Eva M. Heppke, Martin Lerch

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Eva M. Heppke and Martin Lerch*

Na₂MgSnS₄ – a new member of the A₂^IB^{II}C^{IV}X₄ family of compounds

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Abstract: A new member of the A₂^IB^{II}C^{IV}X₄ compound family, Na₂MgSnS₄, has been synthesized by ball milling of the binary sulfides SnS, Na₂S, and MgS with elemental sulfur in a high-energy planetary mill, followed by annealing in an atmosphere of H₂S (*T* = 600 °C/3 h). Na₂MgSnS₄ adopts the NaCrS₂-type structure (rhombohedral, space group *R* $\bar{3}m$) with *a* = 3.7496(11) and *c* = 19.9130(6) Å. The Na atoms occupy Wyckoff position 3*b*, whereas the Mg and Sn atoms are statistically distributed on the cation sites 3*a*; all cations are surrounded by six sulfur atoms.

Keywords: mechanochemical synthesis; multinary sulfides; NaCrS₂ type; Rietveld refinement; tin sulfide; X-ray powder diffraction.

1 Introduction

A₂^IB^{II}C^{IV}X₄ compounds are a well-known class of materials with interesting properties. Cu₂ZnSnS₄, for example, is a candidate as an absorber material for thin-film solar cell applications due to its high absorption coefficient and direct optical band gap [1, 2]. A₂^IB^{II}C^{IV}X₄ compounds belong to the adamantine family, being structurally derived from the cubic or hexagonal diamond structure and forming so-called tetrahedral structures implying tetrahedral surroundings of the contained atoms.

In the tetragonal crystal system, two space groups, *I* $\bar{4}2m$ and *I* $\bar{4}$ (both derived from the cubic diamond-/sphalerite-type structure) [3, 4], are listed for quaternary sulfides of the type A₂^IB^{II}C^{IV}X₄. Cu₂ZnSnS₄ crystallizes in the kesterite-type structure with space group *I* $\bar{4}$ [3, 5, 6], whereas Cu₂MSnS₄ (*M* = Mn, Fe, Co, Cd, Hg) [7] as well as Cu₂MGeS₄ (*M* = Zn, Fe, Co, Hg) [7, 8] and Ag₂MSnS₄ (*M* = Fe, Zn) [9, 10] belong to the stannite-type structure

(space group *I* $\bar{4}2m$). Both crystal structure types exhibit a cubic closest packing of the sulfur anions. The kesterite-type structure consists of alternating A^I-C^{IV} and A^I-B^{II} layers along the crystallographic *c* axis, whereas in the stannite-type structure, the monovalent cation occupies another Wyckoff position, which leads to a different cation stacking along the *c* axis (A^I-B^{II}-C^{IV} layers). It should be mentioned that compressed chalcopyrite-like structures with a larger divalent cation such as Ba²⁺, Pb²⁺, and Eu²⁺ also adopt space group *I* $\bar{4}2m$. The compression along the *c* axis leads to an eightfold instead of a tetrahedral coordination of the divalent cations. This type of structure is realized for Li₂Ba(Ge/Sn)S₄ [11], Li₂(Eu/Pb)GeS₄ [12], and Ag₂BaGeS₄ [13].

Hexagonal diamond-related structures have been reported for quaternary sulfides in the orthorhombic crystal system with space group *Pmn*2₁ as well as in the monoclinic crystal system with space group *Pn* [4]. Especially Si-containing compounds such as Cu₂MSiS₄ with *M* = Mn, Fe, Zn, Cd, Mg, Hg [7, 14], several Ag compounds [15–19], Ge-bearing compounds with partly larger divalent cations such as Cu₂MGeS₄ with *M* = Mn, Zn, Cd, Mg, Hg [7, 14, 20], and Li compounds such as Li₂M(Sn/Ge)S₄ with *M* = Cd, Mn, Zn, Co, Fe [16, 18, 21–24] crystallize either in the orthorhombic wurtzstannite- or the monoclinic wurtzkesterite-type structure. Both structure types exhibit a hexagonal closest packed arrangement of the sulfur anions but differ in their cation stacking sequences (*Pmn*2₁: A^I-B^{II}-C^{IV} layers; *Pn*: A^I-C^{IV}-A^I-B^{II} layers) considering the honeycomb set-up. A further subgroup of *Pmn*2₁ is listed in the literature for A₂^IB^{II}C^{IV}X₄ compounds: Ag₂CdGeS₄ crystallizes in the wurtzstannite-type structure (space group *Pmn*2₁) [19] but has also been reported to exist in space group *Pna*2₁ [25] which shows a different arrangement of the cations.

Apart from these structures, there are a few A₂^IB^{II}C^{IV}X₄ sulfides which crystallize in different space groups. In Cu₂NiSnS₄, a disordered alternative in the form of the sphalerite-type structure (a direct subgroup of the cubic diamond structure) with a statistical distribution of the cations on position 4*a* (0,0,0) is realized [7]. The Si analogue Cu₂NiSiS₄ adopts a deformed sphalerite-type structure with statistically distributed cations comparable to the arrangement in Cu₂NiSnS₄ (monoclinic space group *P*2₁/*m*) [7]. Ag₂CdSnS₄ crystallizes in space group *Cmc*2₁ [4,

*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

Eva M. Heppke: Institut für Chemie, Technische Universität Berlin, Straße des 17. Juni 135, 10623 Berlin, Germany

Figure 1: Scanning electron microscope (SEM) images of $\text{Na}_2\text{MgSnS}_4$ particles showing the distribution of Na (pink), Mg (blue), Sn (green), and S (red).

26] where all cations are located on one Wyckoff position, as well as in space group Pn with an ordering of the cations [27]; both structures are derived from the hexagonal diamond/wurtzite-type structure.

According to literature reports, several compounds with the general formula $A_2B^{II}C^{IV}X_4$ do not form tetrahedral structures but exhibit a higher coordination of the contained atoms (especially the divalent cations (B) and the sulfur atoms (X)) [28–34].

The $A_2B^{II}C^{IV}X_4$ compounds mentioned above contain Cu and Ag as monovalent cations (A). Up to now, several Li-bearing sulfides of the type $A_2B^{II}C^{IV}X_4$ are also known [11, 12, 18, 21–24, 35, 36]. The substitution with Na was less successful and has led to only a few representatives: $\text{Na}_2\text{CdSnS}_4$ crystallizes in the monoclinic space group $C2$ and shows a slightly distorted tetrahedral surrounding of the cations [36]. $\text{Na}_2\text{ZnSnS}_4$ crystallizes in the kesterite-type structure ($I\bar{4}$) and exhibits a slight compression along the c axis [37]. Two more Na-containing $A_2B^{II}C^{IV}X_4$ sulfides with earth-alkaline atoms (B) are known [38]: $\text{Na}_2\text{BaSnS}_4$ belongs to the tetragonal crystal system (space group $I\bar{4}2d$) but forms a tunnel structure with partly higher coordinated

cations instead of a tetrahedral structure. The same applies to the Ge analogue $\text{Na}_2\text{BaGeS}_4$ crystallizing in space group $R3c$.

In this contribution, we present a new Na-bearing $A_2B^{II}C^{IV}X_4$ compound with Mg as the divalent cation. $\text{Na}_2\text{MgSnS}_4$ crystallizes in a space group hitherto unknown for the $A_2B^{II}C^{IV}X_4$ family, the rhombohedral space group $R\bar{3}m$. This space group is more common among ternary chalcogenides like NaCrS_2 [39] or $3R\text{-LiTiS}_2$ [40].

2 Results and discussion

A phase-pure and well-crystallized product of the formula $\text{Na}_2\text{MgSnS}_4$ was synthesized mechanochemically with a subsequent annealing step in H_2S atmosphere as described in Section 4. Energy dispersive X-ray spectroscopy (EDX) measurements showed a homogenous distribution of the contained elements Na, Mg, Sn, and S in the $\text{Na}_2\text{MgSnS}_4$ samples (Figure 1). The analytical data are consistent with the theoretical ones, except for those of Sn which differ slightly from the ideal value due to the difficult fitting of the background around those peaks (Table 1).

The crystal structure of $\text{Na}_2\text{MgSnS}_4$ has been determined using X-ray powder diffraction. The diffraction pattern was analyzed using the software X'PERT HIGHSCORE PLUS (PANalytical, Almelo, The Netherlands) which refers to the Inorganic Crystal Structure Database ICSD (FIZ Karlsruhe). Thereby, the NaCrS_2 -type structure was suggested indicating a rhombohedral symmetry with space group $R\bar{3}m$. Thus, Rietveld refinement [41] was performed in space group $R\bar{3}m$ which turned out to be quite successful exhibiting a statistical mixture of Mg and Sn. Results of the

Table 1: Phase composition of $\text{Na}_2\text{MgSnS}_4$ calculated from EDX analysis compared to the ideal values.

	$\text{Na}_2\text{MgSnS}_4$	
	Ideal (at%)	Measured (at%)
Na	25	24.7
Mg	12.5	12.1
Sn	12.5	14.4
S	50	48.9

Rietveld refinement are depicted in Figure 2. The experimental diffraction pattern is in good agreement with the theoretical one with a residual value $R_{wp} = 0.0308$. The atomic and structural parameters are summarized in Tables 2 and 3. Site occupation factors of positions $3a$, $3b$, and $6c$ as well as the Debye Waller factor of sulfur on position $6c$ were kept fixed during refinement. The structure contains two independent cation sites, Mg and Sn, which are statistically distributed on position $3a$ in a molar ratio of 1:1.

Na_2MgSnS_4 crystallizes rhombohedral in the $NaCrS_2$ -type structure in space group $R\bar{3}m$ with $a = 3.750(3)$ and $c = 19.9130(14)$ Å. The crystal structure is derived from the NaCl structure type and is based on a cubic closest packing of the sulfur anions. Sulfur and Mg/Sn form a $CdCl_2$ -type arrangement where the octahedral voids of every other layer are statistically filled with Mg and Sn. The remaining octahedral voids are occupied by Na (Figure 3). All cations show an octahedral coordination. NaS_6 octahedra are edge-sharing with $(Mg/Sn)S_6$ octahedra, and all octahedra are edge-sharing with each other. The calculated average bond lengths for the NaS_6 polyhedra with 2.873(2) Å and for the $(Mg/Sn)S_6$ polyhedra with 2.595(2) Å (Figure 4) are in accordance with standard ionic radii: Na^+ : 1.16 Å; Mg^{2+} : 0.86 Å; Sn^{4+} : 0.83 Å; and S^{2-} : 1.70 Å [42]. The ionic radii of Mg^{2+} and Sn^{4+} are very close to each other, which allows for a statistical distribution on one position. It should be mentioned that magnesium and sodium cannot be distinguished by conventional X-ray diffractions techniques, but due to their different ionic radii, a significant degree of mixed occupation is not probable. The interatomic Na–S distances correlate quite well with those reported for compounds such as $NaCrS_2$ (Na–S: 2.773(14) Å) [39]. (Mg/Sn)–S bond lengths are in agreement with those of spinel-type chalcogenides where Mg and Sn atoms are also statistically distributed on one position and octahedrally surrounded by sulfur atoms: $Cu_2MgSn_3S_8$: (Mg/Sn)–S: 2.5658(10) Å; and $Ag_2MgSn_3S_8$: (Mg/Sn)–S: 2.5721(16) Å [43]. Sulfur atoms are coordinated by 3 Na and 3 (Mg/Sn) atoms forming slightly distorted octahedra. Due to the larger difference in the electronegativities of the contained cations and anions, Na_2MgSnS_4 tends to a more ionic character and crystallizes in a structure type derived from rocksalt and not from sphalerite or wurtzite [44, 45].

As mentioned above, the $NaCrS_2$ -type structure is derived from the rocksalt type. The corresponding group-subgroup scheme using the Bärnighausen formalism [46, 47] is presented in Figure 5. We start with space group $Fm\bar{3}m$ for the rock salt type exhibiting a cubic closest packing of Cl atoms and an occupation of every octahedral void with Na atoms [48]. The first symmetry reduction leads

Figure 2: X-ray diffraction pattern of Na_2MgSnS_4 with results of the Rietveld refinement.

Table 2: Results of the Rietveld refinement for Na_2MgSnS_4 (standard deviations in parenthesis).

Empirical formula	Na_2MgSnS_4
Color	Olive
Structure type	$NaCrS_2$
Space group	$R\bar{3}m$
Crystal system	Rhombohedral
Z	1.5
$a = b$, Å	3.750(3)
c, Å	19.9130(14)
V, Å ³	242.46(3)
Calculated density, g cm ⁻³	3.26
Diffractometer	PANalytical X'Pert MDP Pro
Radiation	CuK α radiation
Wavelengths λ_1/λ_2 , Å	1.54056/1.54439
R_p	0.0222
R_{wp}	0.0308
R_{exp}	0.0194
R_{Bragg}	0.0289
S	1.59

Table 3: Refined atomic parameters for Na_2MgSnS_4 (standard deviations in parenthesis).

Atom	Wyckoff	x	y	z	s.o.f	B_{iso} (Å ²)
Na1	3b	0	0	1/2	1	2.27(19)
Mg1	3a	0	0	0	0.5	0.45(7)
Sn1	3a	0	0	0	0.5	0.45(7)
S1	6c	0	0	0.26148(19)	1	1

Figure 3: Crystal structure of $\text{Na}_2\text{MgSnS}_4$ (NaCrS_2 type) with NaS_6 and $(\text{Mg/Sn})\text{S}_6$ octahedra.

Figure 4: NaS_6 and $(\text{Mg/Sn})\text{S}_6$ octahedra in $\text{Na}_2\text{MgSnS}_4$ (bond lengths in Å).

already to space group $R\bar{3}m$ via a *translationengleiche* transition of index 4. The face-centered lattice changes here to an R -centered lattice. Two crystallographically independent atom positions are maintained in this case; as an example for this arrangement, antiferromagnetic NiO (af-NiO) can be given [49]. In the next step, we have an *isomorphic* transition with index two resulting in a doubling of the c axis. At this step, Wyckoff position $3a$ splits up into two crystallographic independent positions

Figure 5: Group-subgroup scheme (Bärnighausen formalism) for the group theoretical relation between rocksalt and NaCrS_2 type.

$3a$ (Na) and $3b$ (Cr). The anion position $3b$ changes to Wyckoff position $6c$ in the NaCrS_2 type.

3 Conclusions

Using the mechanochemical synthesis route, a new member of the $A_2B^{II}C^{IV}X_6$ compound family has been synthesized. $\text{Na}_2\text{MgSnS}_4$ exhibits the NaCrS_2 -type structure (space group $R\bar{3}m$) with $a = 3.750(3)$ and $c = 19.9130(14)$ Å. The NaCrS_2 type is derived from the rocksalt type and exhibits an atomic arrangement similar to the CdCl_2 type with additional atoms occupying the remaining voids. The successful synthesis of this compound again shows the large potential of the mechanochemical route for the preparation of multinary sulfides.

4 Experimental section

4.1 Synthesis

$\text{Na}_2\text{MgSnS}_4$ was synthesized by ball milling of Na_2S (Sigma Aldrich), MgS , SnS , and sulfur (Fluka, 99.99%) in a high

energy planetary mill (Pulverisette 7, Fritsch, Idar-Oberstein, Germany) followed by annealing under flowing H_2S gas stream. The reactants were filled in a 45-mL zirconia grinding beaker with six zirconia balls (diameter: 15 mm) and ground at a rotational speed of 450 rpm for 4 h. The milled material was annealed at $T = 600^\circ C$ for 3 h in an atmosphere of H_2S to increase its crystallinity. MgS was prepared using high-temperature sulfidation of amorphous MgO ($750^\circ C$, 3 h); MgO was prepared by a modified Pechini method [50] with a calcination temperature of $450^\circ C$. Solid state reaction of Sn (Merck, 99.9%) and S (Fluka, 99.99%) in an evacuated and sealed SiO_2 ampoule was used for the preparation of SnS .

4.2 Structural and chemical characterization

Na_2MgSnS_4 was structurally characterized by X-ray powder diffraction in Bragg–Brentano geometry using a PANalytical X'Pert MDP Pro diffractometer. The diffractometer operates with $CuK\alpha$ radiation at 40 kV and 40 mA. Structural refinements were carried out using the program suite FULLPROF [51] by applying a pseudo-Voigt function. To determine the phase composition of Na_2MgSnS_4 , EDX was performed using a DSM 982 GEMINI spectrometer (Carl Zeiss AG, Oberkochen, Germany) equipped with a XFlash 6|60 detector (Bruker, Billerica, USA). Three independent measurements were performed, and their average value was used to calculate the chemical composition. Including the determination of the sulfur content, a device error of 5% is presumed for the EDX analysis. The EDX measurements were performed at the Zentrum für Elektronenmikroskopie (ZELMI) of the Technische Universität Berlin.

Further details of the crystal structure investigations may be obtained from the joint CCDC/FIZ Karlsruhe online deposition service: <https://www.ccdc.cam.ac.uk/structures/> by quoting the deposition number CSD-2007152.

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References

1. Katagiri H., Saitoh K., Washio T., Shinohara H., Kurumadani T., Miyajima S. Development of thin film solar cell based on Cu_2ZnSnS_4 thin films. *Sol. Energy Mater. Sol. Cells* 2001, 65, 141–148.
2. Seol J.-S., Lee S.-Y., Lee J.-C., Nam H.-D., Kim K.-H. Electrical and optical properties of Cu_2ZnSnS_4 thin films prepared by rf magnetron sputtering process. *Sol. Energy Mater. Sol. Cells* 2003, 75, 155–162.
3. Hall S. R., Szymanski J. T., Stewart J. M. Kesterite, $Cu_2(Zn,Fe)SnS_4$, and stannite, $Cu_2(Fe,Zn)SnS_4$, structurally similar but distinct minerals. *Can. Mineral.* 1978, 16, 131–137.
4. Parthé E., Yvon K., Deitch R. H. The crystal structure of Cu_2CdGeS_4 and other quaternary normal tetrahedral structure compounds. *Acta Crystallogr. B Struct. Sci.* 1969, 25, 1164–1174.
5. Schorr S., Hoebler H.-J., Tovar M. A neutron diffraction study of the stannite-kesterite solid solution series. *Eur. J. Mineral.* 2007, 19, 65–73.
6. Choubac L., Paris M., Lafond A., Guillot-Deudon C., Rocquefelte X., Jobic S. Multinuclear (^{67}Zn , ^{119}Sn and ^{65}Cu) NMR spectroscopy—an ideal technique to probe the cationic ordering in Cu_2ZnSnS_4 photovoltaic materials. *Phys. Chem. Chem. Phys.* 2013, 15, 10722–10725.
7. Schäfer W., Nitsche R. Tetrahedral quaternary chalcogenides of the type $Cu_2 II IV S_4(Se_4)$. *Mater. Res. Bull.* 1974, 9, 645–654.
8. Moodie A. F., Whitfield H. J. Determination of the structure of Cu_2ZnGeS_4 polymorphs by lattice imaging and convergent-beam electron diffraction. *Acta Crystallogr. B Struct. Sci.* 1986, 42, 236–247.
9. Caye R., Laurent Y., Picot R., Pierrot R., Levy C. La hocartite, Ag_2SnFeS_4 , une nouvelle espèce minérale. *Bull. Soc. Fr. Mineral. Cristallogr.* 1968, 91, 383–387.
10. Zdenek J., Picot P. La pirquitasite, Ag_2ZnSnS_4 , un nouveau membre du groupe de la stannite. *Bull. Mineral.* 1982, 105, 229–235.
11. Wu K., Zhang B., Yang Z., Pan S. New compressed chalcopyrite-like $Li_2BaM^IVQ_4$ ($M^IV = Ge, Sn; Q = S, Se$): promising infrared nonlinear optical materials. *J. Am. Chem. Soc.* 2017, 139, 14885–14888.
12. Aitken J. A., Larson P., Mahanti S. D., Kanatzidis M. G. Li_2PbGeS_4 and Li_2EuGeS_4 : polar chalcopyrites with a severe tetragonal compression. *Chem. Mater.* 2001, 13, 4714–4721.
13. Teske C. L. Darstellung und Kristallstruktur von silber-bariumthiogermanat(IV). Ag_2BaGeS_4 /preparation and crystal structure of silver-barium-thiogermanate(IV). Ag_2BaGeS_4 . *Z. Naturforsch.* 1979, 34b, 544–547.
14. Liu B.-W., Zhang M.-J., Zhao Z.-Y., Zeng H.-Y., Zheng F.-K., Guo G.-C., Huang J.-S. Synthesis, structure, and optical properties of the quaternary diamond-like compounds $II_2-III-IV-VI_4$ ($II=Cu; III=Mg; IV=Si, Ge; VI=S, Se$). *J. Solid State Chem.* 2013, 204, 251–256.
15. Haeuseler H., Himmrich M. Neue Verbindungen Ag_2HgMX_4 mit Wurtzstannitstruktur/new compounds Ag_2HgMX_4 with the Wurtzstannite type structure. *Z. Naturforsch.* 1989, 44b, 1035–1036.
16. Brunetta C. D., Brant J. A., Rosmus K. A., Henline K. M., Karey E., MacNeil J. H., Aitken J. A. The impact of three new quaternary sulfides on the current predictive tools for structure and composition of diamond-like materials. *J. Alloys Compd.* 2013, 574, 495–503.

17. Brunetta C. D., Karuppannan B., Rosmus K. A., Aitken J. A. The crystal and electronic band structure of the diamond-like semiconductor Ag_2ZnSiS_4 . *J. Alloys Compd.* 2012, 516, 65–72.
18. Greil S. *Untersuchungen an ternären und quaternären Kupfer-, Lithium-, und Silbersulfiden mit Diamantstruktur*; Dissertation, Universität Regensburg; Regensburg, 2015.
19. Parasyuk O. V., Piskach L. V., Oleksyuk I. D., Pekhnyo V. I. The quasi-ternary system $Ag_2ScdSgeS_2$ and the crystal structure of Ag_2CdGeS_4 . *J. Alloys Compd.* 2005, 397, 95–98.
20. Oleksyuk I. D., Marchuk O. V., Gulay L. D., Zhabankov O.Y. Isothermal section of the $Cu_2Se-HgSe-GeSe_2$ system at 670K and crystal structures of the compounds $Cu_2HgGeSe_4$ and HT-modification of $Cu_2HgGeSe_4$. *J. Alloys Compd.* 2005, 398, 80–84.
21. Lekse J. W., Moreau M. A., McNerny K. L., Yeon J., Halasyamani P. S., Aitken J. A. Second-harmonic generation and crystal structure of the diamond-like semiconductors Li_2CdGeS_4 and Li_2CdSnS_4 . *Inorg. Chem.* 2009, 48, 7516–7518.
22. Lekse J. W., Leverett B. M., Lake C. H., Aitken J. A. Synthesis, physicochemical characterization and crystallographic twinning of Li_2ZnSnS_4 . *J. Solid State Chem.* 2008, 181, 3217–3222.
23. Brant J. A., Clark D. J., Kim Y. S., Jang J. I., Weiland A., Aitken J. A. Outstanding laser damage threshold in Li_2MnGeS_4 and tunable optical nonlinearity in diamond-like semiconductors. *Inorg. Chem.* 2015, 54, 2809–2819.
24. Brant J. A., Devlin K. P., Bischoff C., Watson D., Martin S. W., Gross M. D., Aitken J. A. A new class of lithium ion conductors with tunable structures and compositions: quaternary diamond-like thiogermanates. *Solid State Ion.* 2015, 278, 268–274.
25. Brunetta C. D., Minsterman W. C., Lake C. H., Aitken J. A. Cation ordering and physicochemical characterization of the quaternary diamond-like semiconductor Ag_2CdGeS_4 . *J. Solid State Chem.* 2012, 187, 177–185.
26. Parasyuk O. V., Oleksyuk I. D., Piskach L. V., Volkov S. V., Pekhnyo V. I. Phase relations in the $Ag_2S-CdS-SnS_2$ system and the crystal structure of the compounds. *J. Alloys Compd.* 2005, 399, 173–177.
27. Heppke E. M., Berendts S., Lerch M. Crystal structure of mechanochemically synthesized Ag_2CdSnS_4 . *Z. Naturforsch.* 2020, 75b, 393–402.
28. Kogut Y. M., Fedorchuk A., Zhabankov O., Romanyuk Y., Kityk I., Piskach L. V., Parasyuk O. V. Isothermal section of the $Ag_2S-PbS-GeS_2$ system at 300K and the crystal structure of Ag_2PbGeS_4 . *J. Alloys Compd.* 2011, 509, 4264–4267.
29. Teske C. L., Vetter O. Präparative und röntgenographische Untersuchung am System $Cu_{2-x}Ag_xBaSnS_4$. *Z. Anorg. Allg. Chem.* 1976, 426, 281–287.
30. Teske C. L. Über die Darstellung und röntgenographische Untersuchung von Cu_2SrGeS_4 und Cu_2BaGeS_4 /on the preparation and X-ray investigation of Cu_2SrGeS_4 and Cu_2BaGeS_4 . *Z. Naturforsch.* 1979, 34b, 386–389.
31. Llanos J., Mujica C., Sánchez V., Peña O. Physical and optical properties of the quaternary sulfides $SrCu_2MS_4$ and $EuCu_2MS_4$ (M=Ge and Sn). *J. Solid State Chem.* 2003, 173, 78–82.
32. Oleksyuk I. D., Piskach L. V., Zhabankov O. Y., Parasyuk O. V., Kogut Y. M. Phase diagrams of the quasi-binary systems Cu_2S-SiS_2 and Cu_2SiS_3-PbS and the crystal structure of the new quaternary compound Cu_2PbSiS_4 . *J. Alloys Compd.* 2005, 399, 149–154.
33. Teske C. L. Darstellung und Kristallstruktur von gold-barium-thiostannat(IV), Au_2BaSnS_4 . *Z. Anorg. Allg. Chem.* 1978, 445, 193–201.
34. Teske C. L., Vetter O. Ergebnisse einer Röntgenstrukturanalyse von silber-barium-thiostannat(IV), Ag_2BaSnS_4 . *Z. Anorg. Allg. Chem.* 1976, 427, 200–204.
35. Kanno R. Synthesis of a new lithium ionic conductor, thio-LISICON—lithium germanium sulfide system. *Solid State Ion.* 2000, 130, 97–104.
36. Devi M. S., Vidyasagar K. First examples of sulfides in the quaternary A/Cd/Sn/S (A = Li, Na) systems: molten flux synthesis and single crystal X-ray structures of Li_2CdSnS_4 , Na_2CdSnS_4 and $Na_6CdSn_4S_{12}$. *J. Chem. Soc. Dalton Trans.* 2002, 9, 2092–2096.
37. He J., Guo Y., Huang W., Zhang X., Yao J., Zhai T., Huang F. Synthesis, crystal structure, and optical properties of noncentrosymmetric Na_2ZnSnS_4 . *Inorg. Chem.* 2018, 57, 9918–9924.
38. Wu K., Yang Z., Pan S. Na_2BaMQ_4 (M=Ge, Sn; Q=S, Se): infrared nonlinear optical materials with excellent performances and that undergo structural transformations. *Angew. Chem. Int. Ed.* 2016, 55, 6713–6715.
39. Rüdorff W., Stegemann K. Kristallstruktur und magnetisches Verhalten der Alkalithiochromite. *Z. Anorg. Allg. Chem.* 1943, 251, 376–395.
40. Nakhil S., Lerch M., Koopman J., Islam M. M., Bredow T. Crystal structure of $3R-LiTiS_2$ and its stability compared to other polymorphs. *Z. Anorg. Allg. Chem.* 2013, 639, 2822–2825.
41. Rietveld H. M. A profile refinement method for nuclear and magnetic structures. *J. Appl. Crystallogr.* 1969, 2, 65–71.
42. Shannon R. D. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Cryst. A* 1976, 32, 751–767.
43. Heppke E. M., Klenner S., Janka O., Pöttgen R., Lerch M. Mechanochemical synthesis of $Cu_2MgSn_3S_8$ and $Ag_2MgSn_3S_8$. *Z. Anorg. Allg. Chem.* 2020, 646, 5–9.
44. Mooser E., Pearson W. B. On the crystal chemistry of normal valence compounds. *Acta Cryst.* 1959, 12, 1015–1022.
45. Goodman C. H. L. The prediction of semiconducting properties in inorganic compounds. *J. Phys. Chem. Solids* 1958, 6, 305–314.
46. Bärnighausen H. Group-subgroup relations between space groups a useful tool in crystal chemistry. *MATCH Commun. Math. Chem.* 1980, 9, 139–175.
47. Müller U. Kristallographische Gruppe-Untergruppe-Beziehungen und ihre Anwendung in der Kristallchemie. *Z. Anorg. Allg. Chem.* 2004, 630, 1519–1537.
48. Bragg W. L. The structure of some crystals as indicated by their diffraction of X-rays. *Proc. R. Soc. Lond. A* 1913, 89, 248–277.
49. Rodic D., Spasojevic V., Kusigerski V., Tellgren R., Rundlof H. Magnetic ordering in polycrystalline $Ni_xZn_{1-x}O$ solid solutions. *Phys. Status Solidi B* 2000, 218, 527–536.
50. Pechini M. P. US Patent No 3330697, 1967.
51. Rodríguez-Carvajal R. FULLPROF, A program for Rietveld refinement and pattern matching analysis. In *Satellite Meeting on Powder Diffraction of the 15th International Congress of the IUCr, Toulouse (France)*, 1990, p. 127.