ISSN 0036-0236, Russian Journal of Inorganic Chemistry, 2008, Vol. 53, No. 8, pp. 1300–1302. © Pleiades Publishing, Ltd., 2008.
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Glass Formation along the $CsHgBr_3$–$CsPbBr_3$, Cs_2HgBr_4–$CsPbBr_3$, and $CsHg_2Br_5$–$CsPbBr_3$ Sections of the $HgBr_2$–$PbBr_2$–CsBr Ternary System

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Received December 12, 2007

Abstract—Glass formation is studied along the $CsHgBr_3$–$CsPbBr_3$, Cs_2HgBr_4–$CsPbBr_3$, and $CsHg_2Br_5$–$CsPbBr_3$ sections of the $HgBr_2$–$PbBr_2$–CsBr ternary system. The glass formation region is demarcated. Characteristic temperatures are determined by differential thermal analysis; the ratio T_g/T_m and the Hruby factor H_R for glassy samples are determined. The data are analyzed, and the most promising glass compositions along the specified sections are determined.

DOI: 10.1134/S0036023608080251

Halide glasses have recently received much attention on account of their potential for use in IR optics and communications. Bromide glasses, which are transparent in the far-IR range (above 20 μm), are particularly important [1–3].

This work studies glass formation along the $CsHgBr_3$–$CsPbBr_3$ (*1*), Cs_2HgBr_4-$CsPbBr_3$ (*2*), and $CsHg_2Br_5$–$CsPbBr_3$ (*3*) sections of the $HgBr_2$–$PbBr_2$–CsBr ternary system. Glass formation in this ternary system has not been mentioned in the literature. In our previous work [4], we studied glass formation in the CsBr–$HgBr_2$ and CsBr–$PbBr_2$ binary subsystems of the $HgBr_2$–$PbBr_2$–CsBr ternary system; we obtained glassy samples with compositions lying near ternary eutectic points, which signified the existence of glasses in this ternary system. Here, we study glass formation along sections *1–3* in order to determine the glass formation region in the $HgBr_2$–$PbBr_2$–CsBr system.

EXPERIMENTAL

The starting chemicals used to study glass formation along sections *1–3* were $CsHgBr_3$, Cs_2HgBr_4, $CsHg_2Br_5$ and $CsPbBr_3$ presynthesized from mercury, lead, and cesium bromides dried at 100°C. The synthesis temperature was chosen on the basis of the melting point of cesium bromide(640°C), which is the highest melting point among the constituent bromides. Synthesis lasted 1 day with melt stirring; then, samples were annealed for 3 days at ~200°C and then cooled in the switched off furnace. The melting points of $CsHgBr_3$, Cs_2HgBr_4, $CsHg_2Br_5$, and $CsPbBr_3$ as determined by differential thermal analysis (DTA) were 310, 435, 250, and 570°C, respectively. The interactions of the components along sections *1–3* in equilibrium were studied in our previous works [5, 6].

Glasses were synthesized as follows. Samples with compositions lying along sections *1–3* synthesized as above inside Stepanov tubes evacuated to 10^{-3} Pa were heated to temperatures 50–70°C higher than the melting point of the sample, exposed to this temperature for 30 min, and then quenched to ice-cold water with NaCl at about ~–10°C. Sample sizes were 1 g. Quenching rates were about 100–150 K/s. Quenching resulted in transparent or semitransparent samples, frequently yellow, and looking like glasses. Glass formation was recognized visually (by transparency, characteristic conchoidal fracture, and other indications) and by DTA (as characteristic glass transition, crystallization, and melting temperatures: T_g, T_c, and T_m, respectively). Differential thermal analysis was carried out on a pyrometer equipped with Pt–Pt/Rh thermocouples with reference to Al_2O_3; heating rates were 8–10 K/min; the temperature determination accuracy was ±5 K.

RESULTS AND DICSUSSION

Our study of glass formation in the $HgBr_2$–$PbBr_2$–CsBr system along sections *1–3* showed a feasibility of synthesizing glassy samples. The results obtained for each section are considered below.

$CsHgBr_3$–$CsPbBr_3$ section (1) was studied over the entire range of compositions. The sample compositions were as follows: 0, 2.5, 7.5, 10, 15, 20, 40, 90, 92.5, 97.5, and 100 mol % $CsPbBr_3$. All samples quenched as described above were glasses. Glass transition temperatures T_g were determined for all samples using DTA; T_c was determined only for three samples (7.5, 10, and

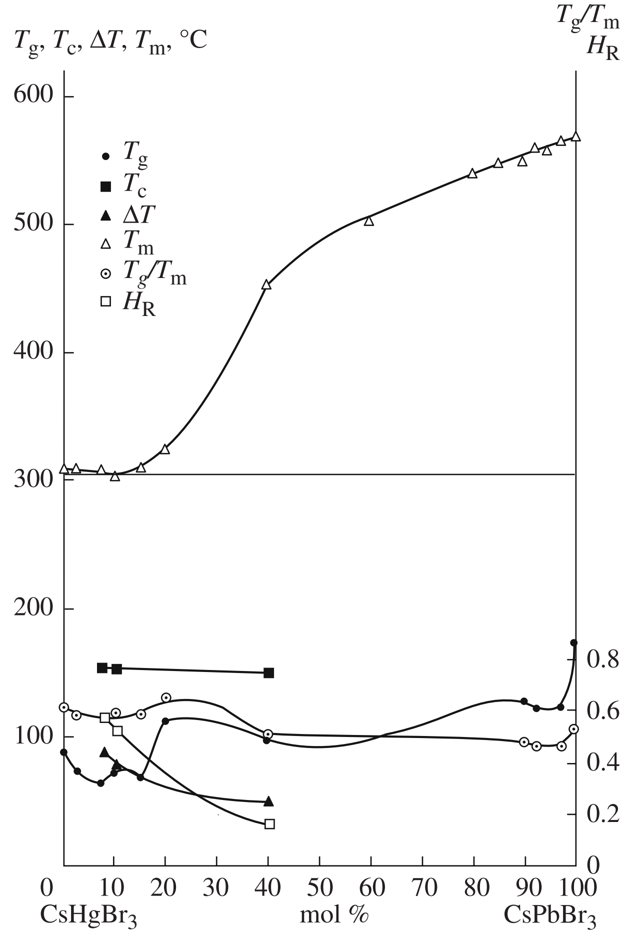

Fig. 1. T_g, T_c, ΔT, T_m, T_g/T_m, and H_R vs. $CsPbBr_3$ concentration along the $CsHgBr_3$–$CsPbBr_3$ section (*1*).

40 mol % $CsPbBr_3$). Figure 1 displays glass formation data for section *1* as T_g, T_c, ΔT, and T_m (in Celsius degrees), as well as T_g/T_m and H_R versus $CsPbBr_3$ plots, where $\Delta T = T_c - T_g$ and Hruby's factor is $H_R = (T_c - T_g)/(T_m - T_c)$. T_g is a wavy function of composition within 65–175°C (Fig. 1); T_g is maximal for 100 mol % $CsPbBr_3$. In near-eutectic compositions (near 10 mol % $CsPbBr_3$), T_g is 65–115°C. T_g determined for three samples is virtually invariable (150–155°C). The highest ΔT (90 and 80 °C) correspond to 7.5 and 10 mol % $CsPbBr_3$ samples. The ratio T_g/T_m along section *1* varies within 0.47–0.65. For 7.5–20 mol % $CsPbBr_3$ samples (near-eutectic samples), T_g/T_m varies insignificantly, within 0.58–0.65. Hruby's factor was calculated for the 7.5, 10, and 40 mol % $CsPbBr_3$ samples; its maximal values were 0.58 and 0.53 for the 7.5 and 10 mol % $CsPbBr_3$ samples and as low as 0.16 for the 40 mol % $CsPbBr_3$ sample. Thus, maximal ΔT and H_R correspond to the 7.5 and 10 mol % $CsPbBr_3$ samples. Analyzing the results obtained for section *1*, we infer that the most stable glass compositions lie near the eutectic (10 mol % $CsPbBr_3$) within ~7.5–20 mol % $CsPbBr_3$ in full agreement with the postulated maximal glass-formation ability of eutectic compositions [7, 8] (Rawson's liquidus-temperature effect).

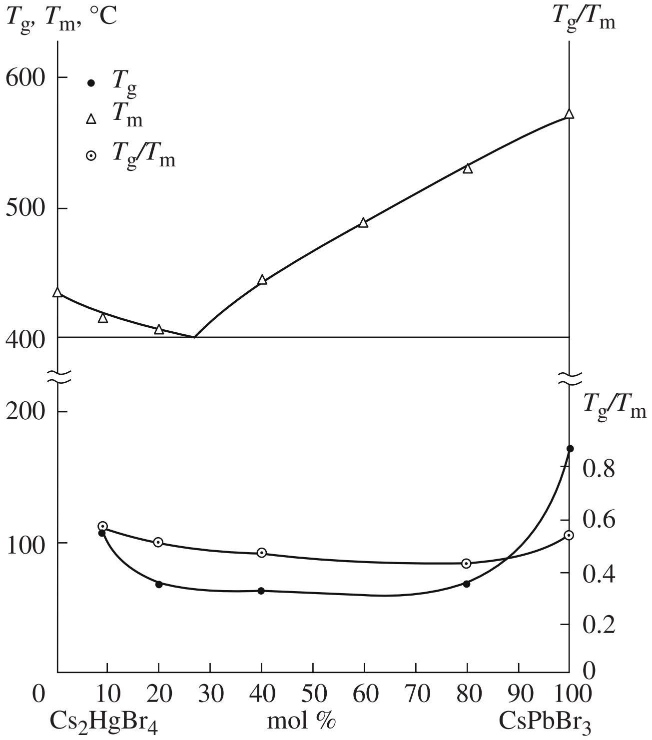

Fig. 2. T_g, T_m, and T_g/T_m vs. $CsHgBr_4$ concentration along the Cs_2HgBr_4–$CsPbBr_3$ section (*2*).

Cs_2HgBr_4–$CsPbBr_3$ section (2) was studied in 0, 8.74, 20, 40, 80, and 100 mol % $CsPbBr_3$ alloys. Glasses were obtained in alloys within 8.74–100 mol % $CsPbBr_3$. Figure 2 displays glass formation data along section *2* as T_g, T_m, and T_g/T_m versus composition plots. T_g drops from 110 to 70°C in 8.74–20 mol % $CsPbBr_3$ samples, virtually does not change up to 80 mol % $CsPbBr_3$, and abruptly increases up to 175°C in $CsPbBr_3$. This T_g trend is likely due to structural rearrangement in glass. The highest T_g/T_m are in 8.74, 20, and 100 mol % $CsPbBr_3$ samples (0.56, 0.51, and 0.54, respectively); the first two samples have low liquidus temperatures, and their compositions are near the 27 mol % $CsPbBr_3$ eutectic. The fact that T_g and T_g/T_m of at least 0.5 are preferable for glasses makes 8.74, 20, and 100 mol % $CsPbBr_3$ the most promising alloys along this section.

$CsHg_2Br_5$–$CsPbBr_3$ section (3) was studied over the entire range of concentrations in 0, 10, 15, 20, 30, 40, 50, 70, 85, and 100 mol % $CsPbBr_3$ samples. Glass formation was observed within 0–40 and 70–100 mol % $CsPbBr_3$. A 50 mol % $CsPbBr_3$ sample after melt quenching was a semitransparent material with some

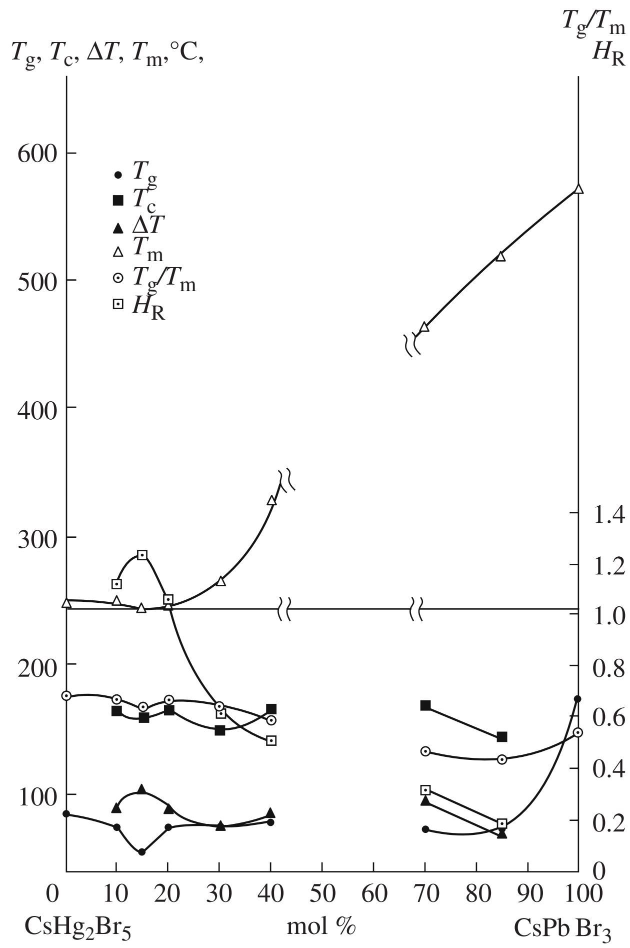

Fig. 3. T_g, T_c, ΔT, T_m, T_g/T_m, and H_R vs. $CsPbBr_3$ concentration along the $CsHg_2Br_{5p}$-$CsPbBr_3$ section (*3*).

crystals; that is, it was a glass + crystal mixture. Thermoanalytical traces did not show T_g and T_c peaks. Fi-gure 3 illustrates the results. Within 0–40 mol % $CsPbBr_3$, the eutectic sample (15 mol % $CsPbBr_3$) seems most promising: it has the maximal glass crystallization indicators ΔT and H_R (105°C and 1.24, respectively). The higher these indicators, the higher the stability of glass to crystallization [9–12]. T_g/T_m in this sample is 0.63, which roughly satisfies the two-thirds rule for glasses [7]. Within 70–100 mol % $CsPbBr_3$, a 70 mol % $CsPbBr_3$ sample has the highest T_c, ΔT, and H_R (170°C, 95°C, and 0.32, respectively); T_g/T_m changes insignificantly, from 0.47 to 0.54. Comparing H_R for 15 and 70 mol % $CsPbBr_3$ samples, we see that H_R in the former is almost four times that in the latter, signifying the higher glass formation ability and a feasibility of preparing more stable glasses.

In summary, having studied glass formation along sections *1–3* of the $HgBr_2$–$PbBr_2$–CsBr ternary system, we demarcated the glass formation region and determined the characteristic temperatures, T_g/T_m, and H_R. These results imply that the most stable glasses can be prepared in samples with the lowest liquidus temperature, that is, in samples with near-eutectic compositions, which verifies the correlation between the liquidus temperature and the glass-formation tendency in bromide systems.

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