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Crystal structures of the $La_3AgSnSe_7$ and $R_3Ag_{1-\delta}SnS_7$ (R = La, Ce; $\delta = 0.18-0.19$) compounds

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Abstract

The crystal structures of new quaternary compounds $La_3AgSnSe_7$ (space group $P6_3$, Pearson symbol $hP24$, $a = 1.0805(4)$ nm, $c = 0.6245(1)$ nm, $R1 = 0.0315$), $La_3Ag_{0.82}SnS_7$ (space group $P6_3$, Pearson symbol $hP23.64$, $a = 1.0399(1)$ nm, $c = 0.6016(1)$ nm, $R1 = 0.0149$) and $Ce_3Ag_{0.81}SnS_7$ (space group $P6_3$, Pearson symbol $hP23.62$, $a = 1.0300(1)$ nm, $c = 0.6002(1)$ nm, $R1 = 0.0151$) were determined by means of X-ray single crystal diffraction. Structural investigations of the $R_3Ag_{1-\delta}SnS_7$ (R = La, Ce; $\delta = 0.18$-$0.19(1)$) compounds at 450 and 530 K were performed. Low temperature data (12 K) for $Ce_3Ag_{0.81}SnS_7$ were also collected. The nearest neighbours of the La(Ce), Ag and Sn atoms are exclusively Se(S) atoms. The latter form distorted trigonal prisms around the La(Ce) atoms, and distorted tetrahedrons around the Sn atoms. The Ag (Ag1) atoms have triangular surroundings: they are located very close to the planes built of three Se(S) atoms. The Ag2 atoms in the structures of the $La_3Ag_{0.82}SnS_7$, $Ce_3Ag_{0.81}SnS_7$ compounds are located practically in the centres of trigonal antiprisms. The pseudo-potentials determined through the Ag atoms show relatively low barrier between two nearest positions which decreases when temperature rises.

Keywords: Rare-earth compounds; Chalcogenides; Crystal structures; X-ray single crystal diffraction

1. Introduction

Production of the compounds with increasingly complex compositions, such as ternary, quaternary, etc., has become a principle direction in a modern science of materials [1]. Among the multicomponent systems an important place belongs to the complex rare-earth chalcogenides. The rare-earth chalcogenides are being intensively studied during last years due to their specific thermal, electrical and optical properties, which for example make them prospective materials in the field of infrared and nonlinear optics. Therefore, the synthesis and the investigation of the crystal structures of complex chalcogenides is important step in the search for new materials.

This paper presents part of our systematic investigation of quaternary rare-earth chalcogenides with transition metals and tin. Previously we reported on the crystal structures of the compounds R_3CuSnS_7 (R = Y, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy and Ho) [2,3] and $R_3CuSnSe_7$ (R = Y, La, Ce, Pr, Nd, Sm, Gd, Tb and Dy) [4–6]. They were determined by means of X-ray single crystal and powder diffraction and shown to be of La_3CuSiS_7 type (space group $P6_3$). Here, we present for the first time the results of the refinement of the crystal structure of $La_3AgSnSe_7$ and $R_3Ag_{1-\delta}SnS_7$ (R = La, Ce; $\delta = 0.18-0.19(1)$) from X-ray single crystal data.

2. Experimental details

The samples with the nominal compositions $La_3AgSnSe_7$, La_3AgSnS_7 and Ce_3AgSnS_7 were prepared by sintering the elemental constituents with the atomic ratio R:Ag:Sn:S = 3:1:1:7 of the purity better than 99.9 wt% in an evacuated

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quartz ampoules. However, the authors made an attempt to prepare $Ce_3AgSnSe_7$ compound, but without much success. The syntheses of the entitled compounds were carried out in a tube furnace. The ampoules were heated with a heating rate of 30 K/h to the maximal temperature, 1420 K. They were kept at the maximal temperature during 3 h. Then they were cooled slowly (10 K/h) to 870 K and annealed at this temperature for 240 h. After annealing the ampoules with the samples were quenched in cold water. The compounds were obtained with satisfying yields (over 90%) and homogeneity of the samples was checked by powder diffraction method. EDAX PV9800 microanalyzer was used for the confirmation of the compositions of the crystals. Calculated for $La_3AgSnSe_7$ (dark red crystals) % (±3%) La: 34.84, Ag: 9.02, Sn: 9.93, Se: 46.21 and found % La: 37.56, Ag: 11.41, Sn: 11.41, Se: 39.62. Calculated for $La_3Ag_{0.82}SnS_7$ (dark red crystals) % La: 49.12, Ag: 10.43, Sn: 13.99, S: 26.46 and found % La: 47.51, Ag: 9.57, Sn: 14.27, S: 28.65. Calculated for $Ce_3Ag_{0.81}SnS_7$ (dark red crystals) % Ce: 49.40, Ag: 10.27, Sn: 13.95, S: 26.38 and found % Ce: 46.57, Ag: 10.70, Sn: 14.09, S: 28.65.

Small single crystals, suitable for crystal structure investigation, were selected from all samples. The X-ray intensities data were collected on a KUMA Diffraction KM-4 four-circle diffractometer equipped with a CCD detector, using graphite-monochromatized Mo*K*α radiation ($\lambda = 0.071073$ nm). Low temperature measurement at 12 K was carried out with a helium-gas-flow cooling system (Oxford Cryosystem controller). High temperature measurements were collected at 450 and 530 K using KUMA Diffraction equipment. The data were worked out by the CrysAlis Data Reduction program [7] taking into account correction on absorption. The absorption coefficient was calculated using special procedure employing appointed shape and dimensions of the sample. The intensities of the reflections were corrected for Lorentz and polarization factors. The crystal structures were solved by Patterson methods [8] and refined by full matrix least squares method using SHELX-97 program [9]. Acentric space group $P6_3$ was checked in PLATON program and no additional symmetry elements were found [10]. The crystal structures for $La_3Ag_{0.82}SnS_7$ and $Ce_3Ag_{0.81}SnS_7$ were also refined using JANA2000 program [11] with four-order anharmonic parameters of Gram-Charlier model for temperature components [12–14] for Ag atom with no splitting for two different positions. For the $Ce_3Ag_{0.81}SnS_7$ crystal structure measured at 12 K three-order parameters were sufficient to described anisotropy in the refinement.

3. Results and discussion

The existence of $La_3AgSnSe_7$ compound was determined during the investigation of the phase relations in the La_2Se_3-Ag_2Se-$SnSe_2$ system. The crystal structure of this compound was investigated using X-ray single crystal diffraction. The extinctions were found to be consistent with the space group $P6_3$. The crystal data and the structure refinement details are summarized in Table 1. The refined atomic coordinates and the temperature factors are given in Table 2. The compound crystallizes in the La_3CuSiS_7 type of structure [15]. The composition of the $La_3AgSnSe_7$ compound was confirmed using EDX analysis.

The formation of the compounds with approximate compositions R_3AgSnS_7 (R = La, Ce) was also determined during the investigation of the phase relations in the R_2S_3–Ag_2S–SnS_2 systems. The crystal structures of both compounds were investigated using X-ray single crystal diffraction. The extinctions were found to be consistent with the space group $P6_3$. One position of R, two positions of Ag, one position of Sn and three positions of S were determined. The second position of the Ag atom was found in difference Fourier map. The positions of the Ag atoms are partially occupied. The final calculated compositions of the compounds are described by formulas $La_3Ag_{0.82}SnS_7$ and $Ce_3Ag_{0.81}SnS_7$. Results of crystal structure determinations of these compounds agree with results of EDX analysis. The crystal data and the structure refinement details of $La_3Ag_{0.82}SnS_7$ are summarized in Table 3, whereas refined atomic coordinates and the temperature factors are given in Table 4. The crystal data and the structure refinement details of $Ce_3Ag_{0.81}SnS_7$ are summarized in Table 5, whereas refined atomic coordinates and the temperature factors are given in Table 6. The crystal structures of the $La_3Ag_{0.82}SnS_7$ and $Ce_3Ag_{0.81}SnS_7$ compounds are similar, but different dependencies with temperature are observed.

Table 1
Crystal data and structure refinement details of the $La_3AgSnSe_7$ compound

Empirical formula	$La_3AgSnSe_7$
Formula weight	1196.01
Space group	$P6_3$ (No. 173)
Unit cell dimensions	$a = 1.0805(4)$ nm $c = 0.6246(1)$ nm
Volume	0.6315(2) nm^3
Number of formula units per unit cell	2
Measurement temperature	298 K
Calculated density	6.290 g/cm^3
Absorption coefficient	33.521 mm^{-1}
F (0 0 0)	1012
Θ range for data collection	3.77–28.69
Index ranges	$-14 \leqslant h \leqslant 14$ $-14 \leqslant k \leqslant 14$ $-8 \leqslant l \leqslant 7$
Reflections collected	7938
Independent reflections	1068 [R (int.) = 0.0904]
Refinement method	Full-matrix least-square on F^2
Absolute structure parameter	−0.01(2)
Data/restraints/parameters	1068/1/38
Goodness-of-fit on F^2	0.796
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0315$, w$R_2 = 0.0350$
R indices (all data)	$R_1 = 0.0540$, w$R_2 = 0.0375$
Extinction coefficient	0.0050(2)
Largest diff. peak and hole × 10^{-3}	1.913 and −1.698 e/nm^3

Table 2
Atomic coordinates and temperature factors for the $La_3AgSnSe_7$ compound

Atom	Position	x/a	Y/b	z/c	Ueq. (10^2, nm2	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
La	6(*c*)	0.1347(1)	0.7768(1)	0.1189(1)	0.0114(1)	0.0124(3)	0.0116(3)	0.0114(3)	−0.0001(4)	0.0004(4)	0.0069(3)
Ag	2(*a*)	0	0	0.0513(3)	0.0251(5)	0.0157(5)	0.0157(5)	0.044(1)	0	0	0.0079(2)
Sn	2(*b*)	1/3	2/3	0.7005(2)	0.0120(3)	0.0138(4)	0.0138(4)	0.0084(7)	0	0	0.0069(2)
Se1	6(*c*)	0.4264(1)	0.9109(1)	0.8672(2)	0.0122(3)	0.0130(6)	0.0132(6)	0.0113(6)	0.0013(4)	−0.0008(5)	0.0073(5)
Se2	6(*c*)	0.8342(1)	0.7308(1)	0.0981(2)	0.0129(2)	0.0130(5)	0.0132(5)	0.0131(6)	0.0002(6)	−0.0004(6)	0.0070(4)
Se3	2(*b*)	1/3	2/3	0.3043(3)	0.0126(5)	0.0147(6)	0.0147(6)	0.0085(11)	0	0	0.0073(3)

Ueq. is definite as one third of the trace of the orthogonalized U_{ij} tensor.
The anisotropic temperature factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+\cdots+2hka^*b^*U_{12}]$.

Table 3
Crystal data and structure refinement details of the $La_3Ag_{1-\delta}SnS_7$ ($\delta = 0.18(1)$) compound at different temperatures

Empirical formula	$La_3Ag_{0.82}SnS_7$	$La_3Ag_{0.82}SnS_7$	$La_3Ag_{0.82}SnS_7$
Formula weight	848.29	848.29	848.29
Space group	$P6_3$ (No. 173)	$P6_3$ (No. 173)	$P6_3$ (No. 173)
Unit cell dimensions	$a = 1.0399(1)$ nm	$a = 1.0404(1)$ nm	$a = 1.0408(1)$ nm
	$c = 0.6016(1)$ nm	$c = 0.6039(1)$ nm	$c = 0.6050(1)$ nm
Volume	0.5635(1) nm^3	0.5661(1) nm^3	0.5676(1) nm^3
Number of formula units per unit cell	2	2	2
Measurement temperature	298 K	450 K	530 K
Calculated density	4.999 g/cm^3	4.976 g/cm^3	4.966 g/cm^3
Absorption coefficient	15.949 mm^{-1}	15.874 mm^{-1}	15.841 mm^{-1}
$F(000)$	743	743	743
Θ range for data collection	4.07–36.94	4.06–37.02	4.06–37.00
Index ranges	$-10 \leqslant h \leqslant 17$	$-17 \leqslant h \leqslant 13$	$-13 \leqslant h \leqslant 17$
	$-17 \leqslant k \leqslant 14$	$-16 \leqslant k \leqslant 13$	$-13 \leqslant k \leqslant 16$
	$-10 \leqslant l \leqslant 9$	$-10 \leqslant l \leqslant 8$	$-8 \leqslant l \leqslant 10$
Reflections collected	8925	9033	9052
Independent reflections	1840 [R(int.) = 0.0228]	1778 [R(int.) = 0.0242]	1786 [R(int.) = 0.0291]
Refinement method	Full-matrix least-square on F^2	Full-matrix least-square on F^2	Full-matrix least-square on F^2
Absolute structure parameter	0.00(1)	−0.01(1)	−0.01(1)
Data/restraints/parameters	1840/1/43	1778/1/43	1786/1/43
Goodness-of-fit on F^2	0.994	0.994	1.022
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0149$, w$R_2 = 0.0276$	$R_1 = 0.0163$, w$R_2 = 0.0263$	$R_1 = 0.0198$, w$R_2 = 0.0342$
R indices (all data)	$R_1 = 0.0165$, w$R_2 = 0.0278$	$R_1 = 0.0191$, w$R_2 = 0.0266$	$R_1 = 0.0230$, w$R_2 = 0.0347$
Extinction coefficient	0.0052(1)	0.0053(1)	0.0056(2)
Largest diff. peak and hole × 10^{-3}	1.866 and −0.890 e/nm^3	1.803 and −0.716 e/nm^3	1.190 and −0.811 e/nm^3

In order to investigate the possibility of ordering/disordering of the positions of the Ag atoms in $La_3Ag_{0.82}SnS_7$ and $Ce_3Ag_{0.81}SnS_7$ the low/high temperature X-ray measurements were performed (Tables 3–6). No ordering of Ce-based compound was observed at 12 K. High temperature measurements (at 450 and 530 K) bring the same structural models for both compounds. Two defect positions of Ag were observed at different temperatures. However, the occupations of both positions of Ag are different at different temperatures, but overall occupations of these positions are similar. The decrease of the occupancy factor of Ag1 and the increase of the occupancy factor of Ag2 with increase of temperature were observed for the La-based compound (Table 4). At the same time the increase of the occupancy factor of Ag1 and the decrease of the occupancy factor of Ag2 with increase of temperature were observed for the Ce-based compound (Table 6). Intriguingly, the crystal structure of the $La_3AgSnSe_7$ is ordered in comparison with its sulphur analogue. Thus, a simple substitution between Se^{2-} and S^{2-} anions leads to an order ↔ disorder effect of the Ag atom. However, complete explanation of this effect seems to be more complicated as the crystal structures of the R_3CuSnS_7 (R = Y, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy and Ho) series [2,3] and $R_3CuSnSe_7$ (R = Y, La, Ce, Pr, Nd, Sm, Gd, Tb and Dy) series [4–6] are ordered.

Relevant interatomic distances (δ, nm) and coordination numbers (C.N.) of the La(Ce), Ag, Sn atoms in the structures of the $La_3AgSnSe_7$ and $La_3Ag_{0.82}SnS_7$, $Ce_3Ag_{0.81}SnS_7$ compounds are listed in Table 7. The interatomic distances are close to the sum of the respective ionic radii [16]. The nearest neighbours of the La(Ce), Ag and Sn atoms are exclusively Se(S) atoms. Basically, the latter form slightly distorted trigonal prisms around the

Table 4
Atomic coordinates and temperature factors for the $La_3Ag_{1-\delta}SnS_7$ ($\delta = 0.18(1)$) compound at different temperatures

Atom	Position	x/a	y/b	z/c	Occupation	Ueq. (10^2, nm^2	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
298 K												
La	6(*c*)	0.35851(1)	0.13233(1)	0.04973(3)	1	0.01067(3)	0.00905(5)	0.01005(5)	0.01266(5)	0.00116(5)	0.00050(5)	0.00460(4)
Ag1	2(*a*)	0	0	0.4660(3)	0.659(3)	0.0318(4)	0.0106(1)	0.0106(1)	0.074(1)	0	0	0.00532(9)
Ag2	2(*a*)	0	0	0.284(1)	0.161(3)	0.0361(18)	0.0116(7)	0.0116(7)	0.085(5)	0	0	0.0058(4)
Sn	2(*b*)	1/3	2/3	0.12629(4)	1	0.01020(5)	0.01163(7)	0.01163(7)	0.00733(9)	0	0	0.00582(3)
S1	6(*c*)	0.51639(6)	0.42295(6)	0.79230(9)	1	0.01084(9)	0.0095(2)	0.0123(2)	0.0110(2)	−0.0009(1)	−0.0009(1)	0.0057(1)
S2	6(*c*)	0.16456(6)	0.26446(6)	0.0267(1)	1	0.0136(1)	0.0120(2)	0.0166(2)	0.0149(3)	0.0016(2)	0.0021(2)	0.0091(1)
S3	2(*b*)	1/3	2/3	0.7365(1)	1	0.0106(1)	0.0121(2)	0.0121(2)	0.0077(4)	0	0	0.0060(1)
450 K												
La	6(*c*)	0.77432(1)	0.13294(1)	0.56685(4)	1	0.01623(3)	0.01512(5)	0.01584(6)	0.01924(5)	0.00168(6)	0.00061(6)	0.00888(4)
Ag1	2(*a*)	0	0	0.9727(7)	0.609(7)	0.0534(9)	0.0174(2)	0.0174(2)	0.125(3)	0	0	0.0087(1)
Ag2	2(*a*)	0	0	0.799(2)	0.213(7)	0.054(3)	0.0205(7)	0.0205(7)	0.122(9)	0	0	0.0103(4)
Sn	2(*b*)	1/3	2/3	0.64311(4)	1	0.01612(6)	0.01844(8)	0.01844(8)	0.01148(9)	0	0	0.00922(4)
S1	6(*c*)	0.51682(7)	0.09334(7)	0.30904(9)	1	0.0167(1)	0.0144(2)	0.0158(3)	0.0176(2)	−0.0005(2)	−0.0020(2)	0.0059(2)
S2	6(*c*)	0.26406(7)	0.16369(6)	0.0423(1)	1	0.0199(1)	0.0230(3)	0.0174(2)	0.0225(3)	0.0032(2)	0.0022(2)	0.0124(2)
S3	2(*b*)	1/3	2/3	0.2545(1)	1	0.0160(1)	0.0183(3)	0.0183(3)	0.0115(4)	0	0	0.0091(1)
530 K												
La	6(*c*)	0.77459(1)	0.13326(1)	0.41002(5)	1	0.01889(4)	0.01776(7)	0.01850(7)	0.02230(7)	−0.00185(7)	−0.00070(7)	0.01048(5)
Ag1	2(*a*)	0	0	0.010(1)	0.59(1)	0.064(1)	0.0201(3)	0.0201(3)	0.154(5)	0	0	0.0100(1)
Ag2	2(*a*)	0	0	0.178(3)	0.23(1)	0.064(4)	0.027(1)	0.027(1)	0.13(1)	0	0	0.0140(5)
Sn1	2(*b*)	1/3	2/3	0.33398(6)	1	0.01894(7)	0.0215(1)	0.0215(1)	0.0137(1)	0	0	0.01077(5)
S1	6(*c*)	0.90688(8)	0.42375(8)	0.6680(1)	1	0.0193(1)	0.0187(3)	0.0212(3)	0.0202(3)	0.0018(3)	−0.0002(3)	0.0114(3)
S2	6(*c*)	0.10060(7)	0.26381(8)	0.4352(1)	1	0.0230(1)	0.0184(3)	0.0262(3)	0.0261(4)	−0.0022(3)	0.0012(3)	0.0124(3)
S3	2(*b*)	1/3	2/3	0.7222(1)	1	0.0189(2)	0.0209(4)	0.0209(4)	0.0148(5)	0	0	0.0104(1)

*U*eq. is definite as one third of the trace of the orthogonalized U_{ij} tensor.
The anisotropic temperature factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + \cdots + 2hka^*b^*U_{12}]$.

Table 5
Crystal data and structure refinement details of the $Ce_3Ag_{1-\delta}SnS_7$ ($\delta = 0.19(1)$) compound at different temperatures

Empirical formula	$Ce_3Ag_{0.81}SnS_7$	$Ce_3Ag_{0.81}SnS_7$	$Ce_3Ag_{0.81}SnS_7$	$Ce_3Ag_{0.81}SnS_7$
Formula weight	851.38	851.38	851.92	851.38
Space group	$P6_3$ (No. 173)	$P6_3$ (No. 173)	$P6_3$ (No. 173)	$P6_3$ (No. 173)
Unit cell dimensions	$a = 1.0300(1)$ nm $c = 0.6002(1)$ nm	$a = 1.0302(1)$ nm $c = 0.5969(1)$ nm	$a = 1.0292(1)$ nm $c = 0.6033(1)$ nm	$a = 1.0299(1)$ nm $c = 0.6041(1)$ nm
Volume	0.5515(1) nm^3	0.5487(1) nm^3	0.5534(1) nm^3	0.5550(1) nm^3
Number of formula units per unit cell	2	2	2	2
Measurement temperature	298 K	12 K	450 K	530 K
Calculated density	5.126 g/cm^3	5.153 g/cm^3	5.112 g/cm^3	5.095 g/cm^3
Absorption coefficient	17.047 mm^{-1}	17.136 mm^{-1}	16.997 mm^{-1}	16.941 mm^{-1}
F (000)	749	749	749	749
Θ range for data collection	4.09–34.28	4.57–30.71	4.08–27.78	3.96–27.88
Index ranges	$-16 \leqslant h \leqslant 13$ $-16 \leqslant k \leqslant 16$ $-9 \leqslant l \leqslant 6$	$-14 \leqslant h \leqslant 14$ $-14 \leqslant k \leqslant 14$ $-6 \leqslant l \leqslant 8$	$-13 \leqslant h \leqslant 13$ $-13 \leqslant k \leqslant 12$ $-5 \leqslant l \leqslant 7$	$-13 \leqslant h \leqslant 12$ $-13 \leqslant k \leqslant 13$ $-7 \leqslant l \leqslant 6$
Reflections collected	8279	5490	6580	6496
Independent reflections	1282 [R(int.) = 0.0316]	917 [*R*(int.) = 0.0841]	799 [*R*(int.) = 0.0772]	828 [*R*(int.) = 0.1029]
Refinement method	Full-matrix least-square on F^2	Full-matrix least-square on F^2	Full-matrix least-square on F^2	Full-matrix least-square on F^2
Absolute structure parameter	0.00(1)	0.03(3)	−0.02(4)	0.00(4)
Data/restraints/parameters	1282/1/43	917/1/43	799/1/43	828/1/43
Goodness-of-fit on F^2	1.005	0.721	1.010	1.000
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0151$, w$R_2 = 0.0247$	$R_1 = 0.0342$, w$R_2 = 0.0321$	$R_1 = 0.0311$, $wR_2 = 0.0726$	$R_1 = 0.0325$, $wR_2 = 0.0739$
R indices (all data)	$R_1 = 0.0170$, w$R_2 = 0.0250$	$R_1 = 0.0590$, w$R_2 = 0.0353$	$R_1 = 0.0323$, w$R_2 = 0.0735$	$R_1 = 0.0336$, w$R_2 = 0.0744$
Extinction coefficient	0.0044(1)	0.00482(7)	0.0066(8)	0.0052(7)
Largest diff. peak and hole × 10^{-3}	0.818 and −0.694 e/nm^3	2.235 and −2.516 e/nm^3	1.613 and –2.123 e/nm^3	1.452 and –1.368 /nm^3

Table 6
Atomic coordinates and temperature factors for the $Ce_3Ag_{1-\delta}SnS_7$ ($\delta = 0.19(1)$) compound at different temperatures

Atom	Position	x/a	y/b	z/c	Occu-pation	Ueq. (10^2, nm^2	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
298 K												
Ce	6(*c*)	0.22476(1)	0.35862(1)	0.42479(4)	1	0.01109(4)	0.01018(6)	0.00910(6)	0.01341(7)	−0.00060(7)	0.00075(7)	0.00439(5)
Ag1	2(*a*)	0	0	0.0347(4)	0.647(4)	0.0421(6)	0.0109(3)	0.0109(3)	0.104(1)	0	0	0.0054(1)
Ag2	2(*a*)	0	0	0.203(1)	0.167(4)	0.027(1)	0.0127(9)	0.0127(9)	0.058(5)	0	0	0.0063(5)
Sn	2(*b*)	1/3	2/3	0.84948(5)	1	0.01057(7)	0.01228(9)	0.01228(9)	0.0071(1)	0	0	0.00614(5)
S1	6(*c*)	0.90857(8)	0.48401(8)	0.1808(1)	1	0.0112(1)	0.0109(3)	0.0104(3)	0.0109(3)	−0.0010(3)	0.0000(3)	0.0041(3)
S2	6(*c*)	0.83672(7)	0.73489(8)	0.4523(1)	1	0.0141(1)	0.0122(3)	0.0174(3)	0.0153(4)	0.0022(3)	0.0025(3)	0.0093(2)
S3	2(*b*)	1/3	2/3	0.2399(1)	1	0.0106(2)	0.0122(3)	0.0122(3)	0.0075(6)	0	0	0.0060(1)
12 K												
Ce	6(*c*)	0.77380(3)	0.64162(3)	0.37408(7)	1	0.00528(7)	0.0041(1)	0.0050(1)	0.0070(1)	0.0001(2)	−0.0009(2)	0.0026(1)
Ag1	2(*a*)	0	0	0.4603(2)	0.596(2)	0.0082(4)	0.0033(5)	0.0033(5)	0.0180(9)	0	0	0.0016(2)
Ag2	2(*a*)	0	0	0.598(1)	0.218(3)	0.057(3)	0.004(1)	0.004(1)	0.163(7)	0	0	0.0022(8)
Sn	2(*b*)	1/3	2/3	0.2984(1)	1	0.0051(1)	0.0048(2)	0.0048(2)	0.0058(4)	0	0	0.0024(1)
S1	6(*c*)	0.5146(1)	0.4229(1)	0.6294(2)	1	0.0057(4)	0.0059(7)	0.0080(7)	0.0031(7)	−0.0005(6)	0.0001(6)	0.0033(6)
S2	6(*c*)	0.1007(1)	0.8353(1)	0.3994(3)	1	0.0081(4)	0.0080(6)	0.0067(6)	0.0078(9)	0.0015(8)	−0.0010(7)	0.0022(5)
S3	2(*b*)	1/3	2/3	0.6910(4)	1	0.0067(7)	0.0082(9)	0.0082(9)	0.003(1)	0	0	0.0041(5)
450 K												
Ce	6(*c*)	0.22380(4)	0.35878(4)	0.0331(1)	1	0.0190(2)	0.0172(3)	0.0146(2)	0.0239(4)	0.0009(1)	−0.0004(1)	0.0070(1)
Ag1	2(*a*)	0	0	0.897(2)	0.68(1)	0.081(4)	0.0203(9)	0.0203(9)	0.202(12)	0	0	0.0102(4)
Ag2	2(*a*)	0	0	0.735(5)	0.12(1)	0.031(6)	0.023(4)	0.023(4)	0.04(1)	0	0	0.011(2)
Sn	2(*b*)	1/3	2/3	0.6080(1)	1	0.0188(3)	0.0205(3)	0.0205(3)	0.0156(6)	0	0	0.0102(1)
S1	6(*c*)	0.5745(2)	0.0909(2)	0.2761(4)	1	0.0184(5)	0.0208(9)	0.0182(9)	0.018(1)	−0.0009(8)	0.0013(8)	0.0112(7)
S2	6(*c*)	0.1621(2)	0.2646(2)	0.5031(4)	1	0.0239(5)	0.0169(9)	0.0254(9)	0.031(1)	0.004(1)	0.0052(9)	0.0119(8)
S3	2(*b*)	1/3	2/3	0.2191(7)	1	0.0192(8)	0.017(1)	0.017(1)	0.022(2)	0	0	0.0089(5)
530 K												
Ce	6(*c*)	0.22339(5)	0.35899(5)	0.2556(1)	1	0.0202(1)	0.0193(2)	0.0161(2)	0.0239(3)	−0.0013(1)	0.0007(1)	0.0076(1)
Ag1	2(*a*)	0	0	0.410(2)	0.73(1)	0.105(4)	0.0226(9)	0.0226(9)	0.27(1)	0	0	0.0113(4)
Ag2	2(*a*)	0	0	0.566(4)	0.07(1)	0.028(8)	0.028(8)	0.028(8)	0.02(1)	0	0	0.014(4)
Sn	2(*b*)	1/3	2/3	0.6807(1)	1	0.0204(3)	0.0232(3)	0.0232(3)	0.0147(5)	0	0	0.0115(1)
S1	6(*c*)	0.5167(2)	0.4255(2)	0.0134(4)	1	0.0201(4)	0.0199(9)	0.023(1)	0.017(1)	0.0024(9)	0.0026(9)	0.0112(8)
S2	6(*c*)	0.2647(2)	0.1031(2)	0.2863(4)	1	0.0244(5)	0.026(1)	0.0207(8)	0.029(1)	0.0012(8)	−0.0032(9)	0.0140(8)
S3	2(*b*)	1/3	2/3	0.0695(6)	1	0.0211(8)	0.021(1)	0.021(1)	0.021(2)	0	0	0.0106(5)

Ueq. is definite as one third of the trace of the orthogonalized U_{ij} tensor.
The anisotropic temperature factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + \cdots + 2hka^*b^*U_{12}]$.

Table 7
Interatomic distances (δ, nm) and coordination numbers (C.N.) of the La, Ag and Sn atoms in the $La_3AgSnSe_7$, $La_3Ag_{0.82}SnS_7$ and $Ce_3Ag_{0.81}SnS_7$ compounds at 298 K

Atoms R = La, Ce; X = Se, S	δ, nm				C.N.
	$La_3AgSnSe_7$	$La_3Ag_{0.82}SnS_7$	$Ce_3Ag_{0.81}SnS_7$		
R	−1 × 2	0.3032(1)	0.29125(7)	0.28802(8)	6
	−1 × 1	0.3049(1)	0.29406(7)	0.29185(8)	
	−1 × 2	0.3075(1)	0.29576(7)	0.29366(8)	
	−1 × 2	0.3109(1)	0.29959(8)	0.2960(1)	
	−1 × 3	0.3150(1)	0.30338(5)	0.30003(6)	
	−1 × 1	0.3153(1)	0.330441(7)	0.30171(7)	
Ag1	−3 × 2	0.2558(1)	0.24331(7)	0.2436(1)	3
Ag2	−3 × 2	—	0.2813(4)	0.2815(4)	6
	−3 × 2	—	0.2862(4)	0.2822(4)	
Sn	−1 × 3	0.2474(2)	0.2344(1)	0.2343(1)	4
	−3 × 1	0.2531(1)	0.24011(6)	0.24030(8)	

La(Ce) atoms. However, coordination sphere can be extended by two additional nearest Se(S)1 and Se(S)2 atoms, ~0.32 nm distanced. Thus, eight coordination sphere creates square antiprism with only ~0.02 nm displacement of the La(Ce) atom from the antiprism's midpoint. Selenium (sulphur) atoms also create trigonally compressed tetrahedron around the Sn atom which lies on the three-fold 3_1-axis. In turn, the Ag (Ag1) atom has triangular surroundings: it is located very close to the planes built by three Se (S) atoms. The Ag2 atom in the structures of the $La_3Ag_{0.82}SnS_7$ and $Ce_3Ag_{0.81}SnS_7$ compounds is located practically in the centre of trigonal antiprism. The unit cells and the coordination polyhedra of the La (a), Ag (Ag1) (b), Ag2 (c), Sn (d), Se(S)1 (e), Se(S)2 (f) and Se(S)3 (g) atoms in the structures of the $La_3AgSnSe_7$ and $La_3Ag_{0.82}SnS_7$ compounds are shown in Fig. 1.

The packing of the cation-centered polyhedra in the crystal structures of the $La_3AgSnSe_7$ and $La_3Ag_{0.82}SnS_7$ compounds is shown in Fig. 2. The arrangement of La-centered trigonal prisms (square antiprism) and Sn-centered tetrahedra are similar in both structures. The Ag atom in $La_3AgSnSe_7$ is located in selenium trigonal antiprism on the 6_3-axis, but it is shifted from the centre of the respective antiprism along *c*-axis. Since three Se atoms are located at the significantly longer distances than remaining three Se atoms, actually a triangular surroundings exists for the Ag atoms. A similar triangular surroundings exists for the Ag1 atoms in $Ce_3Ag_{0.81}SnS_7$ and $La_3Ag_{0.82}SnS_7$. At the same time the Ag2 atom in these compounds is located practically in the centre of sulphur antiprism.

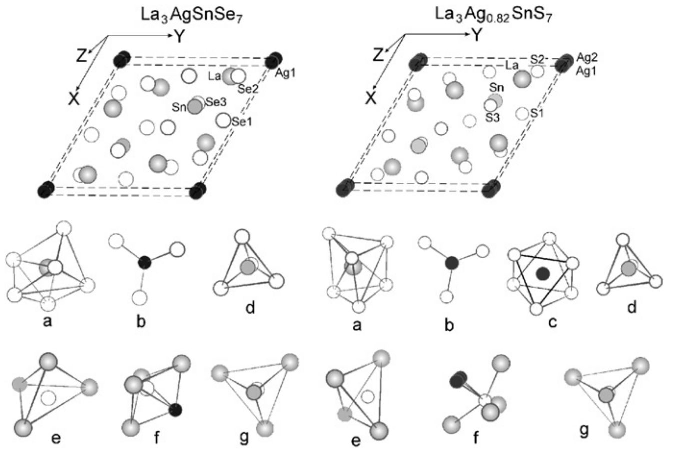

Fig. 1. The unit cells and the coordination polyhedra of the La (a), Ag (Ag1) (b), Ag2 (c), Sn (d), Se(S)1 (e), Se(S)2 (f) and Se(S)3 (g) atoms in the structures of the $La_3AgSnSe_7$ and $La_3Ag_{0.82}SnS_7$ compounds.

As the occupational disorder in the $Ce_3Ag_{0.81}SnS_7$ and $La_3Ag_{0.82}SnS_7$ was observed and U_{33} anisotropic parameter for Ag atom has large values, the crystal structures were also refined by means of JANA2000 program [11]. Large values of the anisotropic parameters were also found e.g. for Cu^+ cations in Cu_6PS_5I ionic conductor [13]. Joint probability density function maps showed Cu^+ diffusion paths which are firmly connected to the ionic conductivity of the Cu_6PS_5I compound.

Fig. 3 shows joint probability density function map in plane of the nearest two Ag and one S2 atoms. The density function map significantly changes with temperature. Both Ag1 and Ag2 atoms are described well at 12 K and Ag2 atom is clearly seen as a maximum. It gradually disappears with rise in temperature and the only one position and more diffused position of the Ag atom is observed at high temperature (Fig. 4). In high temperatures, the position of the Ag atom is much diffused and diffusion paths can be created along *c* direction.

On the basis of probability density function maps the pseudo-potentials through the Ag atoms in *c* direction were determined (Fig. 4). As the anharmonic parameters described the anisotropy of the Ag atom they had to be taken into consideration in a pseudo-potential calculation [17]. In one dimension (x) an anharmonic potential is

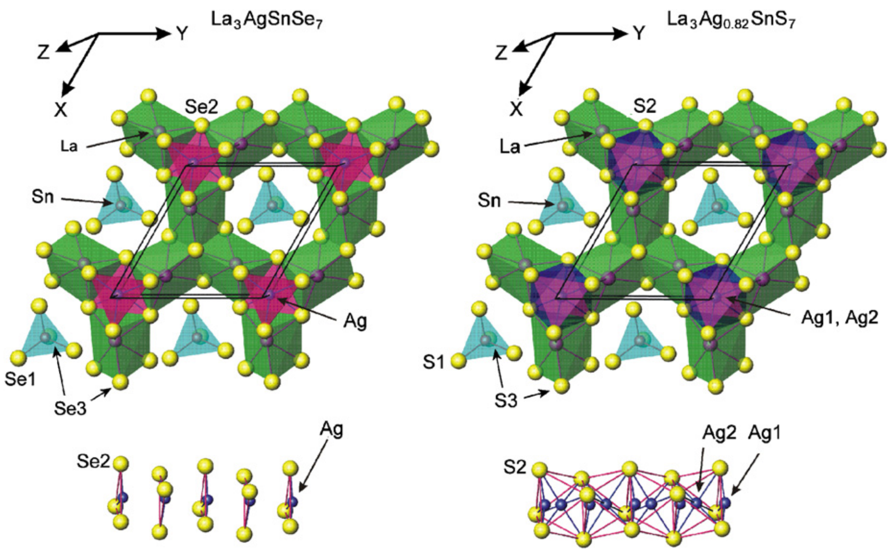

Fig. 2. The packing of the cation-centered polyhedra in the crystal structures of the $La_3AgSnSe_7$ and $La_3Ag_{0.82}SnS_7$ compounds.

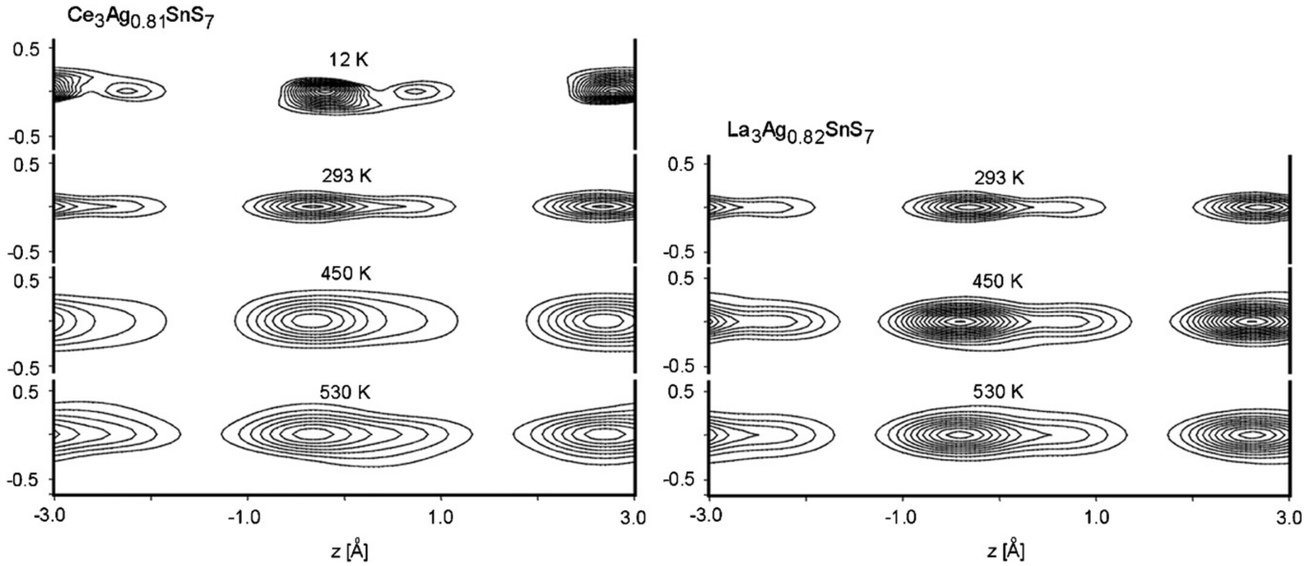

Fig. 3. Joint probability density function maps in plane of the nearest two Ag and one S2 atoms for $Ce_3Ag_{0.81}SnS_7$ and $La_3Ag_{0.82}SnS_7$ compounds.

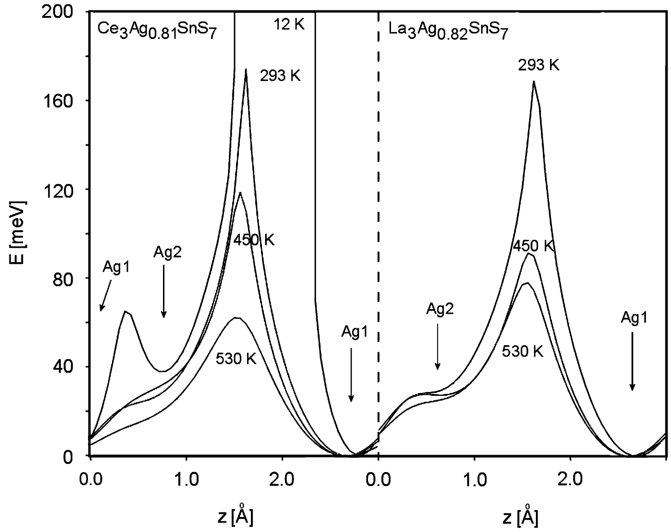

Fig. 4. Pseudo-potentials within the 6_3-axis in the $[Ag(S2)_6]$ trigonal antiprism. The positions of the Ag1 and Ag2 atoms from SHELXL refinement were added.

described as a power expression:

$$V_i(x) = \beta(x - x_i)^2 + \gamma(x - x_i)^3 + \delta(x - x_i)^4.$$

When only third-order anharmonic parameters are considered (see 12 K results) only two first sum parts are used to determine the potential. Fig. 4 shows relatively low barrier between two nearest positions and it decreases when temperature rises. It can be assumed that low barrier and its decrease at high temperatures are connected with high mobility of the Ag^+ cations which are possible charge carriers in the lattice. It is worth mentioning that migration of Ag^+ within the $[Ag(S2)_6]$ triangular antiprism can be facilitated by the nonstoichiometric composition of the crystal. Besides, as the only one direction for migration is privileged (along *c*-axis) some physical properties can show anisotropy. Therefore, $Ce_3Ag_{0.81}SnS_7$ and $La_3Ag_{0.82}SnS_7$ materials are put in a good light in the studies of e.g. ionic conductors [13,14].

4. Supporting information

Further details of the crystal structure investigations can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, (fax: (49) 7247-808-666; e-mail: crysdata@fiz.karlsruhe.de) on quoting the depository numbers CSD 417794–417800 and 417803.

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