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Crystal structures of the $AgGa_2Se_3Cl$ and $AgGa_2Te_3Cl$ compounds

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The crystal structures of the new quaternary compounds $AgGa_2Se_3Cl$ and $AgGa_2Te_3Cl$ have been studied by X-ray powder diffraction. An analysis of the diffraction diagrams indicated the tetragonal crystal system, structure type $CuIn_2Te_3Cl$ (space group *I*-4) with the following unit-cell parameters: $AgGa_2Se_3Cl$, $a = 0.59789(3)$ nm, $c = 1.08592(7)$ nm; $AgGa_2Te_3Cl$, $a = 0.63044(4)$ nm, $c = 1.19562(8)$ nm. The Ga sites have tetrahedral surrounding and their positions (Wyckoff positions 2*a* and 2*c*) are filled to 80 %. The statistic mixtures *M*1, *M*2 (composition: 50 % Ag, 20 % Ga, 30 % vacancies) occupy two Wyckoff positions (2*b* and 2*d*) and center tetrahedra [$M_1$4*X*] and [$M_2$4*X*], where *X* = 75 % Se(Te), 25 % Cl.

Crystal structure / chalcogenides / X-ray powder diffraction

1. Introduction

Complex chalcogenides and chalcohalides with tetrahedral cation coordination are of considerable interest to researchers [1-4]. According to literature data, quaternary compounds AB_2X_3Y (where *A* = Cu, Ag; *B* = In; *X* = S, Se, Te; *Y* = Cl, Br, I) are formed in the quasibinary systems Cu(Ag)Cl(Br,I) – $In_2S(Se,Te)_3$, and their thermodynamic properties were investigated by Moroz *et al.* [3]. In [4] we investigated quaternary compounds, in which Ga atoms replace In atoms, namely $CuGa_2S(Se)_3I$. The analysis of the *hkl* indexes of the reflections indicated space group *I*-4 and structure type $CuIn_2Te_3Cl$ [2,4] and the structures were refined from X-ray powder diffraction data. Other investigations of Ga-containing compounds were not found in the literature. All these results drew our attention to the $AgGa_2X_3Cl$ compounds where *X* = Se, Te.

2. Experimental details

Samples of stoichiometric compositions weighing 1 g were prepared by fusing Ga, Se, and Te with purities not less than 99.99 wt.% The elements and freshly prepared AgCl were melted in quartz ampoules evacuated to a residual pressure of 0.1 Pa and sealed in a vertical furnace with a system to control the temperature. The maximum temperature was 1120 K, exposure 24 h, cooling to 670 K with a rate of 20 K/h, exposure 300 h, quenching of the samples in 20 % aqueous NaCl solution.

The obtained samples were investigated by X-ray diffraction. The crystal structures of the quaternary compounds were refined by the powder method. The experimental intensities were obtained using a diffractometer DRON-4-13 (Cu *K*α-radiation, range $10° \le 2\theta \le 100°$, scan step 0.05°, exposition time 20 s). Refinement of the crystal structures was performed using WinCSD [5] software.

3. Results and discussion

The results of the investigations of the crystal structures are shown in Tables 1-3 and on Figs. 1,2.

The refined positional coordinates and isotropic displacement parameters of the atoms in the structures of the quaternary compounds $AgGa_2Se_3Cl$ and $AgGa_2Te_3Cl$ are given in Table 2. Both of the investigated compounds crystallize with the structure type $CuIn_2Te_3Cl$. The occupation factors were fixed at values similar to those found for the corresponding sites in $CuIn_2Te_3Cl$ [4].

Table 1 Crystallographic characteristics and details of the refinement of the structures of $AgGa_2Se_3Cl$ and $AgGa_2Te_3Cl$.

Empirical formula	$AgGa_2Se_3Cl$	$AgGa_2Te_3Cl$
Space group	*I*-4	*I*-4
Z	2	2
Unit-cell parameters, nm	*a* = 0.59789(3), *c*=1.08592(7)	*a* = 0.63044(4), *c*=1.19562(8)
V, nm^3	0.38818(6)	0.47521(9)
Number of atoms in the unit cell	14	14
Calculated density, g/cm^3	4.4454(6)	4.6510(8)
Absorption coefficient, 1/cm	499.53	1011.11
Radiation type, wavelength, nm	Cu *K*α, 0.154185	Cu *K*α, 0.154185
Diffractometer	DRON 4-13	DRON 4-13
Method of calculation	Full profile	Full profile
Number of free parameters	10	10
R_I, R_p	0.0932, 0.2028	0.1024, 0.3149
Scale factor	1.170(8)	1.19(4)
Texture axis and parameter	[1 0 0], 0.4154	[1 0 0], 1.7(2)

Table 2 Atomic coordinates and isotropic displacement parameters for the $AgGa_2Se_3Cl$ and $AgGa_2Te_3Cl$ compounds.

$AgGa_2Se_3Cl$						
Atom	Wyckoff position	*x/a*	*y/b*	*z/c*	Occupation	$B_{iso}\times10^2$, nm^2
Ga1	2*a*	0	0	0	0.8	0.4(4)
Ga2	2*c*	0	½	¼	0.8	1.1(5)
*M*1	2*b*	0	0	½	0.5 Ag + 0.2 Ga	1.7(8)
*M*2	2*d*	0	½	¾	0.5 Ag + 0.2 Ga	0.4(4)
X	8*g*	0.2161(15)	0.270(3)	0.1236(10)	0.75 Se + 0.25 Cl	2.4(2)
$AgGa_2Te_3Cl$						
Atom	Wyckoff position	*x/a*	*y/b*	*z/c*	Occupation	$B_{iso}\times10^2$, nm^2
Ga1	2*a*	0	0	0	0.8	0.94(6)
Ga2	2*c*	0	½	¼	0.8	0.90(6)
*M*1	2*b*	0	0	½	0.5 Ag + 0.2 Ga	0.84(6)
*M*2	2*d*	0	½	¾	0.5 Ag + 0.2 Ga	0.75(6)
X	8*g*	0.232(2)	0.259(5)	0.1307(4)	0.75 Te + 0.25 Cl	1.32(5)

Table 3 Interatomic distances and coordination numbers (CN) of the Ag and Ga atoms in the structures of the $AgGa_2Se_3Cl$ and $AgGa_2Te_3Cl$ compounds

$AgGa_2Se_3Cl$		
Atoms	Interatomic distances, nm	CN
Ga1 – 4*X*	0.24652	4
Ga2 – 4*X*	0.23334	4
*M*1 – 4*X*	0.25639	4
*M*2 – 4*X*	0.27150	4
$AgGa_2Te_3Cl$		
Atoms	Interatomic distances, nm	CN
Ga1 – 4*X*	0.26921	4
Ga2 – 4*X*	0.25460	4
*M*1 – 4*X*	0.27577	4
*M*2 – 4*X*	0.27487	4

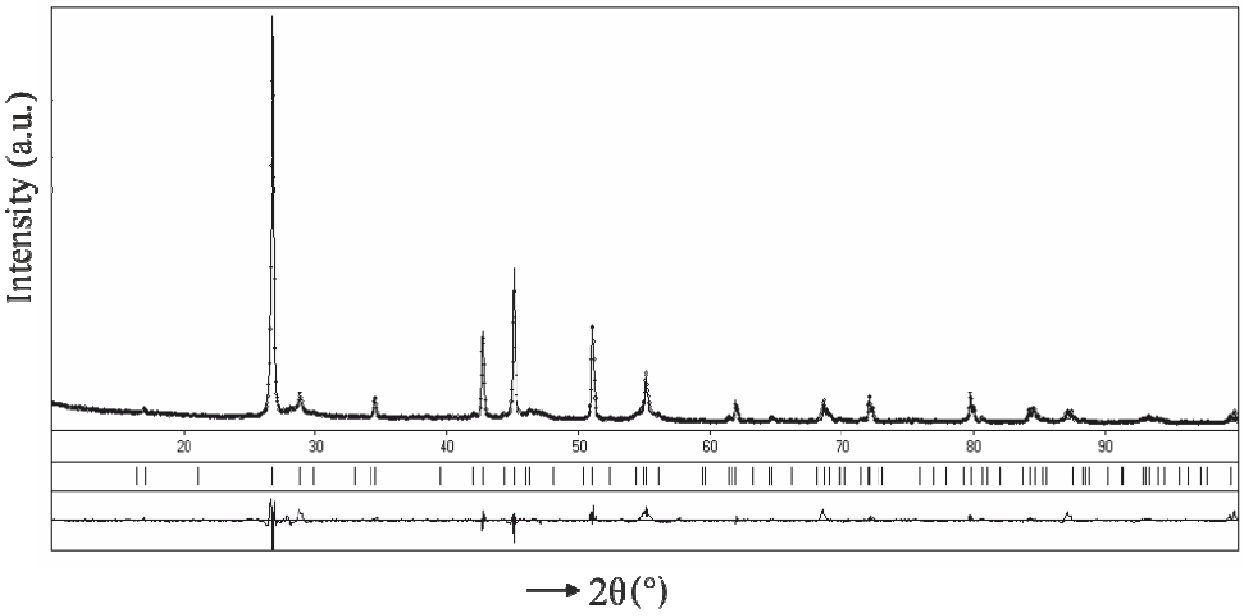

Fig. 1 Experimental (points), calculated (solid) and difference (bottom) profiles of the $AgGa_2Se_3Cl$ compound, Cu *K*α radiation.

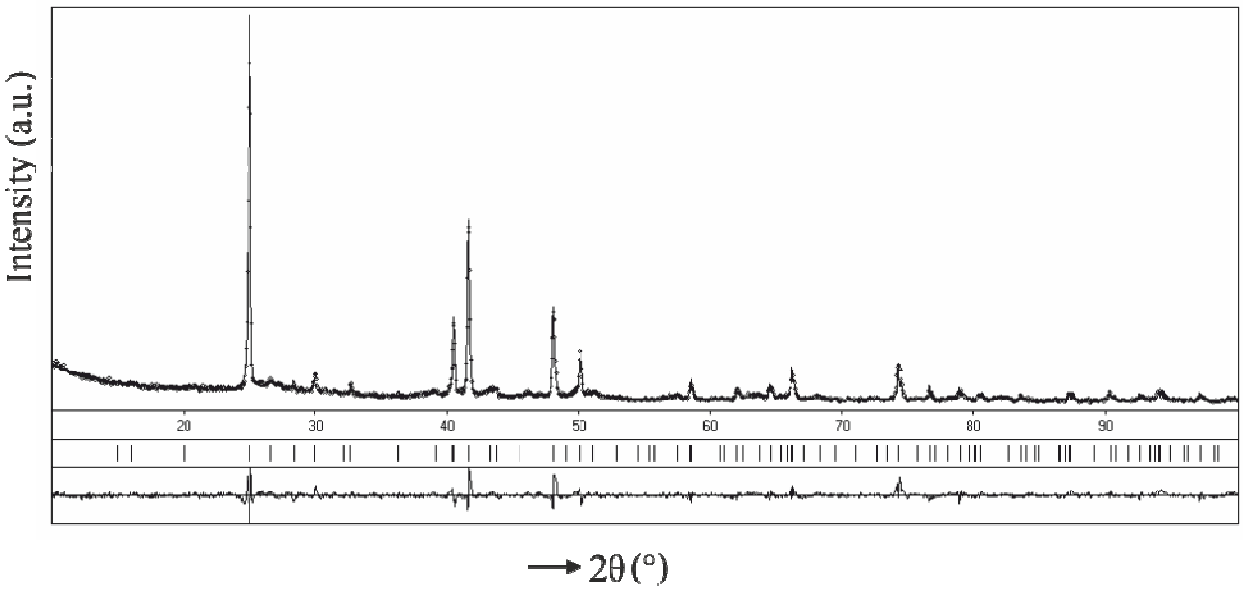

Fig. 2 Experimental (points), calculated (solid) and difference (bottom) profiles of the $AgGa_2Te_3Cl$ compound, Cu *K*α radiation.

In the structures of $AgGa_2Se_3Cl$ and $AgGa_2Te_3Cl$ (Fig. 3) the Ga atoms occupy Wyckoff positions 2*a* and 2*c* and have tetrahedral surroundings, where the anions *X* are 75 % Se(Te), 25 % Cl. By analogy with our refinement of $CuIn_2Te_3Cl$, the sites Ga1 (2*a*) and Ga2 (2*c*) are assumed to be filled to 80 %. Statistic mixtures *M*1 and *M*2 occupy two Wyckoff positions (2*b* and 2*d*) and are surrounded by the tetrahedra [$M_1$4*X*] and [$M_2$4*X*]. The statistic mixtures have the composition: 50 % Ag and 20 % Ga with 30 % not filled positions. The interatomic distances are in good agreement with the sizes of the ions [6].

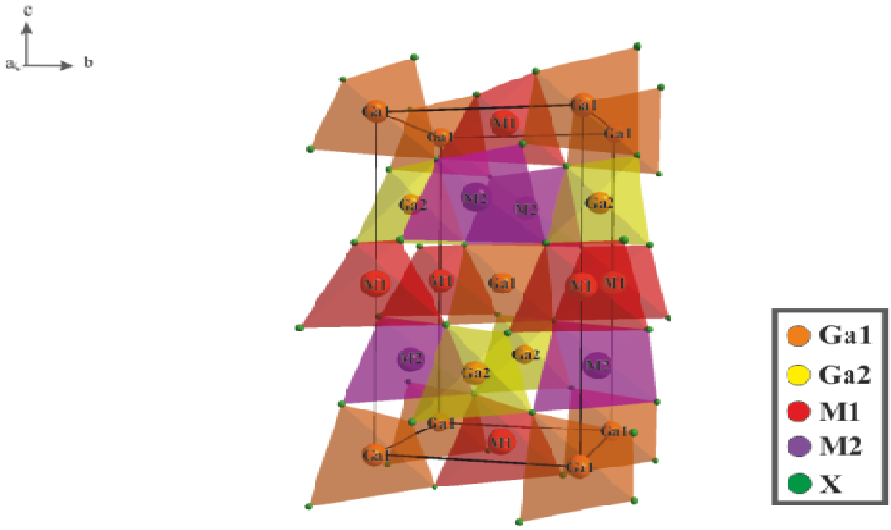

Fig. 3. Unit cell and coordination polyhedra of the Ag and Ga atoms in the crystal structures of the compounds $AgGa_2Se(Te)_3Cl$.

Conclusions

The crystal structures of the quaternary compounds $AgGa_2Se_3Cl$ (a = 0.59789(3) nm, c = 1.08592(7) nm), $AgGa_2Te_3Cl$ (a = 0.63044(4) nm, c = 1.19562(8) nm) have been investigated by X-ray powder diffraction. The structures were refined in space group I-4 (structure type $CuIn_2Te_3Cl$).

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