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$\text{Ln}_3\text{M}_{1-\delta}\text{TX}_7$ – quasi-isostructural compounds: stereochemistry and silver-ion motion in the $\text{Ln}_3\text{Ag}_{1-\delta}\text{GeS}_7$ (Ln = La–Nd, Sm, Gd–Er and Y; $\delta = 0.11$ – 0.50) compounds

Received 28 August 2008
Accepted 12 January 2009

The crystal structures of the $\text{Ln}_3\text{Ag}_{1-\delta}\text{GeS}_7$ (Ln = La–Nd, Sm, Gd–Er, Y; $\delta = 0.11$ – 0.50 , space group $P6_3$) compounds were determined by means of X-ray single-crystal diffraction and the similarities among the crystal structures of all $\text{Ln}_3\text{M}_{1-\delta}\text{TX}_7$ (space group $P6_3$; Ln – lanthanide element, M – monovalent element; T – tetravalent element and X – S, Se) compounds deposited in the Inorganic Crystal Structure Database (ICSD) are discussed. Substitutions of each element in $\text{Ln}_3\text{M}_{1-\delta}\text{TX}_7$ result in a different structural effect. On the basis of the data deposited in the ICSD the large family of the $\text{Ln}_3\text{M}_{1-\delta}\text{TX}_7$ compounds was divided into three groups depending on the position of the monovalent element in the lattice. This position determines what kind of stereoisomer is present in the structure, either the ++ enantiomer or the +- diastereoisomer. Since the silver ions can occupy a different position and the energy barriers between positions are low the ions can move through the channel. It was shown that this movement is not a stochastic process but a correlated one.

1. Introduction

The syntheses of compounds with increasingly complex compositions, such as ternary, quaternary *etc.*, has become a principle direction in modern materials science (Eliseev & Kuzmichyeva, 1990). Among the multicomponent systems are the complex rare-earth chalcogenides which play an important role. Compounds with the general formula Ln_3MTX_7 [space group $P6_3$; Ln – rare-earth element, M – monovalent element (Cu, Ag), T – Si, Ge, Sn and X – S, Se] are interesting owing to their possible application in the field of ionic conductivity.

The formation of quaternary $\text{Ln}_3\text{AgGeS}_7$ (Ln = La, Ce and Pr) compounds has been reported by Guittard & Julien-Pouzol (1970). Lattice parameters have been determined and a $\text{La}_3\text{CuSiS}_7$ -type structure (space group $P6_3$) has been assigned. The crystal structure of the $\text{La}_3\text{AgGeS}_7$ compound has been reinvestigated by means of X-ray single-crystal diffraction (Hwu *et al.*, 1995).

This paper presents part of our systematic investigations of rare-earth chalcogenides with transition metals. Crystal structures of the $\text{Ln}_3\text{Ag}_{1-\delta}\text{GeS}_7$ (Ln = La–Nd, Sm, Gd–Er and Y; $\delta = 0.11$ – 0.50) compounds investigated by means of X-ray single-crystal diffraction are given. The relationships between the crystal structures of all $\text{Ln}_3\text{M}_{1-\delta}\text{TX}_7$ (space group $P6_3$; Ln – rare-earth element, M – monovalent element; T – tetravalent element and X – S, Se) compounds are also described.

Table 1

Crystal data and structure refinement details of the $\text{Ln}_3\text{Ag}_{1-\delta}\text{GeS}_7$ (Ln = La–Nd, Sm, Gd–Er, Y; $\delta = 0.11$ –0.50) compounds.

	$\text{La}_3\text{Ag}_{0.82}\text{GeS}_7$	$\text{Ce}_3\text{Ag}_{0.88}\text{GeS}_7$	$\text{Pr}_3\text{Ag}_{0.90}\text{GeS}_7$	$\text{Nd}_3\text{Ag}_{0.84}\text{GeS}_7$	$\text{Sm}_3\text{Ag}_{0.74}\text{GeS}_7$	
Crystal data						
Chemical formula	$\text{Ag}_{0.82}\text{GeLa}_3\text{S}_7$	$\text{Ag}_{0.88}\text{Ce}_3\text{GeS}_7$	$\text{Ag}_{0.89}\text{GePr}_3\text{S}_7$	$\text{Ag}_{0.84}\text{GeNd}_3\text{S}_7$	$\text{Ag}_{0.74}\text{GeS}_7\text{Sm}_3$	
M_r	802.19	812.30	815.74	819.80	827.34	
Cell setting, space group	Hexagonal, $P6_3$	Hexagonal, $P6_3$	Hexagonal, $P6_3$	Hexagonal, $P6_3$	Hexagonal, $P6_3$	
Temperature (K)	295 (2)	295 (2)	295 (2)	295 (2)	295 (2)	
a, c (Å)	10.4056 (15), 5.8280 (12)	10.3902 (15), 5.8425 (12)	10.2290 (14), 5.7760 (11)	10.1930 (14), 5.7693 (12)	10.0809 (14), 5.7604 (12)	
V (Å ³)	546.49 (16)	546.23 (16)	523.39 (14)	519.11 (15)	506.97 (15)	
Z	2	2	2	2	2	
D_x (Mg m ⁻³)	4.875	4.939	5.176	5.245	5.420	
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	
μ (mm ⁻¹)	16.91	17.79	19.50	20.49	22.80	
Crystal form, colour	Prism, dark red	Prism, dark red	Prism, dark red	Prism, dark red	Prism, dark red	
Crystal size (mm)	0.09 × 0.04 × 0.03	0.09 × 0.08 × 0.06	0.10 × 0.09 × 0.07	0.11 × 0.09 × 0.08	0.13 × 0.11 × 0.09	
Data collection						
Diffraction	KUMA KM-4 with CCD area detector	KUMA KM-4 with CCD area detector	KUMA KM-4 with CCD area detector	KUMA KM-4 with CCD area detector	KUMA KM-4 with CCD area detector	
Data collection method	ω scan	ω scan	ω scan	ω scan	ω scan	
Absorption correction	Numerical	Numerical	Numerical	Numerical	Numerical	
T_{\min}	0.097	0.097	0.163	0.093	0.029	
T_{\max}	0.599	0.599	0.272	0.261	0.242	
No. of measured, independent and observed reflections	5858, 743, 729	6515, 726, 704	5174, 602, 585	5463, 713, 700	4935, 604, 601	
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	
R_{int}	0.039	0.043	0.059	0.038	0.046	
θ_{\max} (°)	26.4	26.4	25.0	26.4	25.3	
Refinement						
Refinement on	F^2	F^2	F^2	F^2	F^2	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.011, 0.022, 1.04	0.021, 0.046, 1.06	0.025, 0.051, 1.09	0.016, 0.035, 1.08	0.014, 0.034, 1.17	
No. of reflections	743	726	602	713	604	
No. of parameters	43	43	43	43	43	
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0107P)^2]^\dagger$	$w = 1/[\sigma^2(F_o^2) + (0.0294P)^2]^\dagger$	$w = 1/[\sigma^2(F_o^2) + (0.0287P)^2 + 1.032P]^\dagger$	$w = 1/[\sigma^2(F_o^2) + (0.0193P)^2]^\dagger$	$w = 1/[\sigma^2(F_o^2) + (0.0181P)^2 + 0.5015P]^\dagger$	
$(\Delta/\sigma)_{\max}$	0.001	0.001	< 0.0001	0.001	0.001	
$\Delta\rho_{\max}, \Delta\rho_{\min}$ (e Å ⁻³)	0.37, -0.44	1.01, -0.70	1.22, -0.73	0.72, -0.74	0.70, -0.51	
Extinction method	<i>SHELXL</i>	<i>SHELXL</i>	<i>SHELXL</i>	<i>SHELXL</i>	<i>SHELXL</i>	
Extinction coefficient	0.0042 (2)	0.0122 (6)	0.0145 (7)	0.0335 (7)	0.0097 (4)	
Friedel pairs (Flack, 1983)	334	319	265	320	270	
Flack parameter	0.014 (12)	-0.04 (2)	0.05 (3)	-0.027 (19)	-0.029 (18)	
<hr/>						
	$\text{Gd}_3\text{Ag}_{0.63}\text{GeS}_7$	$\text{Tb}_3\text{Ag}_{0.59}\text{GeS}_7$	$\text{Dy}_3\text{Ag}_{0.51}\text{GeS}_7$	$\text{Ho}_3\text{Ag}_{0.50}\text{GeS}_7$	$\text{Er}_3\text{Ag}_{0.50}\text{GeS}_7$	$\text{Y}_3\text{Ag}_{0.50}\text{GeS}_7$
Crystal data						
Chemical formula	$\text{Ag}_{0.63}\text{Gd}_3\text{GeS}_7$	$\text{Ag}_{0.59}\text{GeS}_7\text{Tb}_3$	$\text{Ag}_{0.51}\text{Dy}_3\text{GeS}_7$	$\text{Ag}_{0.50}\text{GeHo}_3\text{S}_7$	$\text{Ag}_{0.50}\text{Er}_3\text{GeS}_7$	$\text{Ag}_{0.50}\text{GeS}_7\text{Y}_3$
M_r	836.18	836.87	840.06	845.73	852.72	617.67
Cell setting, space group	Hexagonal, $P6_3$	Hexagonal, $P6_3$	Hexagonal, $P6_3$	Hexagonal, $P6_3$	Hexagonal, $P6_3$	Hexagonal, $P6_3$
Temperature (K)	295 (2)	295 (2)	295 (2)	295 (2)	295 (2)	295 (2)
a, c (Å)	9.9637 (14), 5.7660 (12)	9.9003 (14), 5.7654 (12)	9.8003 (14), 5.7879 (12)	9.7401 (14), 5.7994 (12)	9.6921 (14), 5.8308 (12)	9.8090 (14), 5.8059 (12)
V (Å ³)	495.73 (14)	489.39 (14)	481.43 (14)	476.48 (14)	474.35 (14)	483.78 (14)
Z	2	2	2	2	2	2
D_x	5.602	5.679	5.795	5.895	5.970	4.240
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ (mm ⁻¹)	25.41	27.01	28.56	30.22	31.87	23.31
Crystal form, colour	Prism, dark red	Prism, dark red	Prism, dark red	Prism, dark red	Prism, dark red	Prism, dark red
Crystal size	0.13 × 0.12 × 0.10	0.12 × 0.11 × 0.08	0.12 × 0.10 × 0.09	0.09 × 0.07 × 0.03	0.13 × 0.10 × 0.08	0.09 × 0.06 × 0.05
Data collection						
Diffraction	KUMA KM-4 CCD area detector	KUMA KM-4 CCD area detector	KUMA KM-4 CCD area detector	KUMA KM-4 CCD area detector	KUMA KM-4 CCD area detector	KUMA KM-4 CCD area detector
Data collection method	ω scan	ω scan	ω scan	ω scan	ω scan	ω scan

Table 1 (continued)

	Gd ₃ Ag _{0.63} GeS ₇	Tb ₃ Ag _{0.59} GeS ₇	Dy ₃ Ag _{0.51} GeS ₇	Ho ₃ Ag _{0.50} GeS ₇	Er ₃ Ag _{0.50} GeS ₇	Y ₃ Ag _{0.50} GeS ₇
Absorption correction	Numerical	Numerical	Numerical	Numerical	Numerical	Numerical
T_{\min}	0.024	0.044	0.035	0.061	0.038	0.107
T_{\max}	0.192	0.187	0.244	0.304	0.131	0.210
No. of measured, independent and observed reflections	5095, 658, 657	4229, 602, 597	5667, 655, 644	5792, 649, 630	4994, 633, 628	5168, 657, 641
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.044	0.039	0.046	0.045	0.049	0.050
θ_{\max} (°)	26.2	25.6	26.4	26.7	26.4	26.3
Refinement						
Refinement on $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	F^2 0.013, 0.029, 1.12	F^2 0.017, 0.038, 1.17	F^2 0.015, 0.032, 1.12	F^2 0.017, 0.033, 1.19	F^2 0.022, 0.053, 1.15	F^2 0.021, 0.044, 1.12
No. of reflections	658	602	655	649	633	657
No. of parameters	43	39	39	38	38	38
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0143P)^2 + 0.2664P]^\dagger$	$w = 1/[\sigma^2(F_o^2) + (0.0175P)^2 + 1.1981P]^\dagger$	$w = 1/[\sigma^2(F_o^2) + (0.0114P)^2 + 0.9002P]^\dagger$	$w = 1/[\sigma^2(F_o^2) + (0.004P)^2 + 2.2568P]^\dagger$	$w = 1/[\sigma^2(F_o^2) + (0.0131P)^2 + 7.731P]^\dagger$	$w = 1/[\sigma^2(F_o^2) + (0.0228P)^2]^\dagger$
$(\Delta/\sigma)_{\max}$	0.001	0.001	0.001	0.001	0.001	< 0.0001
$\Delta\rho_{\max}, \Delta\rho_{\min}$ (e Å ⁻³)	0.58, -0.81	0.84, -1.39	0.99, -1.03	0.79, -2.25	0.86, -2.84	0.60, -1.38
Extinction method	<i>SHELXL</i>	<i>SHELXL</i>	<i>SHELXL</i>	<i>SHELXL</i>	<i>SHELXL</i>	<i>SHELXL</i>
Extinction coefficient	0.0047 (3)	0.0055 (3)	0.0034 (2)	0.0054 (2)	0.0081 (5)	0.0058 (9)
Friedel pairs	296	265	293	275	280	294
Flack parameter	0.006 (15)	0.00 (2)	-0.005 (19)	-0.04 (2)	-0.03 (3)	-0.036 (11)

Computer programs used: *CrysAlis 1.171.32.6* (Oxford Diffraction, 2007), *SHELXS97* and *SHELXL97* (Sheldrick, 2008). † $P = (F_o^2 + 2F_c^2)/3$.

2. Experimental details

The samples were prepared by sintering the elemental constituents with the atomic ratio Ln:Ag:Ge:S = 3:1:1:7 with a purity better than 99.9 wt %, in evacuated silica ampoules in a tube furnace. The ampoules were heated at a rate of 30 K h⁻¹ to a maximum temperature of 1420 K and kept at this temperature for 3 h. Afterwards the ampoules were cooled slowly (10 K h⁻¹) to 870 K, annealed at this temperature for 240 h and then quenched in cold water.

For the structure determination, diffraction-quality single crystals were selected from the samples prepared. All the crystals were a dark red colour with a prismatic habit. The ω -scan method was used at 295 (2) K on a Kuma Diffraction KM-4 four-circle single-crystal diffractometer equipped with a CCD detector and a Mo $K\alpha$ tube (graphite monochromator; $\lambda = 0.71073$ Å). The raw data collected were treated with the *CrysAlis* Data Reduction program (Oxford Diffraction, 2007), taking into account the numerical absorption correction from crystal shape. The intensities of the reflections were corrected for Lorentz and polarization effects. The crystal structures were solved using the Patterson method (Sheldrick, 2008) and refined by full-matrix least-squares (on F^2) using *SHELX97* (Sheldrick, 2008). The criterion for observed reflections was $I > 2\sigma(I)$. The extinction coefficient was also refined. All the

compounds crystallize in the space group $P6_3$ ($Z = 2$) which was checked with *PLATON* (Spek, 2007) and no additional symmetry elements were found. The compositions of all single crystals were confirmed by EDX analysis (EDAX PV9800 microanalyzer). Calc. for La₃Ag_{0.82}GeS₇: La 51.94, Ag 11.03, Ge 9.05, S 27.98%; found: La 51.98, Ag 10.97, Ge 9.11, S 27.94%. Calc. for Ce₃Ag_{0.88}GeS₇: Ce 51.75, Ag 11.69, Ge 8.94, S 27.62%; found: Ce 51.63, Ag 11.68, Ge 8.97, S 27.72%. Calc. for Pr₃Ag_{0.90}GeS₇: Pr 51.75, Ag 11.88, Ge 8.89, S 27.48%; found: Pr 51.62, Ag 11.85, Ge 8.95, S 27.58%. Calc. for Nd₃Ag_{0.84}GeS₇: Nd 52.74, Ag 11.04, Ge 8.86, S 27.36%; found: Nd 52.62, Ag 10.98, Ge 8.95, S 27.45%. Calc. for Sm₃Ag_{0.74}GeS₇: Sm 54.48, Ag 9.64, Ge 8.77, S 27.11%; found: Sm 54.39, Ag 9.71, Ge 8.74, S 27.16%. Calc. for Gd₃Ag_{0.63}GeS₇: Gd 56.38, Ag 8.12, Ge 8.68, S 26.82%; found: Gd 56.46, Ag 8.11, Ge 8.56, S 26.87%. Calc. for Tb₃Ag_{0.59}GeS₇: Tb 56.93, Ag 7.60, Ge 8.67, S 26.80%; found: Tb 56.80, Ag 7.69, Ge 8.63, S 26.88%. Calc. for Dy₃Ag_{0.51}GeS₇: Dy 58.06, Ag 6.55, Ge 8.65, S 26.74%; found: Dy 58.14, Ag 6.60, Ge 8.59, S 26.67%. Calc. for Ho₃Ag_{0.50}GeS₇: Ho 58.50, Ag 6.38, Ge 8.58, S 26.54%; found: Ho 58.55, Ag 6.45, Ge 8.54, S 26.46%. Calc. for Er₃Ag_{0.50}GeS₇: Er 58.84, Ag 6.32, Ge 8.52, S 26.32%; found: Er 58.73, Ag 6.40, Ge 8.45, S 26.42%. Calculated for Y₃Ag_{0.51}GeS₇: Y 43.10, Ag 8.89, Ge 11.73, S 36.28%; found: Y 43.22, Ag 8.85, Ge 11.78, S 36.15%.

3. Results and discussion

3.1. Crystal structure of the $\text{Ln}_3\text{AgGeS}_7$ compounds

The formation of quaternary compounds with approximate compositions $\text{Ln}_3\text{AgGeS}_7$ ($\text{Ln} = \text{La-Nd, Sm, Gd-Er and Y}$) was observed during the investigation of the phase relations in the respective quasi-ternary systems. The crystal structures of these compounds were investigated using X-ray single-crystal diffraction. A hexagonal unit cell was determined (Table 1¹) and the space group $P6_3$ was applied to the crystal-structure solution and refinement. Initially all the positions were determined. However, the high value of the U^{33} anisotropic displacement parameter for the silver ion was observed as well as residual electron density near this cation. Thus, two positions with partial occupation of the silver ion were assumed. Reasonable values of the anisotropic displacement parameters for Ag1 and Ag2 were finally obtained. The value of R1 was also improved significantly. Reduced silver content for all $\text{Ln}_3\text{Ag}_{1-\delta}\text{GeS}_7$ ($\delta = 0.11-0.50$) compounds was observed when compared with initial $\text{Ln}_3\text{AgGeS}_7$ compositions. The silver content slightly increases when going from La to Pr and decreases from Pr to Er. The latter range agrees with the previously reported data for the large series of hexagonal chalcogenides *e.g.* $\text{Ln}_3\text{Ag}_{1-\delta}\text{SnS}_7$ ($\text{Ln} = \text{La, Ce; } \delta = 0.18-0.19$; Daszkiewicz *et al.*, 2007), $\text{Ln}_3\text{Ag}_{1-\delta}\text{SiS}_7$ ($\text{Ln} = \text{La-Nd, Sm; } \delta = 0.10-0.23$; Daszkiewicz *et al.*, 2008), $\text{Ln}_3\text{Ag}_{1-\delta}\text{GeSe}_7$ ($\text{Ln} = \text{La-Nd, Sm, Gd-Dy; } \delta = 0.06-0.28$) and $\text{Ln}_3\text{Ag}_{1-\delta}\text{SiSe}_7$ ($\text{Ln} = \text{La-Nd, Sm, Gd-Dy; } \delta = 0-0.30$; Daszkiewicz *et al.*, 2009). The charge neutrality of these compounds can be realised when an existence of the $\text{Ag}^{2+}/\text{Ag}^{3+}$ ions is assumed (Curda *et al.*, 2001; van Wüllen *et al.*, 2005).

The dependence of the lattice parameters (a and c) and unit-cell volume (V) of the $\text{Ln}_3\text{Ag}_{1-\delta}\text{GeS}_7$ ($\text{Ln} = \text{La-Nd, Sm, Gd-Er and Y; } \delta = 0.11-0.50$) compounds on the ionic radius of the rare-earth elements is shown in Fig. 1. A gradual decrease of the unit-cell volume agrees well with the decrease in ionic radius of the rare-earth element. It reflects the well known lanthanide contraction. The size of the lanthanide ion considerably affects the unit-cell dimension in the ab plane, but the change in the c parameter is not significant. The opposite effect is observed when different tetravalent elements substitute at the germanium position in the structure leading to the $\text{Ln}_3\text{Ag}_{1-\delta}\text{SiS}_7$ and $\text{Ln}_3\text{Ag}_{1-\delta}\text{SnS}_7$ compounds (Daszkiewicz *et al.*, 2008). This substitution affects the c parameter and the a parameter insignificantly, and there is a small change in volume, *e.g.* $\sim 0.6\%$ between $\text{La}_3\text{Ag}_{1-\delta}\text{GeS}_7$ and $\text{La}_3\text{Ag}_{1-\delta}\text{SiS}_7$, and $\sim 3\%$ between $\text{La}_3\text{Ag}_{1-\delta}\text{GeS}_7$ and $\text{La}_3\text{Ag}_{1-\delta}\text{SnS}_7$ (Daszkiewicz *et al.*, 2007). Overall, based on the literature data, the larger change of the unit-cell volume amounting to $\sim 13\%$ is caused by the substitution of either lanthanide or sulfur (Daszkiewicz *et al.*, 2008, 2009). This change is rather a two-dimensional effect in the former case and a three-dimensional one in the latter case. Besides, when the silver $\text{La}_3\text{Ag}_{1-\delta}\text{GeS}_7$ and copper $\text{La}_3\text{CuGeS}_7$ series are

compared with each other, it appears that the differences between the lattice parameters are not significant. The unit-cell volumes differ by only $\sim 1\%$, despite the fact that the Ag^+ ionic radius of 0.67 \AA is $\sim 50\%$ larger than the Cu^+ radius of 0.46 \AA (Shannon, 1976). However, these ions lie in a channel built by the face-sharing trigonal antiprismatic arrangement of the sulfur anions (Fig. 2), and the silver or copper ions can occupy different positions in this channel. Therefore, the occurrence of more silver ions is compensated in this simple manner. The silver ions occupy the positions near the centres of the antiprisms which are further from the triangular bases.

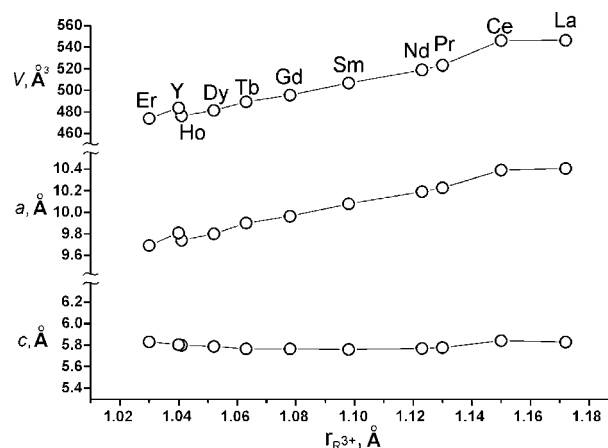


Figure 1

Dependence of the lattice parameters (a and c) and unit-cell volume (V) of the $\text{Ln}_3\text{Ag}_{1-\delta}\text{GeS}_7$ ($\text{Ln} = \text{La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Y}$ and $\text{Er; } \delta = 0.11-0.50$) compounds on the ionic radii of the rare-earth elements.

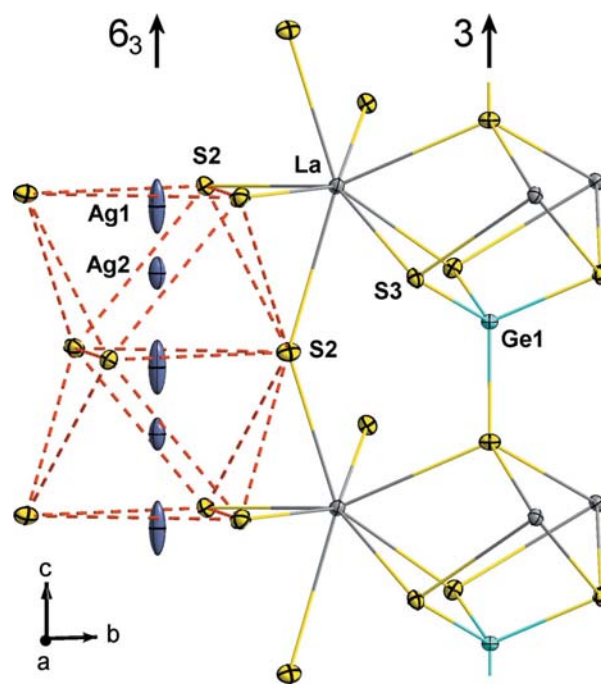


Figure 2

Atomic coordination of the La, Ag1, Ag2 and Ge ions in the $\text{La}_3\text{Ag}_{0.82}\text{GeS}_7$ structure.

¹ Supplementary data for this paper are available from the IUCr electronic archives (Reference: BP5017). Services for accessing these data are described at the back of the journal.

Table 2

Interatomic distances (δ , Å) and coordination numbers (CN) of the ions in the structures of $\text{Ln}_3\text{Ag}_{1-\delta}\text{GeS}_7$ (Ln = La–Nd, Sm, Gd–Er, Y; $\delta = 0.11$ – 0.50).

	CN	La	Ce	Pr	Nd	Sm	Gd
Ln–1S3	8	2.9145 (9)	2.909 (1)	2.863 (2)	2.853 (1)	2.833 (1)	2.816 (1)
Ln–1S2		2.9399 (9)	2.942 (1)	2.893 (2)	2.879 (1)	2.833 (1)	2.790 (1)
Ln–1S2		2.9452 (9)	2.944 (1)	2.905 (2)	2.893 (1)	2.860 (1)	2.830 (1)
Ln–1S2		2.966 (1)	2.957 (2)	2.918 (3)	2.902 (1)	2.878 (1)	2.844 (1)
Ln–1S3		3.0319 (9)	3.025 (1)	2.980 (2)	2.966 (1)	2.938 (1)	2.909 (1)
Ln–1S3		3.0732 (9)	3.075 (1)	3.037 (3)	3.031 (1)	3.012 (1)	3.004 (1)
Ln–1S1		3.0878 (7)	3.080 (1)	3.029 (1)	3.017 (1)	2.982 (1)	2.9466 (9)
Ln–1S2		3.122 (1)	3.131 (2)	3.097 (3)	3.105 (1)	3.124 (1)	3.161 (1)
Ag1–3S2	3	2.4136 (9)	2.439 (1)	2.405 (2)	2.404 (2)	2.378 (4)	2.413 (8)
Ag2–3S2	6	2.805 (4)	2.79 (1)	2.50 (3)	2.76 (2)	2.724 (9)	2.672 (5)
Ag–3S2		2.811 (4)	2.85 (1)	3.19 (3)	2.79 (2)	2.751 (9)	2.743 (5)
Ge–1S1	4	2.175 (1)	2.190 (3)	2.172 (4)	2.174 (3)	2.177 (2)	2.176 (1)
Ge–3S3		2.2245 (9)	2.239 (1)	2.217 (3)	2.225 (1)	2.228 (1)	2.225 (1)
	CN	Tb	Dy	Ho	Y	Er	
Ln–1S3	8	2.805 (1)	2.794 (1)	2.861 (1)	2.794 (1)	2.784 (3)	
Ln–1S2		2.769 (1)	2.733 (1)	2.714 (1)	2.736 (1)	2.699 (3)	
Ln–1S2		2.814 (1)	2.787 (1)	2.768 (2)	2.790 (1)	2.753 (3)	
Ln–1S2		2.818 (2)	2.792 (1)	2.773 (1)	2.794 (1)	2.761 (3)	
Ln–1S3		2.893 (1)	2.872 (1)	2.784 (1)	2.875 (1)	2.853 (3)	
Ln–1S3		2.999 (1)	2.997 (1)	3.006 (1)	3.008 (1)	3.020 (3)	
Ln–1S1		2.925 (1)	2.892 (1)	2.873 (1)	2.894 (1)	2.856 (1)	
Ln–1S2		3.189 (2)	3.243 (1)	3.281 (2)	3.261 (1)	3.329 (3)	
Ag1–3S2	3						
Ag2–3S2	6	2.504 (3)	2.511 (3)	2.535 (4)	2.516 (2)	2.560 (7)	
Ag2–3S2		2.909 (4)	2.816 (4)	2.743 (5)	2.824 (3)	2.688 (7)	
Ge–1S1	4	2.175 (3)	2.185 (2)	2.181 (3)	2.188 (2)	2.190 (4)	
Ge–3S3		2.225 (1)	2.220 (1)	2.216 (1)	2.224 (1)	2.223 (3)	

Relevant interatomic distances and coordination numbers of the ions are listed in Table 2 and related coordination polyhedra for Ln, Ag1, Ag2 and Ge are shown in Fig. 2. Each lanthanide ion is surrounded by eight sulfur anions to form a bicapped trigonal prism. The shortest Ln–S distance decreases from 2.9145 (9) Å for La to 2.784 (3) Å for Er and reflects the well known lanthanide contraction. Overall, the interatomic distances agree well with the respective sum of the ionic radii (Shannon, 1976). Particularly, the longest Ln–S2 distance is acceptable for $\text{La}_3\text{Ag}_{1-\delta}\text{GeS}_7$ [3.122 (1) Å], but it seems to be too long for $\text{Er}_3\text{Ag}_{1-\delta}\text{GeS}_7$ [3.329 (3) Å] to consider it as a bonding interaction. However, a bond-valence sum calculation for the eight-coordination sphere of the Er^{3+} ion (2.79) remains smaller than 3 and the longest Er–S2 distance still contributes 0.09 of a valence unit (Brown, 1996). Therefore, this S2 ion is reckoned among the coordination sphere of the Er^{3+} and a bicapped trigonal prismatic arrangement for the lanthanide atom in other $\text{Ln}_3\text{Ag}_{1-\delta}\text{GeS}_7$ compounds can justifiably be considered. The germanium ion lies on the threefold axis and its coordination sphere is created by one S1 and three S3 anions generated by symmetry transformations. Since the Ge–S1 distance is slightly shorter than the Ge–S3 distances, the tetrahedron is compressed

along the threefold axis. The Inorganic Crystal Structure Database contains 88 structures of chalcogenides (S and Se) with the space group $P6_3$. They crystallize in five types of ANX formula² ABC_3X_7 (62 structures), $AB_2C_6X_{14}$ (19), $A_2B_3X_7$ (3), AB_3X_7 (3) and $AB_4C_{12}X_{28}$ (1), of which 9, 1, 1, 0 and 0 structures contain an elongated tetrahedron around the tetravalent element. Besides, an almost perfect tetrahedron is observed in $\text{Tb}_3\text{CuSiSe}_7$ (Gulay, Lychmanyuk, Olekseyuk, Daszkiewicz, Stępień-Damm & Pietraszko, 2007). However, an angular deformation occurs for $[\text{SiSe}_4]$ despite the fact that the four Si–Se distances are equal. Therefore, a compression of the $[\text{GeS}_4]$ tetrahedron appears to be normal in the title compounds $\text{Ln}_3\text{Ag}_{1-\delta}\text{GeS}_7$. One Ge, three Ln and four S ions create cube-shaped $[\text{Ln}_3\text{GeS}_4]$ blocks, which are connected to each other by the Ge–S1 bonds along the c axis (Fig. 2).

The main feature of the $\text{Ln}_3\text{Ag}_{1-\delta}\text{GeS}_7$ compounds are $[\text{S}_3]_n$ channels created by the sulfur anions along the c axis. The silver ions lie on the 6_3 axis in the channel and occupy Ag1 and Ag2 positions with coordination numbers CN = 3 and 6, respectively. The coordination triangle of the Ag1 is slightly distorted because of the Ag1 displacement from the triangular sulfur plane. The Ag1–S distances lie in the range 2.378 (4)–2.439 (1) Å and they correlate well with the sum of the respective ionic radii (Shannon, 1976). Six S2 ions ($\text{S}_{2_3} + \text{S}_{2_3}$) form a trigonal antiprismatic arrangement around the Ag2 which is displaced from the centre of the antiprism. Two types of

Ag2–S2 distances describe this displacement which becomes larger for the heavier rare-earth elements. Since two positions of the silver ion occur in the trigonal antiprism, short Ag1–Ag2 distances can be observed in the structures of $\text{Ln}_3\text{Ag}_{1-\delta}\text{GeS}_7$ (Ln = La–Nd, Sm and Gd; $\delta = 0.11$ – 0.38) compounds. Actually, when one antiprism is centered by Ag2, the next antiprism must be either occupied in the same manner or left empty (see §3.4). The nearest Ag1 position could not be occupied, because a Ag2–Ag1 distance which is too short would occur. Only the third trigonal antiprism can contain a silver ion in the Ag1 position. Thus, the occurrence of two symmetrically independent positions of the silver is related to the non-stoichiometry of the compounds.

3.2. Ln_3MTX_7 – quasi-isostructural compounds

The existence of some quaternary Ln_3MTX_7 (Ln – lanthanide element, M – Cu, Ag; T – Si, Ge, Sn and X – S, Se) compounds with $\text{La}_3\text{CuSiS}_7$ structure type (space group $P6_3$) has been reported by Guittard & Julien-Pouzol (1970) and Collin & Flahaut (1972). Only lattice parameters have been determined for these compounds. However, complete struc-

² ANX formula notation derives from the ICSD.

Table 3

Three groups of the $\text{Ln}_3\text{M}_{1-\delta}\text{TX}_7$ (Ln – lanthanide element, M – Cu, Ag, T – Si, Ge, Sn and X – S, Se) compounds.

1 - first group, 2 - second group, 3 - third group (see §3.2).

Compounds	Lanthanide element													
	La	Ce	Pr	Nd	Sm	Gd	Tb	Dy	Ho	Y	Er	Tm	Yb	Lu
$\text{Ln}_3\text{Cu}_{1-\delta}\text{SiS}_7$ ($\delta = 0$)	1	1	1	1	1	1	1	1	1	1	1	–	–	–
$\text{Ln}_3\text{Cu}_{1-\delta}\text{GeS}_7$ ($\delta = 0$)	1	1	1	1	1	1	1	1	1	1	1	–	–	–
$\text{Ln}_3\text{Cu}_{1-\delta}\text{SnS}_7$ ($\delta = 0$)	1	1	1	1	1	1	1	1	1	1	–	–	–	–
$\text{Ln}_3\text{Cu}_{1-\delta}\text{SiSe}_7$ ($\delta = 0$)	1	1	1	1	1	1	1	1	1	1	1	–	–	–
$\text{Ln}_3\text{Cu}_{1-\delta}\text{GeSe}_7$ ($\delta = 0$)	1	1	1	1	1	1	1	1	–	1	–	–	–	–
$\text{Ln}_3\text{Cu}_{1-\delta}\text{SnSe}_7$ ($\delta = 0$)	1	1	1	1	1	1	1	1	–	1	–	–	–	–
$\text{Ln}_3\text{Ag}_{1-\delta}\text{SiS}_7$ ($\delta = 0.10\text{--}0.23$)	2	2	2	2	2	–	–	–	–	–	–	–	–	–
$\text{Ln}_3\text{Ag}_{1-\delta}\text{GeS}_7$ ($\delta = 0.11\text{--}0.50$)	2	2	2	2	2	2	3	3	3	3	3	–	–	–
$\text{Ln}_3\text{Ag}_{1-\delta}\text{SnS}_7$ ($\delta = 0.18\text{--}0.19$)	2	2	–	–	–	–	–	–	–	–	–	–	–	–
$\text{Ln}_3\text{Ag}_{1-\delta}\text{SiSe}_7$ ($\delta = 0\text{--}0.30$)	1	1	1	1	2	2	2	2	–	–	–	–	–	–
$\text{Ln}_3\text{Ag}_{1-\delta}\text{GeSe}_7$ ($\delta = 0.06\text{--}0.28$)	2	2	2	2	2	2	2	2	–	–	–	–	–	–
$\text{Ln}_3\text{Ag}_{1-\delta}\text{SnSe}_7$ ($\delta = 0$)	1	–	–	–	–	–	–	–	–	–	–	–	–	–

ture determinations have been performed using both single-crystal and powder X-ray data for $\text{Ln}_3\text{CuSiS}_7$ (Ln = La–Nd, Sm, Gd–Er and Y; Collin & Laruelle, 1971; Gulay, Lychmanyuk, Stępień-Damm, Pietraszko & Olekseyuk, 2005; Hartenbach, Müller & Schleid, 2006; Gulay, Lychmanyuk, Olekseyuk, Daszkiewicz, Stępień-Damm & Pietraszko, 2007), $\text{Ln}_3\text{CuGeS}_7$ (Ln = La–Nd, Sm, Gd–Er and Y; Poduska *et al.*, 2002; Gulay, Lychmanyuk, Stępień-Damm, Pietraszko & Olekseyuk, 2006; Lychmanyuk *et al.*, 2007; Gulay, Lychmanyuk, Wołczyr, Pietraszko & Olekseyuk, 2007), $\text{Ln}_3\text{CuSnS}_7$ (Ln = La–Nd, Sm, Gd–Ho and Y; Gulay, Shemet & Olekseyuk, 2005; Gulay, Olekseyuk, Wołczyr & Stępień-Damm, 2005), $\text{Ln}_3\text{CuSiSe}_7$ (Ln = La–Nd, Sm, Gd–Ho and Y; Gulay, Lychmanyuk, Stępień-Damm, Pietraszko & Olekseyuk, 2005; Gulay, Lychmanyuk, Olekseyuk, Daszkiewicz, Stępień-Damm & Pietraszko, 2007; Lychmanyuk *et al.*, 2007), $\text{Ln}_3\text{CuGeSe}_7$ (Ln = La–Nd, Sm, Gd–Dy and Y; Huang & Ibers, 1999; Poduska *et al.*, 2002; Gulay, Lychmanyuk, Olekseyuk & Pietraszko, 2006; Lychmanyuk *et al.*, 2006), $\text{Ln}_3\text{CuSnSe}_7$ (Ln = La–Nd, Sm, Gd–Dy and Y; Gulay *et al.*, 2004; Gulay & Olekseyuk, 2005; Gulay, Kaczorowski & Pietraszko, 2006). The $\text{La}_3\text{AgSiS}_7$ (Wu & Huang, 2005), $\text{La}_3\text{AgSiSe}_7$ (Lin *et al.*, 1997) and $\text{La}_3\text{AgGeS}_7$ (Hwu *et al.*, 1995) compounds have been investigated by means of X-ray single-crystal diffraction. Extremely high values of anisotropic displacement parameters for Ag have been observed in the structures of these compounds. The crystal structures of the $\text{Ln}_3\text{Ag}_{1-\delta}\text{SiS}_7$ (Ln = La–Nd, Sm, $\delta = 0.10\text{--}0.23$; Daszkiewicz *et al.*, 2008), $\text{Ln}_3\text{Ag}_{1-\delta}\text{GeS}_7$ (Ln = La–Nd, Sm, Gd–Er and Y; $\delta = 0.11\text{--}0.50$; this work), $\text{Ln}_3\text{Ag}_{1-\delta}\text{SnS}_7$ (Ln = La, Ce; $\delta = 0.18\text{--}0.19$; Daszkiewicz *et al.*, 2007), $\text{Ln}_3\text{Ag}_{1-\delta}\text{SiSe}_7$ (Ln = La–Nd, Sm,

Gd–Dy; $\delta = 0\text{--}0.30$; Daszkiewicz *et al.*, 2009), $\text{Ln}_3\text{Ag}_{1-\delta}\text{GeSe}_7$ (Ln = La–Nd, Sm, Gd–Dy, $\delta = 0.06\text{--}0.28$; Huang & Ibers, 1999; Poduska *et al.*, 2002; Gulay, Lychmanyuk, Olekseyuk & Pietraszko, 2006; Lychmanyuk *et al.*, 2006), $\text{La}_3\text{AgSnSe}_7$ (Daszkiewicz *et al.*, 2007) compounds have been investigated recently. For most of them a reduction in the Ag content has been observed. Crystal structures of all these compounds are similar. However, positions of the monovalent elements (Cu, Ag) in the trigonal antiprism differ in various series of the compounds. Thus, all the $\text{Ln}_3\text{M}_{1-\delta}\text{TX}_7$ compounds can be divided into three groups (Table 3):

(i) Only one position for Cu (or Ag) exists. Copper (or silver) ions have a triangular coordination. Stoichiometric Ln_3MTX_7 compounds (a large majority of the ABC_3X_7 compounds deposited in the ICSD) belong to the first group.

(ii) Two positions are occupied, Ag1 and Ag2, which have a triangular and trigonal antiprismatic coordination. The $\text{Ln}_3\text{Ag}_{1-\delta}\text{TX}_7$ ($0.06 \leq \delta \leq 0.38$) compounds belong to the second group.

(iii) Only one position exists in the structure with the trigonal antiprismatic arrangement of the X anion. Several compounds belong to this group:

(a) non-stoichiometric silver chalcogenides $\text{Ln}_3\text{Ag}_{1-\delta}\text{TX}_7$ ($0.06 \leq \delta \leq 0.50$) and $\text{Ce}_3\text{Fe}_{1.94}\text{S}_7$ ($\text{A}_2\text{B}_3\text{X}_7$ general formula; Mills & Ruck, 2004) where mixed-valence silver or iron atoms occupy central positions in the antiprisms;

(b) the compounds which contain di-, tri- or tetravalent elements provided that the site-occupancy factor of the element is equal to an inverse of its oxidation state, e.g. $\text{La}_3\text{Sn}_{0.25}\text{SiS}_7$ ($\text{AB}_4\text{C}_{12}\text{X}_{28}$ general formula; Collin *et al.*, 1973), $\text{La}_3\text{In}_{0.33}\text{SiS}_7$ ($\text{AB}_2\text{C}_6\text{X}_{14}$ general formula; Collin *et al.*, 1973),

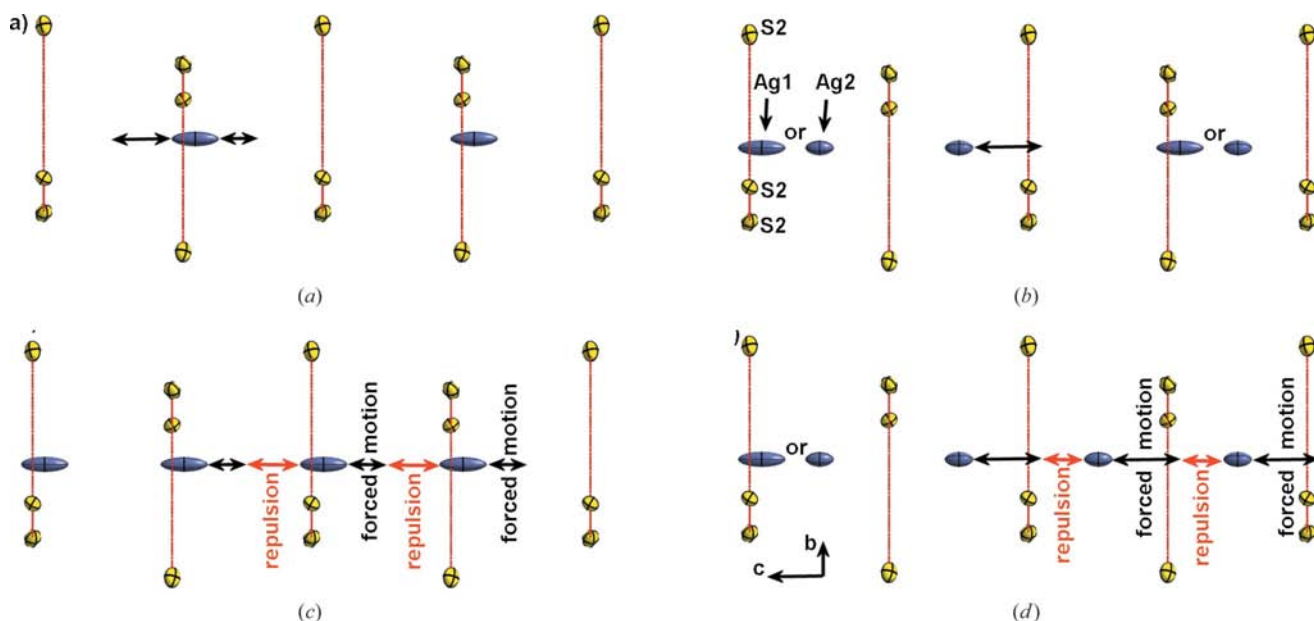


Figure 3
A model of the silver-ion motion through the $[S_3]_n$ channel viewed down $[100]$.

$\text{Pr}_3\text{Ge}_{1.25}\text{S}_7$ (AB_3X_7 general formula; Bakakin & Ipatova, 1974);

(c) stoichiometric Ln_3MTX_7 compounds where a monovalent element with small ionic radius is located in the centre of the antiprism, e.g. Y_3NaSi_7 (ABC_3X_7 general formula; Hartenbach & Schleid, 2003) or stoichiometric Ln_3MTX_7 compounds where monovalent and tetravalent elements are substituted by the di- and trivalent elements, e.g. $\text{La}_3\text{MnFeS}_7$ (ABC_3X_7 general formula; Nanjundaswamy & Gopalakrishnan, 1983).

Hartenbach and co-workers recently published the crystal structure of $\text{Ce}_3\text{Ag}_{0.63}\text{Si}_{6.63}\text{Cl}_{0.37}$, where the chloride and sulfide ions shared one position and, therefore, a disordered $[(S/Cl)_3]_n$ channel was created (Hartenbach, Nilges & Schleid, 2006). This substitution involves a non-stoichiometric amount of silver. Thus, some trigonal antiprisms are occupied and some of them remain empty, likewise for the compounds belonging to the (ii), and (iii*a*) and (iii*b*) groups. The crystal structure of $\text{Ce}_3\text{Ag}_{0.63}\text{Si}_{6.63}\text{Cl}_{0.37}$ was refined assuming one position of the silver ion, but the second was very well established by means of the third-order anharmonic parameters for the low-temperature data. Therefore, this compound should be incorporated into the second group.

An important feature of the Ln_3MTX_7 compounds is that each trigonal antiprism is occupied by the M ion in the (i) and (iii*c*) groups, and thus the $[X_3]_n$ channel is saturated. A non-stoichiometric amount of the M element occurs in all the other groups resulting in some antiprisms being occupied and some remaining empty. This unsaturation can facilitate ionic movement through the channel. Besides, ionic conductivity should be greater when the chemical composition is disordered, e.g. $[(S/Cl)_3]_n$ in $\text{Ce}_3\text{Ag}_{0.63}\text{Si}_{6.63}\text{Cl}_{0.37}$ (Hartenbach,

Nilges & Schleid, 2006). Indeed, the energy barrier between Ag1 and Ag2 positions for the disordered channel (45 meV; 298 K; Hartenbach, Nilges & Schleid, 2006) is approximately half that for the $\text{Ce}_3\text{Ag}_{0.82}\text{Si}_7$ (105 meV; 298 K)³ (Petricek *et al.*, 2000).

3.3. Stereoisomerism

Hwu *et al.* (1995) paid attention to the stereoisomerism of the Ln_3MTX_7 compounds. The crystal structure can be treated as linked parallel chains of $[MX_3]$ and cube-shaped $[\text{Ln}_3\text{TX}_4]$ motifs (Fig. 2). However, the cube can be oriented with a tetravalent (Ge) ion in the upper (+) or lower (−) position, likewise the displacement direction of the monovalent (Ag) ion towards the $[X_3]$ plane can be in the same or opposite direction. When both chains are oriented in the upper or both in the lower direction, they create the same enantiomer (+/+−−). When an antiparallel configuration occurs, the crystal lattice is built by the +− diastereoisomer.

Since the monovalent element can occupy only one of two positions at the same time (see Ag1 and Ag2 in Fig. 2), its accurate position is important for the stereochemistry of the Ln_3MTX_7 compounds. The Ag1 position is occupied for the compounds belonging to the first and second group (see §3.2). All these compounds create ++ isomers with the exception of $\text{Sm}_3\text{CuSiSe}_7$ and $\text{Gd}_3\text{CuSiSe}_7$ (Gulay, Lychmanyuk, Oleksyuk, Daszkiewicz, Stępień-Damm & Pietraszko, 2007), where the Cu ion is displaced 0.132 and 0.114 Å from the $[\text{Se}_3]$ plane in the opposite direction towards the cube orientation.

³ The energy barrier was determined by means of the JANA2000 program on basis of the published data on $\text{Ce}_3\text{Ag}_{0.82}\text{Si}_7$ (Daszkiewicz *et al.*, 2008). Third-order anharmonic parameters were considered to determine a displacement of the silver ion with no splitting for two different positions. The Ag2 position from SHELXL was determined by means of the third-order approximation.

For the third group of the Ln_3MTX_7 compounds, the Ag2 position lies nearby the centre of the antiprism. Therefore, even small displacements from the centre result in the ++ or +- stereoisomer. Indeed, many belonging to the third group structures (see §3.2), which are deposited in the ICSD database, are ++ as well as +- and there is no simple rule which connects the chemical constitution and stereochemistry of the Ln_3MTX_7 compounds. However, the most interesting compounds appear to be silver chalcogenides with a non-stoichiometric composition, where two symmetrically independent positions of the silver were found. Low-energy barriers between two positions occur and the silver ions can easily move through the channel. The ions also occupy intermediate positions during this process. Thus, ++ and +- stereoisomers coexist in the crystal (not necessarily in equal amounts), because the movement has dynamic character by its nature. However, it appears that a stereoisomeric excess is determined to a large extent by the site occupancy factors of the Ag1 and Ag2 positions.

3.4. Model of silver-ion motion

Overall, the sulfur trigonal antiprismatic units $[\text{S}_3]_2$ can either be occupied by Ag1 or Ag2, or left empty (see §3.1). The energy barriers between Ag positions are very small and the silver ions can move through the channel. However, silver does not occupy Ag1 and Ag2 positions in a completely random manner. When the Ag2 position is occupied, the next antiprism is also occupied by Ag2 or left empty. Therefore, the shift to Ag1 is possible provided that the adjacent antiprisms are empty or two silver ions are located in the furthestmost positions (Figs. 3a and b). If adhering to this condition does not result in a silver motion, $\text{Ag1} \leftrightarrow \text{Ag2}$ and $\text{Ag2} \leftrightarrow \text{Ag1}$, a forced motion of the other silver ions occurs (Figs. 3c and d) owing to the repulsive interaction between the ions. Thus, all the silver ions move through the channel in a correlated manner.

One of the authors (MD) is the laureate of The Domestic Grant for Young Scientists awarded by the Foundation for Polish Science.

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