MnTi₃S₈ and Cu₂NiTi₃S₈ with thiospinel structure. *Mater. Res. Bull.* 2007, *42*, 143–148.
- Kormosh Z., Fedorchuk A., Wojciechowski K., Tataryn N., Parasyuk O. The Cu₂FeTi₃S₈ and Cu₂FeZr₃S₈ compounds: Crystal structure and electroanalytical application. *Mater. Sci. Eng. C* 2011, *31*, 540–544.
- Branci C., Sarradin J., Olivier-Fourcade J., Jumas J. C. Structural modifications related to lithium intercalation into iron thiospinels. *J. Power Sources* 1999, *81–82*, 282–285.
- Krykhovets O. V., Sysa L. V., Olekseyuk I. D., Glowyak T. Crystal structure of Ag₂In₂GeSe₆. J. Alloys Compd. 1999, 287, 181–184.
- Besse R., Da Silva J. L. F. The role of the alkali and chalcogen atoms on the stability of the layered chalcogenide A₂M["]M₃[™]Q₈ (A = alkali-metal; M = metal-cations; Q = chalcogen) compounds: a density functional theory investigation within van der Waals corrections. *J. Phys.: Condens. Matter* 2017, *29*, 035402.
- Sabrowsky H., Thimm A., Vogt-Mertens P. NaLiS: Ein weiteres interalkalimetallsulfid / NaLiS: A nother inter alkaline metal sulphide. Z. Naturforsch. 1985, 40b, 1759–1760.
- Aitken J. A., Larson P., Mahanti S. D., Kanatzidis M. G. Li₂PbGeS₄ and Li₂EuGeS₄ polar chalcopyrites with a severe tetragonal compression. *Chem. Mater.* 2001, *13*, 4714–4721.
- Garg G., Bobev S., Roy A., Ghose J., Das D., Ganguli A. K. Single crystal structure and Mössbauer studies of a new cation-deficient thiospinel: Cu_{5.47}Fe_{2.9}Sn_{13.1}S₃₂. *Mater. Res. Bull.* 2001, *36*, 2429–2435.
- Garg G., Bobev S., Ganguli A. K. Single crystal structures of two new cation-deficient thiospinels: Cu_{7.38(11)}Mn₄Sn₁₂S₃₂ and Cu_{7.07(6)}Ni₄Sn₁₂S₃₂. Solid State lonics 2002, 146, 195–198.
- Heppke E. M., Klenner S., Janka O., Pöttgen R., Lerch M. Mechanochemical Synthesis of Cu₂MgSn₃S₈ and Ag₂MgSn₃S₈. *Z. Anorg. Allg. Chem.* 2020, *646*, 5–9.
- 20. Shannon R. D. Bond distances in sulfides and a preliminary table of sulfide crystal radii. In *Structure and Bonding in Crystals*;

O'Keeffe M., Navrotsky A., Eds., Vol. 2. Academic Press, Inc.: New York, 1981; pp. 53–70.

- 21. Tauc J. Optical properties and electronic structure of amorphous Ge and Si. *Mater. Res. Bull.* 1968, *3*, 37–46.
- Tauc J., Grigorovici R., Vancu A. Optical properties and electronic structure of amorphous germanium. *Phys. Status Solidi B* 1966, 15, 627–637.
- 23. Pechini M. P. US Patent No. 3330697, 1967.
- 24. Rietveld H. M. A profile refinement method for nuclear and magnetic structures. J. Appl. Crystallogr. 1969, 2, 65–71.
- 25. Rodríguez-Carvajal J. FullProf, A Program for Rietveld Refinement and Pattern Matching Analysis. *Abstracts of the Satellite Meeting on Powder Diffraction of the 15th International Congress of the IUCr, Toulouse, France*, 1990; p. 127.