

Phase diagrams of the $\text{Cs}_3\text{Sb}_2\text{I}_9\text{-Cs}_2\text{TeI}_6$ and $\text{Rb}_3\text{Sb}_2\text{I}_9\text{-Rb}_2\text{TeI}_6$ systems

I.P. STERCHO¹, I.E. BARCHIY¹, E.YU. PERESH¹, V.I. SIDEY², T.O. MALAKHOVSKA^{2*}

¹ Department of Chemistry, Uzhhorod National University,
Pidhirna St. 46, 88000 Uzhhorod, Ukraine

² Research Institute of Physics and Chemistry of Solid State, Uzhhorod National University,
Pidhirna St. 46, 88000 Uzhhorod, Ukraine

* Corresponding author. Tel.: +380-312-237163; fax: +380-312-235091; e-mail: malakhovska@rambler.ru

Received December 02, 2013; accepted December 25, 2013; available on-line August 30, 2014

The $\text{Cs}_3\text{Sb}_2\text{I}_9\text{-Cs}_2\text{TeI}_6$ and $\text{Rb}_3\text{Sb}_2\text{I}_9\text{-Rb}_2\text{TeI}_6$ systems were investigated by DTA and X-ray diffraction, and the phase diagrams were constructed. The binary systems are of the invariant eutectic type and characterized by the formation of limited solid solutions. New complex compounds do not form.

Phase diagram / Thermal analysis / X-ray diffraction / Complex halides

Introduction

The search for new materials that are characterized by a set of interesting magnetic, luminescent, acousto-optical and other properties is an important task in modern inorganic chemistry. Complex halides attract sustained interest among inorganic materials that are promising for use in modern semiconductor devices. Investigation of the $\text{Cs}_3\text{Sb}_2\text{I}_9\text{-Cs}_2\text{TeI}_6$ and $\text{Rb}_3\text{Sb}_2\text{I}_9\text{-Rb}_2\text{TeI}_6$ systems is a necessary stage in the study of systems with cation-cationic substitution based on $A_3^I B_2^V C^{VII}_9$ and $A_2^I B^VI C^{VII}_6$ ternary compounds.

The $\text{Rb}(\text{Cs})\text{I-SbI}_3$ systems feature compounds of the $\text{Rb}_3(\text{Cs}_3)\text{Sb}_2\text{I}_9$ type, which melt congruently at 760 K and 892 K [1]. The $\text{Cs}_3\text{Sb}_2\text{I}_9$ ternary compound crystallizes with hexagonal symmetry, space group $P6_3/mmc$, lattice parameters $a = 0.835$, $c = 2.094$ nm [2], $\text{Rb}_3\text{Sb}_2\text{I}_9$ with monoclinic symmetry, s.g. Pc , lattice parameters $a = 1.448$; $b = 0.818$; $c = 2.522$ nm, $\beta = 125.4^\circ$. The $\text{Rb}(\text{Cs})\text{I-TeI}_4$ systems are also characterized by the formation of two-cation $\text{Rb}_2(\text{Cs}_2)\text{TeI}_6$ ternary compounds (which melt congruently at 757 K and 831 K respectively) [3]. The Cs_2TeI_6 ternary compound crystallizes with cubic symmetry, s.g. $Fm-3m$, lattice parameter $a = 1.170$ nm [4], Rb_2TeI_6 with tetragonal symmetry, s.g. $P4/mnc$, lattice parameters $a = 0.814$, $c = 1.181$ nm [5].

Experimental

Binary $\text{Cs}(\text{Rb})\text{I}$ compounds were prepared by reaction of the carbonate $\text{Rb}_2(\text{Cs}_2)\text{CO}_3$ with acid HI . Synthesis of the binary compounds SbI_3 and TeI_4 was carried out by the two-temperature method from stoichiometric amounts of the initial elements in evacuated two-section quartz containers; the products were purified by the zone melting method.

Using the direct single-temperature method, the $\text{Rb}_3(\text{Cs}_3)\text{Sb}_2\text{I}_9$ and $\text{Rb}_2(\text{Cs}_2)\text{TeI}_6$ ternary compounds and 22 multicomponent alloys of the $\text{Cs}_3\text{Sb}_2\text{I}_9\text{-Cs}_2\text{TeI}_6$ and $\text{Rb}_3\text{Sb}_2\text{I}_9\text{-Rb}_2\text{TeI}_6$ systems were synthesized in quartz ampoules evacuated to a residual pressure of 0.13 Pa. The highest temperature for synthesis was 1023 K. After thermal treatment at the highest temperature for 10-12 h, the samples were slowly cooled (25-30 K per hour) down to 573 K and homogenized at this temperature for 336 h. Subsequently the ampoules were quenched in cold water. The samples were heated and cooled in a furnace using an RIF-101 programmer, which provided a linear temperature variation. The phase equilibria were studied by DTA (chromel-alumel thermocouple with an accuracy of ± 5 K) and X-ray powder diffraction (DRON-3, $\text{Cu K}\alpha$ radiation, Ni filter).

Results and discussion

Based on the DTA and XRD results, the phase diagram of the $\text{Cs}_3\text{Sb}_2\text{I}_9\text{-Cs}_2\text{TeI}_6$ system was constructed. It belongs to the Rozeboom V type (Fig. 1). It contains an α -solid solution (based on $\text{Cs}_3\text{Sb}_2\text{I}_9$) and a β -solid solution (based on Cs_2TeI_6). There is a eutectic point $L_e \leftrightarrow \alpha + \beta$ in the system with the coordinates 20 mol.% Cs_2TeI_6 , 757 K. The extent of the α -solid solution range decreases from 15 mol.% $\text{Cs}_3\text{Sb}_2\text{I}_9$ at the eutectic temperature to 8 mol.% $\text{Cs}_3\text{Sb}_2\text{I}_9$ at 573 K. The extent of the β -solid solution range varies from 10 to 4 mol.% Cs_2TeI_6 with decreasing temperature.

The $\text{Rb}_3\text{Sb}_2\text{I}_9\text{-Rb}_2\text{TeI}_6$ system (Fig. 2) is also characterized by eutectic process (V type diagram by Rozeboom) with formation of a γ -solid solution (based on $\text{Rb}_3\text{Sb}_2\text{I}_9$) and a δ -solid solution (based on Rb_2TeI_6). The lines of primary crystallization intersect

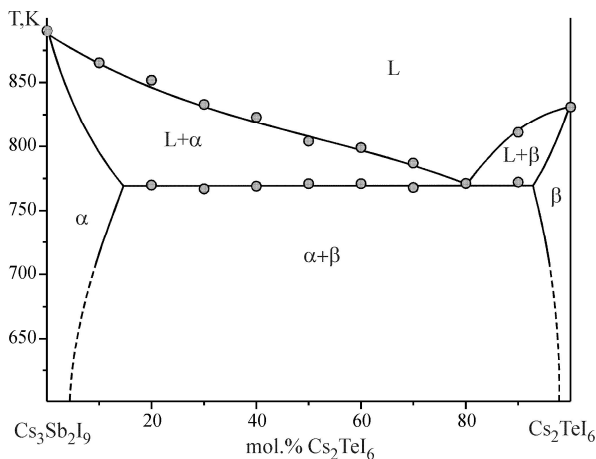


Fig. 1 Phase diagram of the $\text{Cs}_3\text{Sb}_2\text{I}_9\text{-Cs}_2\text{TeI}_6$ system.

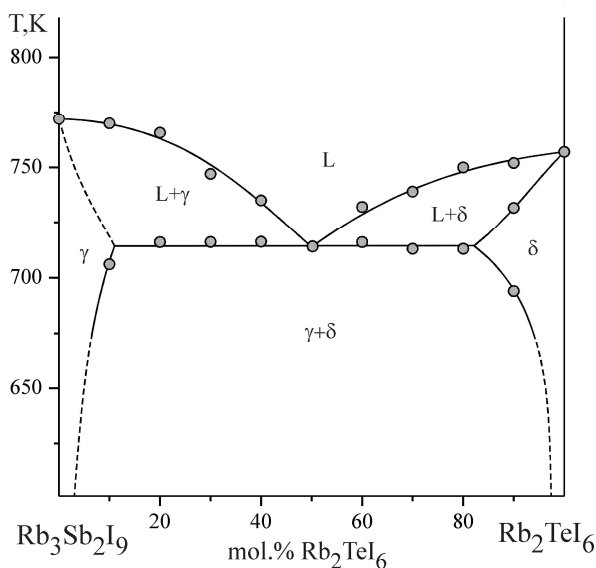


Fig. 2 Phase diagram of the $\text{Rb}_3\text{Sb}_2\text{I}_9\text{-Rb}_2\text{TeI}_6$ system.

in an invariant eutectic point ($L_e \leftrightarrow \gamma + \delta$) with coordinates: 50 mol.% Rb_2TeI_6 , 713 K. At this temperature the extent of the γ -solid solution range is 10 mol.% $\text{Rb}_3\text{Sb}_2\text{I}_9$; that of the δ -solid solution range is 18 mol.% Rb_2TeI_6 . At the homogenization temperature 573 K the solid solutions ranges do not exceed 5 mol.%.

Based on a comparison of the ionic radii, we expected that the quasibinary systems under investigation, $\text{Cs}_3\text{Sb}_2\text{I}_9\text{-Cs}_2\text{TeI}_6$ and $\text{Rb}_3\text{Sb}_2\text{I}_9\text{-Rb}_2\text{TeI}_6$, would be characterized by the formation of extended solid solutions. However, the analysis of the synthesized samples showed that two-phase samples are formed even at 10 mol.% of the other component.

Analysis of the crystal structures of the ternary compounds $\text{Rb}_2(\text{Cs}_2)\text{TeI}_6$ and $\text{Rb}_3(\text{Cs}_3)\text{Sb}_2\text{I}_9$ revealed that all these compounds are halide derivatives of the perovskite ABC_3 structure [6]. The crystal structures of perovskites and related phases considered in this paper are built up of close-packed infinite $\{AC_3\}$ layers, where A is a cation and C is an anion (Fig. 3). The $\{AC_3\}$ layers are stacked so that each A cation is closely surrounded by 12 C (*i.e.* direct contact between A cations is precluded) anions in the form of an $[AC_{12}]$ cuboctahedron or anticuboctahedron. The $[AC_{12}]$ coordination polyhedra share square faces to form an infinite three-dimensional framework (Fig. 4). The free space between the $[AC_{12}]$ polyhedra has the form of octahedral voids formed by halide ions. The number of such voids is equal to the number of A atoms. Filling all the octahedral interstices with B atoms leads to the general formula ABC_3 (usual perovskites and their polytypes); filling half or two-thirds of the interstices leads to the A_2BC_6 or $A_3B_2C_9$ stoichiometry, respectively.

Taking into account the unlimited number of possible stacking sequences (cubic and hexagonal) for the $\{AC_3\}$ layers and the diversity of filling octahedral holes with B elements, an exhaustive crystallochemical classification of the perovskite structure family is clearly impossible. Nevertheless, the experimental results show that

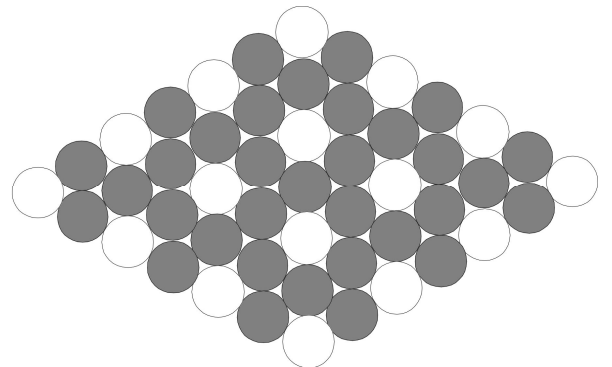


Fig. 3 Idealized representation of infinite $\{AC_3\}$ layers in A_2BC_6 and $A_3B_2C_9$ structures (A atoms are represented by open circles and C by filled circles).

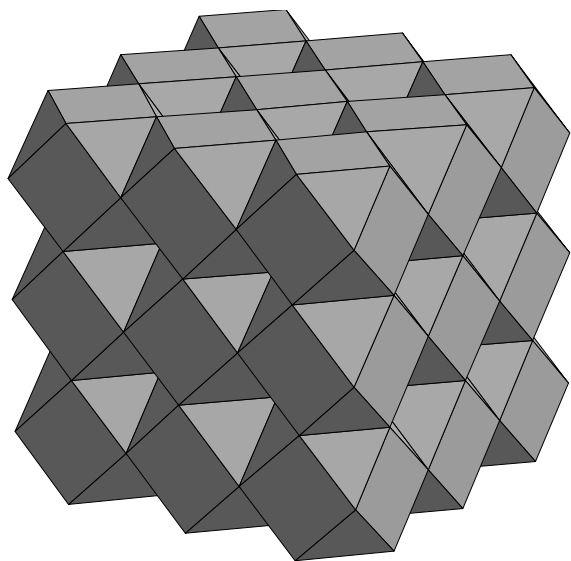


Fig. 4 $[\text{AC}_{12}]$ coordination polyhedra forming the framework of the perovskite structure.

cubic stacking (**c**) is dominant for A_2BC_6 ternary halides, while three stacking modes (**c**, **h**, **hcc**) are typical for $\text{A}_3\text{B}_2\text{C}_9$ structures [6]. The above structural peculiarities are inherent to the ternary compounds that have been investigated in our laboratory for about two decades [7-11].

Within one phase, the effective sizes of the particles (*A* and *C*) forming the close-packing in the A_2BC_6 structures can be changed in two different ways. First, on heating and/or cooling the magnitudes of thermal motion of the cations and anions may vary differently, so that the ratio of the ionic radii can be changed. Such changes of ionic radii can be seen, for example, in the structure of K_2SnCl_6 [13] which undergoes the following polymorphic transformation on heating: monoclinic phase \rightarrow tetragonal phase \rightarrow cubic phase (Fig. 5). Furthermore, partial replacement of the ions in the close-packing by their chemical

analogues can also change the average ionic radii of A^+ and C^- .

Both ternary compounds in the systems under investigation have related crystal structures belonging to the perovskite family; the difference between the ionic radii of Sb^{3+} and Te^{4+} is only 0.01 Å ($\text{Sb}^{3+} - 0.90$ Å; $\text{Te}^{4+} - 0.89$ Å). However, in the $[\text{TeI}_6]$ octahedron the ionic type of chemical bonding prevails, and, as a result, Te^{4+} is placed at the center of a regular polyhedron and all the Te-I distances are equal. In turn, in the $[\text{SbI}_6]$ polyhedron covalent bonding dominates, so that *Sb* and *I* form three shorter and three longer bonds, resulting in a distorted octahedron $[\text{SbI}_6]$. Partial substitution of *Sb* for *Te* atoms in the structure of Cs_2TeI_6 (Rb_2TeI_6) leads to substantial (inconsistent with the cubic symmetry of Cs_2TeI_6) distortion of the $[\text{BI}_6]$ coordination polyhedra; under these conditions, the formation of two different phases, cubic (Cs_2TeI_6) and trigonal/hexagonal ($\text{Cs}_3\text{Sb}_2\text{I}_9$), is probably energetically more favorable than the formation of one phase of a solid solution. Analogous substitution and phenomena apparently occur in the system $\text{Rb}_3\text{Sb}_2\text{I}_9\text{--Rb}_2\text{TeI}_6$.

Conclusions

Differential thermal, X-ray phase analysis was used to construct phase diagrams of the $\text{Cs}_3\text{Sb}_2\text{I}_9\text{--Cs}_2\text{TeI}_6$ and $\text{Rb}_3\text{Sb}_2\text{I}_9\text{--Rb}_2\text{TeI}_6$ systems for the first time. The character of the monovariant processes, and the temperatures and coordinates of the invariant processes in the quasibinary systems were determined. The existence of solid solutions of the $\text{Cs}_3(\text{Rb}_3)\text{Sb}_2\text{I}_9$, $\text{Cs}_2(\text{Rb}_2)\text{TeI}_6$ ternary phases were established. New complex compounds were not observed in the quasibinary systems. The solid solutions that form in the $\text{Cs}_3\text{Sb}_2\text{I}_9\text{--Cs}_2\text{TeI}_6$ and $\text{Rb}_3\text{Sb}_2\text{I}_9\text{--Rb}_2\text{TeI}_6$ systems may serve as new semiconductor materials with a combination of appropriate physical and optical properties.

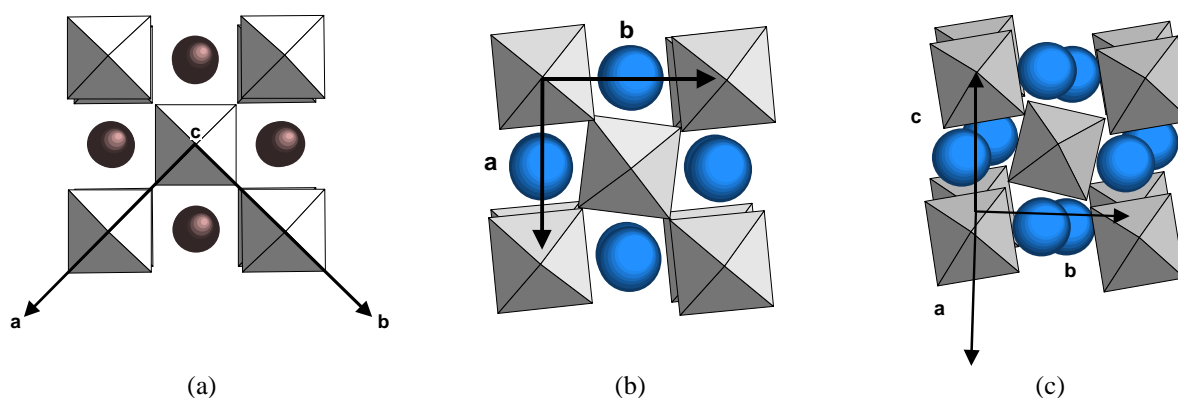


Fig. 5 Arrangement of $[\text{BC}_6]$ octahedra and *A* atoms in typical A_2BC_6 crystal structures: (a) cubic K_2PtCl_6 [12]; (b) tetragonal $\beta\text{-K}_2\text{SnCl}_6$ structure type [13]; (c) monoclinic $\alpha\text{-K}_2\text{TeBr}_6$ structure type [14,15].

References

- [1] V. Zirianov, E. Petrov, *Izv. Akad. Nauk SSSR, Ser. Khim.* 4 (1974) 109-111.
- [2] B. Chabot, E. Parthé, *Acta Crystallogr. B* 34 (1978) 645-648.
- [3] V.V. Safonov, O.V. Lemeshko, B.G. Korshunov, *Zh. Neorg. Khim.* 16 (1971) 2283-2285.
- [4] L.M. Manojlovic, *Bull. Boris Kidric Inst. Nucl. Sci.* 6 (1956) 149-152.
- [5] W. Abriel, *Mater. Res. Bull.* (1982) 1341-1346.
- [6] K.S. Aleksandrov, A.T. Anistratov, B.V. Beznosikov, N.B. Fedoseeva, *Phase Transitions in Crystals of ABX₃ Compounds*, Nauka, Novosibirsk, 1981, 266 p. (in Russian).
- [7] S.V. Kun, E.Yu. Peresh, V.B. Lazarev, A.V. Orinchay, V.I. Gorvat, *Izv. Akad. Nauk SSSR, Neorg. Mater.* 24 (1988) 1899-1903.
- [8] S.V. Kun, V.B. Lazarev, E.Yu. Peresh, A.V. Kun, Yu.V. Voroshilov, *Neorg. Mater.* 29 (1993) 410-413.
- [9] E.Yu. Peresh, V.B. Lazarev, S.V. Kun, I.E. Barchiy, A.V. Kun, V.I. Sidey, *Neorg. Mater.* 33 (1997) 431-435.
- [10] V.I. Sidey, Yu.V. Voroshilov, S.V. Kun, E.Yu. Peresh, *J. Alloys Compd.* 296 (2000) 53-58.
- [11] I.P. Stercho, V.V. Tzygyka, V.I. Sidey, E.Yu. Peresh, *Ukr. Khim. Zh.* 71 (2005) 29-33.
- [12] R.J. Williams, D.R. Dillin, W.O. Milligan, *Acta Crystallogr. B* 29 (1973) 1369-1372.
- [13] H. Boysen, A.W. Hewat, *Acta Crystallogr. B* 34 (1978) 1412-1418.
- [14] I.D. Brown, *Can. J. Chem.* 42 (1964) 2758-2767.
- [15] S.C. Abrahams, J. Ihringer, P. Marsh, *Acta Crystallogr. B* 45 (1989) 26-34.