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Crystal structure of $R_3Mg_{0.5}DSe_7$ (R = Ce, Pr; D = Si, Ge)

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The crystal structures of four quaternary $R_3Mg_{0.5}DSe_7$ compounds (structure type $La_3Mn_{0.5}SiS_7$, space group $P6_3$, Pearson code $hP23$, a = 10.669(1) Å, c = 6.0611(8) Å, $R1$ = 0.0252 for $Ce_3Mg_{0.5}SiSe_7$; a = 10.531(1) Å, c = 6.0420(1) Å, $R1$ = 0.0275 for $Pr_3Mg_{0.5}SiSe_7$; a = 10.6579(7) Å, c = 6.0430(7) Å, $R1$ = 0.0249 for $Ce_3Mg_{0.5}GeSe_7$; a = 10.615(1) Å, c = 6.0329(7) Å, $R1$ = 0.0406 for $Pr_3Mg_{0.5}GeSe_7$) were determined by means of X-ray single-crystal diffraction. The R atoms occupy trigonal prisms capped by two additional atoms. The Mg atoms are located in octahedra and the D atoms in tetrahedra.

Rare-earth compounds / Chalcogenides / Crystal structure / X-ray single-crystal diffraction

Introduction

The production of new materials with increasingly complex compositions has become a principle direction in modern science and technology. Among the multicomponent systems, an important place is occupied by complex rare-earth chalcogenides [1,2]. The compounds with the general formula R_3MDX_7 (space group $P6_3$) (R = lanthanide element, M = 1 mono-valent element (Cu, Ag) or 1/2 of a di-valent element (Mn, Fe, Mg), D = Si, Ge, Sn, and X = S, Se) are interesting due to possible applications in the field of nonlinear optics.

The existence of quaternary $R_3Mg_{0.5}Si(Ge)S_7$ (R = Y, La) compounds (space group $P6_3$) was reported in [3]. Lattice parameters were determined for these compounds. Complete crystal structure determinations of the quaternary rare-earth sulfides $La_3Mg_{0.5}Si(Ge)S_7$ and $R_3Mg_{0.5}GeS_7$ (R = Y, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, and Er) were reported in [4] and [5], respectively.

In this paper we present our results of the structure refinement of $R_3Mg_{0.5}DSe_7$ (R = Ce, Pr; D = Si, Ge) on single-crystal X-ray diffraction data.

Experimental

Samples with the nominal compositions $R_3Mg_{0.5}DSe_7$ (R = Ce, Pr; D = Si, Ge) were prepared by fusion of the high-purity elemental constituents in evacuated silica ampoules. The purity of the starting materials was better than 99.9 wt.%. In order to exclude the reaction of magnesium with quartz, the ampoules were lined with graphite. The synthesis was carried out in a tube resistance furnace. The ampoules were gradually heated at a rate of 30°C per hour up to a maximal temperature of 1150°C, and kept at this temperature for 3 h. After that they were slowly cooled (10°C per h) to 600°C, and annealed at this temperature for 720 h. Subsequently, the ampoules were quenched in air.

X-ray powder diffraction patterns of the samples were recorded using a DRON-4-13 powder diffractometer (Cu$K\alpha$ radiation, $10° \leq 2\theta \leq 90°$, step scan mode with a step size of 0.05° and a counting time of 5 s per data point). The similarity of the X-ray powder diffraction patterns of $R_3Mg_{0.5}DSe_7$ (R = Ce, Pr; D = Si, Ge) to those investigated in [3-5] allowed us to conclude that these compounds are isostructural. Small single crystals, with the shape of hexagonal prisms, suitable for crystal structure investigations, were selected from the samples. The compositions of these single crystals were determined by microprobe analysis performed with an EDAX PV9800 microanalyzer.

The X-ray intensities data were collected on a KUMA Diffraction KM-4 four-circle diffractometer equipped with a CCD camera (graphite-monochromatized Mo$K\alpha$ radiation, λ = 0.71073 Å).

The raw data were treated with the CrysAlis Data Reduction program [6], taking into account an absorption correction. The intensities of the reflections were corrected for Lorentz and polarization factors. The crystal structures were solved by Patterson methods and refined by the full-matrix least-squares method using SHELXL-97 [7]. The acentric space group $P6_3$ was checked with the PLATON program [8] and no additional symmetry elements were found.

Results and discussion

Hexagonal unit cells with similar lattice parameters (Table 1) were observed during testing of the single crystals of $R_3Mg_{0.5}DSe_7$ (R = Ce, Pr; D = Si, Ge). The extinctions were found to be consistent with the space group $P6_3$, which was used for the crystal structure solution and refinement for all the compounds. One site occupied by R, one site by Mg, one site by Si (Ge) and three sites by Se were determined. The positions of the R, Si (Ge) and Se atoms are fully occupied. The site occupancy factors for the Mg atoms refined to values close to 0.50 for all the investigated compounds. In the final cycles the occupancy factors of the Mg sites were fixed to 0.50 to satisfy charge balance requirements. The crystallographic data and refinement information for $R_3Mg_{0.5}DSe_7$ (R = Ce, Pr; D = Si, Ge) are summarized in Table 1, whereas the atomic coordinates and the atomic displacement factors are given in Table 2. The results of the crystal structure refinement for $R_3Mg_{0.5}DSe_7$ (R = Ce, Pr; D = Si, Ge) are in good accordance with the structure type $La_3Mn_{0.5}SiS_7$ [9].

Table 1 Crystallographic data and experimental details for $R_3Mg_{0.5}DSe_7$ (R = Ce, Pr; D = Si, Ge).

Empirical formula	$Ce_3Mg_{0.5}SiSe_7$	$Pr_3Mg_{0.5}SiSe_7$	$Ce_3Mg_{0.5}GeSe_7$	$Pr_3Mg_{0.5}GeSe_7$
Space group	$P6_3$ (No. 173)	$P6_3$ (No. 173)	$P6_3$ (No. 173)	$P6_3$ (No. 173)
Unit cell dimensions:				
a (Å)	10.669(1)	10.531(1)	10.6579(7)	10.615(1)
c (Å)	6.0611(8)	6.0420(8)	6.0430(7)	6.0329(7)
V (Å^3)	599.15(8)	580.3(1)	594.4(8)	588.7(1)
Number of formula units per unit cell Z	2	2	2	2
Calculated density (g cm^{-3})	5.697	5.812	5.910	5.980
Absorption coefficient (mm^{-1})	32.999	34.414	35.169	36.323
F(000)	864	870	900	906
Crystal color	dark red	dark red	dark red	dark red
Crystal size (mm^3)	0.06×0.04×0.04	0.08×0.06×0.05	0.06×0.04×0.03	0.10×0.06×0.05
θ range for data collection	3.82-27.48	3.87-27.42	4.03-28.67	4.04-35.63
Index ranges	$-13 \le h \le 13$ $-13 \le k \le 13$ $-7 \le l \le 7$	$-13 \le h \le 13$ $-13 \le k \le 13$ $-7 \le l \le 7$	$-14 \le h \le 14$ $-14 \le k \le 14$ $-8 \le l \le 8$	$-13 \le h \le 15$ $-17 \le k \le 14$ $-8 \le l \le 9$
Reflections collected	8361	7383	9341	8989
Independent reflections	903 [R(int.) = 0.0524]	886 [R(int.) = 0.0522]	1026 [R(int.) = 0.0725]	1677 [R(int.) = 0.0541]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Absolute structure parameter	-0.03(3)	0.05(3)	0.00(3)	0.03(3)
Data/restraints/parameters	903/1/37	886/1/37	1026/1/38	1677/1/38
Goodness-of-fit on F^2	0.995	0.984	1.001	0.870
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0227$, $wR2 = 0.0369$	$R1 = 0.0237$, $wR2 = 0.0399$	$R1 = 0.0224$, $wR2 = 0.0425$	$R1 = 0.0288$, $wR2 = 0.0423$
R (all data)	$R1 = 0.0252$, $wR2 = 0.0373$	$R1 = 0.0275$, $wR2 = 0.0407$	$R1 = 0.0249$, $wR2 = 0.0431$	$R1 = 0.0406$, $wR2 = 0.0438$
Extinction coefficient	–	–	0.0101(3)	0.0037(1)
Largest diff. peak and hole (e Å^{-3})	0.870 and -1.077	1.698 and -1.229	1.900 and -1.302	1.777 and -2.989

Table 2 Atomic coordinates and thermal displacement factors (Å^2) for $R_3Mg_{0.5}DSe_7$ (R = Ce, Pr; D = Si, Ge).

Atom	Wyckoff	*x/a*	*y/b*	*z/c*	Occupancy	$U_{\text{eq.}}$ [a]
$Ce_3Mg_{0.5}SiSe_7$						
Ce	6*c*	0.12660(4)	0.35753(4)	0.0138(1)	1	0.00913(9)
Mg	2*a*	0	0	0.277(3)	0.50	0.012(1)
Si	2*b*	⅓	⅔	0.4273(6)	1	0.0096(8)
Se1	2*b*	⅓	⅔	0.7995(2)	1	0.0112(3)
Se2	6*c*	0.24899(7)	0.16135(7)	0.0280(1)	1	0.0105(1)
Se3	6*c*	0.10777(7)	0.58604(7)	0,2820(1)	1	0.00948(1)
$Pr_3Mg_{0.5}SiSe_7$						
Pr	6*c*	0.12936(4)	0.35702(4)	0.0126(1)	1	0.0177(1)
Mg	2*a*	0	0	0.285(3)	0.50	0.019(1)
Si	2*b*	⅓	⅔	0.4271(5)	1	0.0098(8)
Se1	2*b*	⅓	⅔	0.7987(2)	1	0.0141(3)
Se2	6*c*	0.25084(9)	0.16022(8)	0.0332(1)	1	0.0204(1)
Se3	6*c*	0.10534(7)	0.58333(8)	0.2814(1)	1	0.0125(1)
$Ce_3Mg_{0.5}GeSe_7$						
Ce	6*c*	0.12943(4)	0.35737(3)	0.01435(9)	1	0.0086(1)
Mg	2*a*	0	0	0.282(2)	0.50	0.005(1)
Ge	2*b*	⅓	⅔	0.4297(2)	1	0.0083(3)
Se1	2*b*	⅓	⅔	0.8114(1)	1	0.0101(3)
Se2	6*c*	0.25035(7)	0.15961(7)	0.0304(1)	1	0.0100(1)
Se3	6*c*	0.10040(7)	0.58182(7)	0.2762(1)	1	0.0084(1)
$Pr_3Mg_{0.5}GeSe_7$						
Pr	6*c*	0.13014(3)	0.35744(3)	0.01420(7)	1	0.00932(7)
Mg	2*a*	0	0	0.280(1)	0.50	0.003(1)
Ge	2*b*	⅓	⅔	0.4293(1)	1	0.0088(2)
Se1	2*b*	⅓	⅔	0.8119(1)	1	0.0101(2)
Se2	6*c*	0.25153(6)	0.15964(5)	0.0319(1)	1	0.0106(1)
Se3	6*c*	0.09919(6)	0.58105(6)	0.2744(1)	1	0.0092(1)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
$Ce_3Mg_{0.5}SiSe_7$						
Ce	0.0098(1)	0.0079(1)	0.0097(1)	-0.0008(3)	-0.0007(3)	0.0044(1)
Mg	0.011(2)	0.011(2)	0.015(4)	0	0	0.005(1)
Si	0.009(1)	0.009(1)	0.008(1)	0	0	0.0050(6)
Se1	0.0130(4)	0,0130(4)	0.0074(7)	0	0	0.0065(2)
Se2	0.0111(3)	0.0096(3)	0.0122(4)	-0.0015(4)	-0.0004(5)	0.0062(3)
Se3	0,0087(4)	0.0097(4)	0.0106(4)	-0.0012(4)	-0.0004(3)	0.0051(3)
$Pr_3Mg_{0.5}SiSe_7$						
Pr	0.0141(2)	0.0179(2)	0.0237(2)	-0.0019(3)	-0.0041(3)	0.0097(1)
Mg	0.015(2)	0.015(2)	0.026(5)	0	0	0.007(1)
Si	0.012(1)	0.012(1)	0.005(1)	0	0	0.0060(6)
Se1	0.0179(4)	0.0179(4)	0.0065(6)	0	0	0.0090(2)
Se2	0.0292(4)	0.0199(4)	0.0213(4)	-0.0080(5)	-0.0082(5)	0.0191(3)
Se3	0.0111(4)	0.0173(4)	0.0105(3)	-0.0003(4)	-0.0001(3)	0.0082(3)
$Ce_3Mg_{0.5}GeSe_7$						
Ce	0.0094(1)	0.0074(1)	0.0091(1)	-0.0008(2)	-0.0008(2)	0.0042(1)
Mg	0.003(1)	0.003(1)	0.010(4)	0	0	0.0018(9)
Ge	0.0093(4)	0.0093(4)	0.0062(5)	0	0	0.0047(2)
Se1	0.0114(4)	0.0114(4)	0.0075(6)	0	0	0.0057(1)
Se2	0.0113(3)	0.0088(3)	0.0121(3)	-0.0012(3)	-0.0006(4)	0.0065(3)
Se3	0.0083(3)	0.0089(3)	0.0089(3)	-0.0012(3)	-0.0002(3)	0.0048(3)
$Pr_3Mg_{0.5}GeSe_7$						
Pr	0.0096(1)	0.0078(1)	0.0105(1)	-0.0010(1)	-0.0009(1)	0.0043(1)
Mg	0.001(1)	0.001(1)	0.009(3)	0	0	0.0006(7)
Ge	0.0099(3)	0.0099(3)	0.0066(5)	0	0	0.0049(1)
Se1	0.0115(3)	0.0115(3)	0.0073(6)	0	0	0.0057(1)
Se2	0.0116(2)	0.0096(2)	0.0127(3)	-0.0016(3)	-0.0004(3)	0.0067(2)
Se3	0.0092(3)	0.0097(3)	0.0099(3)	-0.0011(2)	0.0002(2)	0.0054(2)

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

Relevant interatomic distances and the coordination numbers of the *R*, Mg, and Si (Ge) atoms are listed in Table 3. All the distances are close to the sums of the respective ionic radii [10].

The unit cell and the coordination polyhedra of the *R*, Mg, *D*, Se1, Se2, and Se3 atoms in the structure of the $R_3Mg_{0.5}DSe_7$ (R = Ce, Pr; D = Si, Ge) compounds are shown in Fig. 1. The *R* atoms occupy trigonal prisms capped by two additional atoms. The Mg atoms are located in octahedra and the *D* atoms in tetrahedra. Every Se1 and Se3 atom is surrounded by a tetrahedron. The Se2 atoms are surrounded by tetragonal bi-pyramids.

Table 3 Interatomic distances (δ) and coordination numbers (C.N.) of the *R*, Mg and *D* atoms in $R_3Mg_{0.5}Se_7$ (R = Ce, Pr; D = Si, Ge).

Atoms		δ (Å)				C.N.
		$Ce_3Mg_{0.5}SiSe_7$	$Pr_3Mg_{0.5}SiSe_7$	$Ce_3Mg_{0.5}GeSe_7$	$Pr_3Mg_{0.5}GeSe_7$	
R	-1Se2	2.9710(8)	2.9326(8)	2.9699(7)	2.9580(6)	8
	-1Se2	2.9820(8)	2.9379(8)	2.9714(7)	2.9643(6)	
	-1Se3	3.0095(8)	2.9973(9)	3.0105(8)	2.9980(7)	
	-1Se2	3.082(1)	3.058(1)	3.090(1)	3.0721(9)	
	-1Se3	3.1114(9)	3.0909(9)	3.1048(8)	3.0895(7)	
	-1Se3	3.1703(8)	3.1638(8)	3.1746(8)	3.1677(7)	
	-1Se1	3.1809(8)	3.1489(8)	3.1510(6)	3.1364(5)	
	-1Se2	3.244(1)	3.294(1)	3.275(1)	3.2754(9)	
Mg	-3Se2	2.77(1)	2.761(9)	2.780(8)	2.778(6)	6
	-3Se2	2.77(1)	2.771(9)	2.791(8)	2.790(6)	
D	-1Se1	2.230(4)	2.245(4)	2.306(1)	2.308(1)	4
	-3Se3	2.284(1)	2.281(1)	2.3657(9)	2.3703(7)	

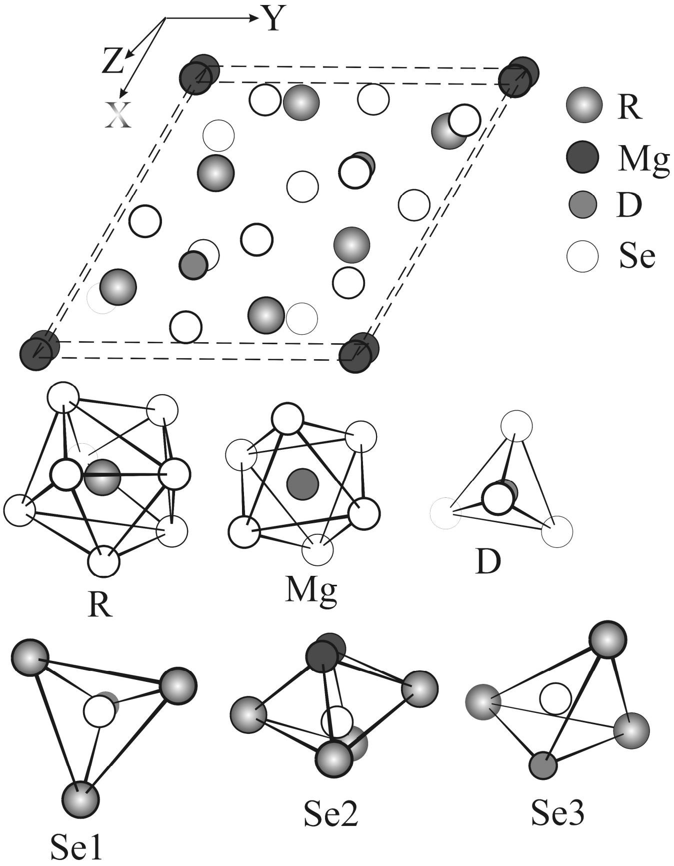

Fig. 1 Unit cell of the structure of the $R_3Mg_{0.5}DSe_7$ (R = Ce, Pr; D = Si, Ge) compounds and coordination polyhedra of the *R*, Mg, *D*, Se1, Se2, and Se3 atoms.

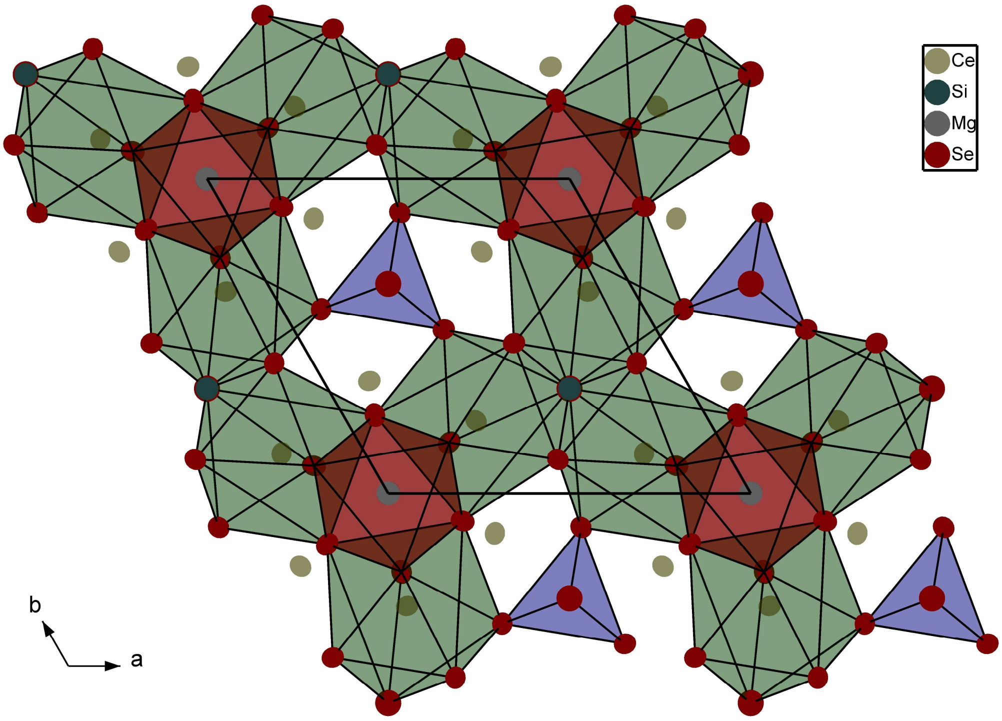

Fig. 2 Packing of $[CeSe1_1Se2_4Se3_3]$ bi-capped trigonal prisms, $[MgSe2_6]$ octahedra and $[SiSe1_1Se3_3]$ tetrahedra in the structure of $Ce_3Mg_{0.5}SiSe_7$.

The crystal structures of $R_3Mg_{0.5}DSe_7$ (R = Ce, Pr; D = Si, Ge) may be seen as built up by different coordination polyhedra, *e.g.* $[RSe1_1Se2_4Se3_3]$ bi-capped trigonal prisms, $[MgSe2_6]$ octahedra and $[DSe1_1Se3_3]$ tetrahedra (see Fig. 2), sharing common corners or faces. Structurally the $R_3Mg_{0.5}DSe_7$ (R = Ce, Pr; D = Si, Ge) compounds investigated in the present paper are members of a large family of compounds with the general formula R_3MDX_7 (space group $P6_3$), where R = lanthanide element; M = 1 mono-valent element (for example, Cu or Ag), 1/2 of a di-valent element (for example, Mg, Fe or Mn), or 1/4 of a four-valent element (Si, Ge, Sn); D = Si, Ge, Sn; and X = S, Se. All these compounds have similar structural motifs. The packing of $[RX_8]$ trigonal prisms and $[DX_4]$ tetrahedra is similar for all the structures and the differences are only in the occupation of the octahedra located along the c axis. The compounds can be divided into three groups (see [1]). The $R_3Mg_{0.5}DSe_7$ (R = Ce, Pr; D = Si, Ge) compounds belong to the third group. Two series of the recently investigated $R_3Mn_{0.5}GeS_7$ (R = Y, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, and Er) [11] and $R_3Fe_{0.5}GeS_7$ (R = Y, La, Ce, Pr, Sm, Gd, Tb, Dy, Ho, Er, and Tm) [12] compounds are also members of the third group of R_3MDX_7.

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