Interaction of Components in the \( \text{Cs}_2\text{HgBr}_4 - \text{Cs}_2\text{ZnBr}_4 - \text{CsBr} \)

Ternary System

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Abstract—The interaction of components in the \( \text{Cs}_2\text{HgBr}_4 - \text{Cs}_2\text{ZnBr}_4 - \text{CsBr} \) ternary system was studied by differential thermal and X-ray powder diffraction analyses. The liquidus surface consists of the crystallization fields of three phases: \( \text{CsBr} \), a solid solution of \( \text{Cs}_2\text{HgBr}_4 \) with \( \text{Cs}_2\text{ZnBr}_4 \) (\( \alpha \)), and solid solution \( \beta \) based on \( \text{Cs}_2\text{ZnBr}_4 \). The ternary eutectic near \( \text{Cs}_2\text{HgBr}_4 \) has the coordinates \(~36.5 \text{ mol } \% \text{CsBr}, 520°C\) and \(~15 \text{ mol } \% \text{CsBr} \) and the melting point \(~415°C\). The triangulating section \( \text{Cs}_2\text{HgBr}_4 - \text{Cs}_2\text{ZnBr}_4 - \text{CsBr} \) is characterized by the eutectic interaction with the eutectic that is degenerate near \( \text{Cs}_2\text{HgBr}_4 \), contains \(~3 \text{ mol } \% \text{Cs}_2\text{ZnBr}_4 \) and melts at \( 420°C \). This section divides the \( \text{Cs}_2\text{HgBr}_4 - \text{Cs}_2\text{ZnBr}_4 - \text{Cs}_2\text{ZnBr}_5 \), \( \text{Cs}_2\text{ZnBr}_4 - \text{CsBr} \), and \( \text{Cs}_2\text{ZnBr}_5 - \text{Cs}_2\text{ZnBr}_5 \) ternary systems into two ternary systems \( \text{Cs}_2\text{HgBr}_4 - \text{Cs}_2\text{ZnBr}_4 - \text{CsBr} \) and \( \text{Cs}_2\text{HgBr}_4 - \text{Cs}_2\text{ZnBr}_5 - \text{Cs}_2\text{ZnBr}_5 \).

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Compounds of bromides of zinc, mercury, and cesium in the crystalline and glassy states transmit in the far IR (above \( 25 \mu \text{m} \)) range and have large refractive indices, which makes them promising materials for IR devices. Therefore, physicochemical investigation of interactions in bromide systems is important.

The purpose of this work was to study the interaction of components in the \( \text{Cs}_2\text{HgBr}_4 - \text{Cs}_2\text{ZnBr}_4 - \text{CsBr} \) ternary system. The binary systems bordering this ternary system were investigated previously [1–4]. The \( \text{Cs}_2\text{HgBr}_4 - \text{Cs}_2\text{ZnBr}_4 - \text{CsBr} \) binary system is eutectic, and the eutectic contains \(~39 \text{ mol } \% \text{CsBr}, 520°C\) and \(~15 \text{ mol } \% \text{CsBr} \) and the melting point \(~415°C\). The coordinates of the eutectics \( \text{Cs}_2\text{HgBr}_4 - \text{Cs}_2\text{ZnBr}_4 \) show [5] that this compound crystallizes in the tetragonal system with the space group \( \text{I}4/\text{mcm} \).

EXPERIMENTAL

The initial compounds \( \text{Cs}_2\text{HgBr}_4 \), \( \text{Cs}_2\text{ZnBr}_4 \), and \( \text{Cs}_2\text{ZnBr}_5 \) were synthesized mercury and zinc bromides, which were produced according to a published procedure [6], purified by vacuum sublimation, and dried. Chemically pure cesium bromide was purified by recrystallization. The compounds were synthesized in quartz ampoules evacuated to a residual pressure of \( 10^{-1} \text{ Pa} \) at \( 650°C \) while stirring for a day. The alloys were annealed for 3 days at \( 400°C \) for equilibration and then cooled in a switched-off furnace mode.

In the \( \text{Cs}_2\text{HgBr}_4 - \text{Cs}_2\text{ZnBr}_4 \) section, we synthesized and tested samples of the compositions 0, 5, 7.5, 10, 20, 30, 40, 45, 50, 55, 60, 70, 80, and 100 mol \% \( \text{Cs}_2\text{ZnBr}_4 \). The samples were produced on Stepanov quartz vessels evacuated to \( 10^{-1} \text{ Pa} \). The sample weight was 0.5 g.

The samples were studied by differential thermal and X-ray powder diffraction analyses. The differential thermal analysis was performed with an NTR-75 pyrometer using Pt–Pt/Rh thermocouples with calcined \( \text{Al}_2\text{O}_3 \) as a standard. The heating rate was \( 8–10 \text{ deg/min} \). The temperature was determined with an accuracy of \( ±5°C \). The X-ray powder diffraction analysis was carried out with diffractometers DRON-1.0 (\( \text{CuK}_α \) radiation, Ni filter, recording rate 1 deg/min, measurement accuracy \( ±3' \)) and Rigaku (\( \text{CuK}_α \) radiation, Ni filter, measurement accuracy \( ±1' \)).

RESULTS AND DISCUSSION

The melting points of the initial compounds \( \text{Cs}_2\text{HgBr}_4 \), \( \text{Cs}_2\text{ZnBr}_4 \), \( \text{Cs}_2\text{ZnBr}_5 \), and \( \text{CsBr} \) according to the differential thermal analysis data are \( 435, 560, 530, \) and \( 640°C \), respectively, which agrees with the published data [1–4]. The study of the state diagram of the \( \text{Cs}_2\text{HgBr}_4 - \text{Cs}_2\text{ZnBr}_4 \) binary system by differential thermal analysis showed that this system is quasi-binary and eutectic with the eutectic that is degenerate near \( \text{Cs}_2\text{HgBr}_4 \), contains \(~3 \text{ mol } \% \text{Cs}_2\text{ZnBr}_5 \) and melts at \( 420°C \). Two branches of the liquidus correspond to the crystallization of solid solutions \( \alpha \) and \( \beta \) from liquid, which are based on \( \text{Cs}_2\text{HgBr}_4 \) and \( \text{Cs}_2\text{ZnBr}_5 \), respectively (Fig. 1). The narrow region of
solid solution \(\alpha\) is within \(0–1.5\) mol \% \(Cs_3ZnBr_5\), whereas the region of solid solution \(\beta\) is wide and is within the range \(50–100\) mol \% \(Cs_3ZnBr_5\) (~55–100 mol \% \(Cs_3ZnBr_5\) at room temperature).

To confirm the construction of the melting diagram of the \(Cs_2HgBr_4–Cs_3ZnBr_5\) system, the X-ray powder diffraction analysis was performed on samples of the compositions 0, 20, 30, 40, 50, 60, 70, 80, and 100 mol \% \(Cs_3ZnBr_5\). Analysis of the diffractograms of these samples showed that the samples of the compositions 20–50 mol \% \(Cs_3ZnBr_5\) contain two phases: solid solutions \(\alpha\) based on \(Cs_2HgBr_4\) and solid solutions \(\beta\) based on \(Cs_3ZnBr_5\). This is indicated by the fact that the diffractograms exhibit lines with \(hkl\) that are characteristic of both \(Cs_2HgBr_4\) and \(Cs_3ZnBr_5\). The samples of the compositions 60–100 mol \% \(Cs_3ZnBr_5\) contain only one phase: solid solution \(\beta\) based on \(Cs_3ZnBr_5\), which confirms the construction of the state diagram of the \(Cs_2HgBr_4–Cs_3ZnBr_5\) system in Fig. 1.

The table presents the results of the X-ray powder diffraction analysis of the initial compounds \(Cs_2HgBr_4\) and \(Cs_3ZnBr_5\) and the samples of the compositions 20, 40, 60, and 80 mol \% \(Cs_3ZnBr_5\). The samples of the compositions 20 and 40 mol \% \(Cs_3ZnBr_5\) are mixtures of two phases: \(Cs_2HgBr_4\)-based solid solution \(\alpha\), which crystallizes in the rhombohedral system with the space group \(Pnma\), and \(Cs_3ZnBr_5\)-based solid solution \(\beta\), which crystallizes in the tetragonal system with the space group \(I4/mcm\). The samples of the compositions 60–100 mol \% \(Cs_3ZnBr_5\) contain only one phase: solid solution \(\beta\). Using the computer program PDIR for each of the phases of the samples of the compositions 0, 20, 30, 40, 50, 60, 70, 80, and 100 mol \% \(Cs_3ZnBr_5\) in the \(Cs_2HgBr_4–Cs_3ZnBr_5\) system, we calculated their unit cell parameters and volume. The following values were obtained: for \(Cs_2HgBr_4\): \(a = 10.2556\) Å, \(b = 7.9428\) Å, \(c = 13.8890\) Å, and \(V = 1131.4\) Å\(^3\); for \(Cs_3ZnBr_5\): \(a = b = 9.6337\) Å, \(c = 15.1450\) Å, and \(V = 1405.6\) Å\(^3\). For the samples of the compositions 20–50 mol \% \(Cs_3ZnBr_5\) (in the region of two phases, \(\alpha\) and \(\beta\)), the unit cell parameters for each phase vary insignificantly; for the samples of the compositions 60–100 mol \% \(Cs_3ZnBr_5\) (in the region of solid solution \(\beta\)), the parameters \(a = b\) remain almost unchanged and \(c\) increases linearly from 15.1450 Å for \(Cs_3ZnBr_5\) to 15.4040 Å for the sample of the composition 60 mol \% \(Cs_3ZnBr_5\).

The studied section \(Cs_2HgBr_4–Cs_3ZnBr_5\), being a triangulating section of the \(Cs_2HgBr_4–Cs_2ZnBr_4–CsBr\) ternary system (Fig. 2), divides this ternary system into two quasi-ternary systems \(Cs_2HgBr_4–Cs_3ZnBr_5–CsBr\) and \(Cs_2HgBr_4–Cs_3ZnBr_5–Cs_2ZnBr_4\). The projection of the liquidus surface of the \(Cs_2HgBr_4–Cs_2ZnBr_4–CsBr\) ternary system in Fig. 2 was constructed using the published data [1–4] and the studied section \(Cs_2HgBr_4–Cs_3ZnBr_5\). The eutectic point at \(420°C\) in the \(Cs_2HgBr_4–Cs_3ZnBr_5\) section is a transition point in the \(Cs_2HgBr_4–Cs_2ZnBr_4–CsBr\) system. The ternary eutectic in the \(Cs_2HgBr_4–Cs_2ZnBr_4–CsBr\) system is near \(Cs_2HgBr_4\) and has the coordinates ~83 mol \% \(Cs_2HgBr_4\), 2 mol \% \(Cs_2ZnBr_4\), and 15 mol \% \(CsBr\) and the melting point ~415°C. Thus, the projection of the liquidus surface of the \(Cs_2HgBr_4–Cs_2ZnBr_4–CsBr\) ternary system consists of three phase fields: \(CsBr\) and two solid solutions, one of which is based on \(Cs_2HgBr_4\) and the other is on \(Cs_3ZnBr_5\) (Fig. 2).