Journal of Alloys and Compounds 503 (2010) 40–43

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Crystal structure of the phases $Hg_5C^{III}{}_2X_8$ ($C^{III} = Ga, In; X = Se, Te$)

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ARTICLE INFO

Article history:
Received 22 February 2010
Received in revised form 29 April 2010
Accepted 30 April 2010
Available online 10 May 2010

Keywords:
Crystal structure
Chemical synthesis
X-ray diffraction

ABSTRACT

Crystal structure of the chalcogenide compounds $Hg_5Ga_2Se_8$, $Hg_5In_2Se_8$, $Hg_5Ga_2Te_8$ and $Hg_5In_2Te_8$ was investigated by X-ray structural analysis (powder method) of alloys annealed at 500 K. These phases crystallize in space group $F\bar{4}3m$ with unit cell parameters $a \approx 2a$ ($Hg^{II}X$) – 11.6876(2) Å ($Hg_5Ga_2Se_8$), 11.8876(2) Å ($Hg_5In_2Se_8$), 12.4738(2) Å ($Hg_5Ga_2Te_8$) and 12.6723(2) Å ($Hg_5In_2Te_8$).

1. Introduction

The phases of the composition $B^{II}{}_5C^{III}{}_2X_8$ form at the sections $B^{II}X–C^{III}{}_2X_3$ and belong to cation-deficient compounds that contain one cation vacancy per eight anion atoms in the crystal lattice ($B^{II}{}_5–C^{III}{}_2X_8$). This class of compounds was currently discovered in the investigation of a series of sections ZnS–In_2S_3 [1], ZnSe–In_2Se_3 [2], CdS–Ga_2S_3 [3], CdS–In_2S_3 [4], HgSe–Ga_2Se_3 [5], HgSe–In_2Se_3 [6], HgTe–Ga_2Te_3 [7], HgTe–In_2Te_3 [8]. The majority of such compounds ($Zn_5In_2S_8$, $Zn_5In_2Se_8$, $Cd_5Ga_2S_8$ and $Cd_5In_2S_8$) exist in a limited temperature range, and their existence can only be established by DTA investigation of the phase diagrams of the sections $B^{II}X–C^{III}{}_2X_3$. At low temperatures, these phases decompose. No information on the crystal structure of such compounds was found.

The compounds $Hg_5Ga_2Se_8$, $Hg_5In_2Se_8$ and $Hg_5In_2Te_8$ form by the ordering of the solid solution range of the respective binary chalcogenide $Hg^{II}X$ (space group $F\bar{4}3m$). $Hg_5Ga_2Te_8$ forms in a peritectic reaction. The phases can be obtained by annealing and quenching from an appropriate temperature.

2. Experimental procedure

The batches were composed of high-purity (better than 99.99 wt%) In, Ga, S, Se, Te and previously synthesized HgS (HgSe, HgTe). The compounds were synthesized by the single-temperature method in evacuated quartz containers in a shaft-type furnace. The maximum heating temperature was 1273 K, with 6 h exposure. The alloys were annealed at 500 K for 500 h followed by quenching into cold water. XRD reflection spectra were recorded by DRON 4-13 diffractometer with CuKα radiation ($10 \leq 2\theta \leq 100^\circ$, with a step size of 0.02° and counting time of 20 s). The computation of the diffraction patterns was performed using WINCSD software package [9].

3. Results and discussion

The crystal structure of the $Hg_5C^{III}{}_2X_8$ phases was investigated using the powder method. The structure was refined by the Rietveld method of the approximation of the experimental data to the theoretical model.

XRD investigation of the sulfide samples showed that the alloys are two-phase. The $Hg_5Ga_2S_8$ sample contained low-temperature modification of HgS and $HgGa_2S_4$ with the thiogallate structure ($I\bar{4}$), and the $Hg_5In_2S_8$ sample was composed of the phases HgS and $HgIn_2S_4$ with the thiospinel structure ($Fd\bar{3}m$).

Selenide and telluride systems exhibited the formation of the phases $Hg_5Ga_2Se_8$, $Hg_5In_2Se_8$, $Hg_5Ga_2Te_8$ and $Hg_5In_2Te_8$. Microstructure analysis of these alloys showed that they were single-phase.

The crystal structure of these compounds was investigated by X-ray structure analysis. All four compounds $Hg_5Ga_2Se_8$, $Hg_5In_2Se_8$, $Hg_5Ga_2Te_8$ and $Hg_5In_2Te_8$ crystallize in cubic space group $F\bar{4}3m$.

Experimental and calculated diffraction patterns for $Hg_5Ga_2Se_8$, $Hg_5In_2Se_8$, $Hg_5Ga_2Te_8$ and $Hg_5In_2Te_8$ and their difference are presented in Fig. 1.

The crystal structure of the $Hg_5In_2Se_8$ compound was already refined in [6] in the assumption of the following atom positions: Se1 in the 24*g* site (x 1/4 1/4), $x = 0.0$; Hg2 in the 16*e* site ($x\,x\,x$), $x = 0.125$; 0.75 M3 in the 16*e* site, $x = 0.625$, where M3 = 0.667In + 0.333Hg; Se4 in the 4*b* site (½ ½ ½); Se5 in the 4*a* site (0 0 0), with space group no. 216 ($F\bar{4}3m$). Attempts to calculate the crystal structure of $Hg_5In_2Se_8$ in the known coordinate system [6] led to unsatisfac-

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doi:10.1016/j.jallcom.2010.04.248

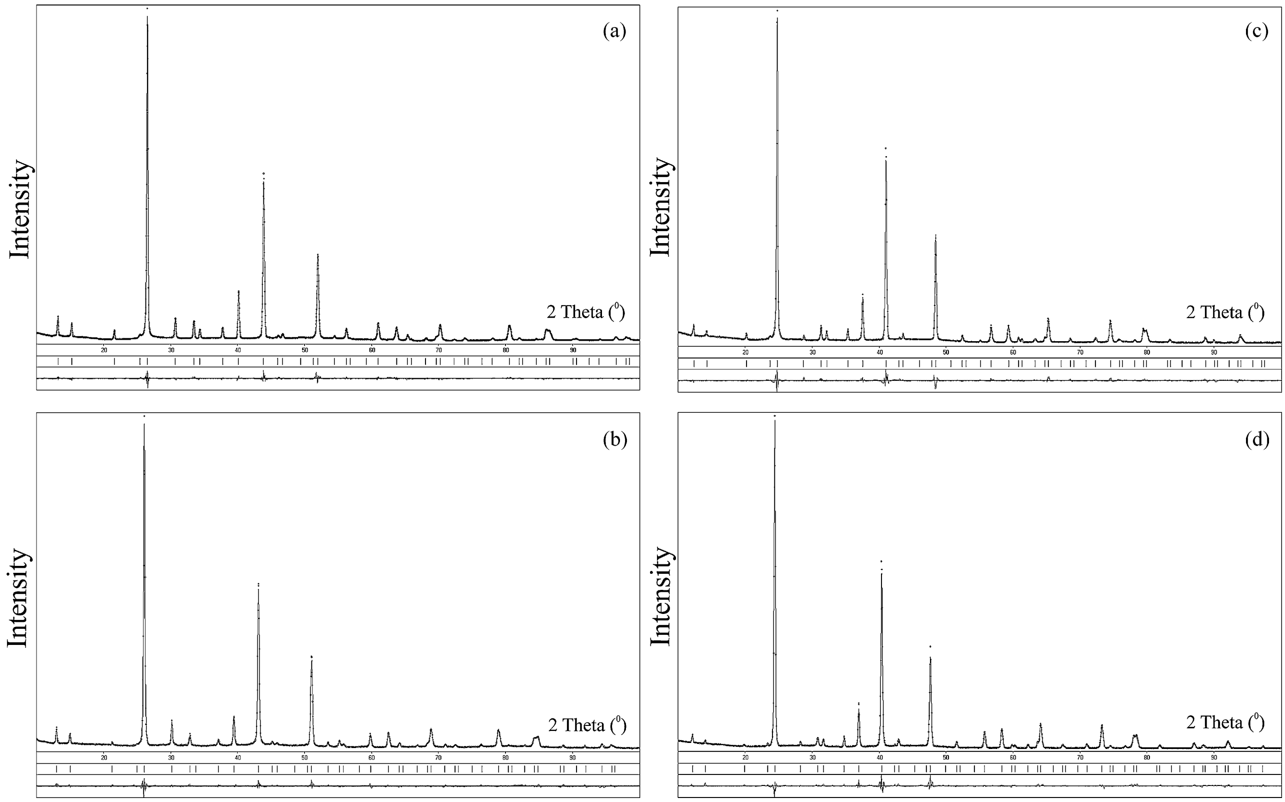


Fig. 1. Experimental and calculated diffraction patterns and their difference for $Hg_5Ga_2Se_8$ (a), $Hg_5In_2Se_8$ (b), $Hg_5Ga_2Te_8$ (c) and $Hg_5In_2Te_8$ (d).

tory fit factor values (obtained Ri/Rp parameters were 12.75/19.23), and the atom location and surrounding was rather uncommon for selenides. Additionally, the refinement of the occupation of crystallographic sites in this model gave unsatisfactory results.

The telluride systems in [7,8] were calculated in the tetragonal structure, space group $I\bar{4}2m$. We have also computed the data in space group $I\bar{4}2m$, with unsatisfactory results. The splitting of the reflections that is typical of a tetragonal structure was not observed, therefore this model was abandoned. Other papers [10,11] discuss the telluride systems in the cubic structure ($F\bar{4}3m$); these articles report also main physical properties of obtained compounds. The authors of [12] investigated $Hg_5In_2Te_8$ in the cubic structure using electron diffraction.

The crystal structure of obtained compounds was studied on the example of $Hg_5Ga_2Se_8$, and the best fit factor values and the most acceptable occupation of the crystallographic sites were produced with the following positions of atoms within the same space group no. 216 ($F\bar{4}3m$).

The atomic coordinates and inter-atomic distances in the crystal structure of $Hg_5Ga_2Se_8$ are listed in Table 1. The cations in the $Hg_5Ga_2Se_8$ crystal lattice are tetrahedrally surrounded by the selenium atoms.

These are the atom positions that follow from the genealogical relation of obtained compounds and the HgSe structure [13] which agrees well with the Barnighausen tree shown in Fig. 2.

The structure of the Cu_3AsS_4 compound (Lazarevicite) [14] can be considered as the intermediate between these two structures. Such a representation of the $Hg_5Ga_2Se_8$ structure is a result of the internal deformation of a structure obtained by doubling the parameter *a* of the Cu_3AsS_4 unit cell.

The coordination surroundings of all atoms in the structure of the $Hg_5Ga_2Se_8$ compound are variously distorted tetrahedra; their packing and inter-atomic distances are presented in Fig. 3.

Empty octahedra of Hg atoms can be marked out in the $Hg_5Ga_2Se_8$ structure; the packing of these is presented in Fig. 4. The shortest distance between the octahedra is 6.443 Å, while their height is 5.242 Å. Such a representation considers the $Hg_5Ga_2Se_8$ structure as a result of merging 4 empty (light cubes) and 4 filled (dark cubes) fragments (hypothetical $GaSe_4$ of the Fe_4C type and hypothetical Hg_6GaSe_4).

Table 2 combine the atomic coordinates and inter-atomic distances in the crystal structure of $Hg_5In_2Se_8$, $Hg_5Ga_2Te_8$ and $Hg_5In_2Te_8$.

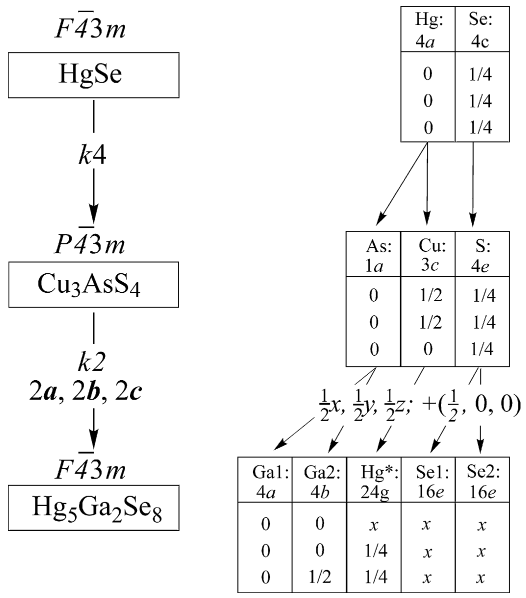


Fig. 2. Graphical representation of the group-subgroup relationships between $HgSe$–Cu_3AsS_4–$Hg_5Ga_2Se_8$. Hg* site is occupied partially.

Table 1
Crystallographic data for $Hg_5Ga_2Se_8$, $Hg_5In_2Se_8$, $Hg_5Ga_2Te_8$ and $Hg_5In_2Te_8$.

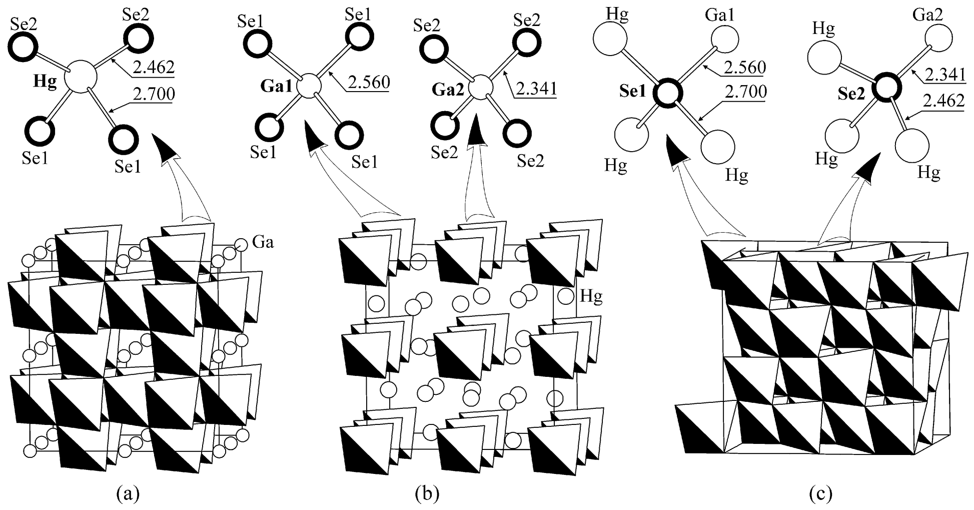
Radiation and wavelength	CuKα, λ = 1.54185 Å			
Diffractometer	Powder			
Mode of refinement	Full profile			
Space group	$F\bar{4}3m$			
Number of atoms in cell	60.0			
	Compounds			
	$Hg_5Ga_2Se_8$	$Hg_5In_2Se_8$	$Hg_5Ga_2Te_8$	$Hg_5In_2Te_8$
a (Å)	11.6876(2)	11.8876(2)	12.4738(2)	12.6723(2)
Volume (Å^3)	1596.51(4)	1679.9(1)	1940.9(1)	2035.0(1)
Calculated density (g/cm^3)	7.3806(3)	7.3917(4)	7.3047(4)	7.4069(4)
Absorption coefficient (1/cm)	1180.88	1309.95	1737.70	1840.00
2ϑ, $\sin\vartheta/\lambda$ (max)	98.57, 0.497	98.84, 0.489	98.29, 0.491	98.82, 0.493
R (intensity)	0.0406	0.0505	0.0564	0.0459
R (profile)	0.0690	0.0972	0.0921	0.0990

Table 2
Atomic parameters and distances for the $Hg_5C^{III}{}_2X_8$ compounds.

Atom	*x/a*	*y/b*	*z/c*	*N*	Occup.
Hg1	1/4	0.0247(3)[*] 0.0211(8)[**] 0.0263(1)[***] 0.0227(1)[****]	1/4	24	0.833
$C^{III}1$	0	0	0	4	1
$C^{III}2$	0	0	1/2	4	1
X1	0.8735(6)[*] 0.8657(2)[**] 0.8745(1)[***] 0.8750(1)[****]	*x*	*x*	16	1
X2	0.3843(7)[*] 0.3752(2)[**] 0.3853(1)[***] 0.3911(2)[****]	*x*	*x*	16	1

Distances for $Hg_5Ga_2Se_8$		Distances for $Hg_5In_2Se_8$		Distances for $Hg_5Ga_2Te_8$		Distances for $Hg_5In_2Te_8$	
Hg1–2Se1	2.700(7)	Hg1–2 Se1	2.682(2)	Hg1–2Te1	2.898(2)	Hg1–2Te1	2.919(2)
Hg1–2Se2	2.461(9)	Hg1–2Se2	2.439(2)	Hg1–2Te2	2.642(2)	Hg1–2Te2	2.754(2)
Ga1–4Se1	2.560(7)	In1–4Se1	2.766(2)	Ga1–4Te1	2.720(1)	In1–4Te1	2.743(1)
Ga2–4Se2	2.341(9)	In2–4Se2	2.570(2)	Ga2–4Te2	2.453(2)	In2–4Te2	2.391(2)
Se1–1Ga1	2.560(7)	Se1–1In1	2.766(2)	Te1–1Ga1	2.720(1)	Te1–1In1	2.743(1)
Se1–3Hg1	2.700(7)	Se1–3Hg1	2.682(2)	Te1–3Hg1	2.898(2)	Te1–3Hg1	2.919(2)
Se2–1Ga2	2.341(9)	Se2–1In2	2.570(2)	Te2–1Ga2	2.453(2)	Te2–1In2	2.391(2)
Se2–3Hg1	2.461(9)	Se2–3Hg1	2.439(2)	Te2–3Hg1	2.642(2)	Te2–3Hg1	2.754(2)

[*] For $Hg_5Ga_2Se_8$.
[**] For $Hg_5In_2Se_8$.
[***] For $Hg_5Ga_2Te_8$.
[****] For $Hg_5In_2Te_8$.



(a) (b) (c)

Fig. 3. Coordination surrounding of Hg (a), Se (b) and Ga (c) atoms in the $Hg_5Ga_2Se_8$ structure and inter-atomic distances.

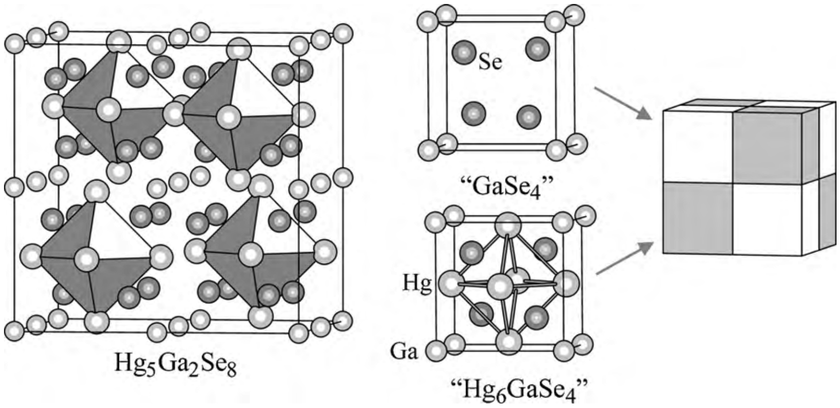


Fig. 4. Positions of octahedra of Hg atoms, and packing of empty and filled cubes in the Hg$_5$Ga$_2$Se$_8$ structure.

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