ISSN 0036-0236, Russian Journal of Inorganic Chemistry, 2009, Vol. 54, No. 2, pp. 294–298. © Pleiades Publishing, Ltd., 2009.
Original Russian Text © I.Ya. Zaitseva, I.S. Kovaleva, V.A. Fedorov, 2009, published in Zhurnal Neorganicheskoi Khimii, 2009, Vol. 54, No. 2, pp. 338–343.

PHYSICOCHEMICAL ANALYSIS OF INORGANIC SYSTEMS

Glass Formation in the $HgBr_2$–$PbBr_2$–CsBr Ternary

I. Ya. Zaitseva, I. S. Kovaleva, and V. A. Fedorov

Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Leninskii pr. 31, Moscow, 119991 Russia

Received February 14, 2008

Abstract—Results of investigation of glass formation in the $HgBr_2$–$PbBr_2$–CsBr system are presented. The glass formation region has been outlined. Characteristic temperatures have been determined by differential thermal analysis, and the ratio T_g/T_m and factor H_R have been calculated for vitreous samples of the $HgBr_2$–$PbBr_2$–CsBr ternary.

DOI: 10.1134/S0036023609020223

Increased interest observed currently to bromide compounds in both crystalline and vitreous states is due to the possibility of their use in IR optics because of their transparency in the far-IR spectral region (above 20 μm) [1]. We choose to study the ternary system consisting of mercury, lead, and cesium bromides because cations of heavy metals shift the absorption band edge to a long-wavelength region, which is important to the use of such materials in IR engineering.

The purpose of this work was to investigate glass formation in the $HgBr_2$–$PbBr_2$–CsBr ternary system. We previously investigated interactions in binary systems bordering the $HgBr_2$–$PbBr_2$–CsBr system. In the $HgBr_2$–CsBr and $PbBr_2$–CsBr systems, compounds $CsHg_2Br_5$, $CsHgBr_3$, Cs_2HgBr_4, $CsPb_2Br_5$, $CsPbBr_3$, and Cs_4PbBr_6 are formed; two of them ($CsPb_2Br_5$ and Cs_4PbBr_6) melt incongruently. As a result of the investigation of interactions in the mentioned ternary system, we outlined the fields of primary crystallization of phases, determined the coordinates of ternary invariant points, and lined isotherms [2]. These data were used in the investigation of glass formation in the ternary system since it is known that samples with the compositions close to eutectic ones have a larger ability to glass formation. First, we investigated glass formation in binary systems bordering the $HgBr_2$–$PbBr_2$–CsBr ternary system. Upon quenching samples to an ice–water mixture at ~100–150 K/s in the CsBr–$HgBr_2$ system, we obtained glasses in the concentration range of 46–76 mol % $HgBr_2$; in the CsBr–$PbBr_2$ system, in the concentration range of 50–95 mol % $PbBr_2$; and in the $HgBr_2$–$PbBr_2$ system, no glasses were obtained. Of the six ternary compounds of the $HgBr_2$–$PbBr_2$–CsBr system, only two, namely, Cs_2HgBr_4 and Cs_4PbBr_6, were not obtained in a vitreous state. To determine glass formation in the $HgBr_2$–$PbBr_2$–CsBr ternary system, we investigated three samples with compositions close to ternary eutectics E_2, E_3, and E_4 (Fig. 1). Quenching of these samples showed that they are vitreous [3]. In [4], we presented the results of the investigation of glass formation along three joins: of the $HgBr_2$–$PbBr_2$–CsBr ternary system $CsHgBr_3$–$CsPbBr_3$ (1), Cs_2HgBr_4–$CsPbBr_3$ (2), and $CsHg_2Br_5$– $CsPbBr_3$ (3). Quenching gave glassy samples in the following ranges: along join 1, over the whole concentration range; along join 2, within 8.7–100 mol % $CsPbBr_3$; and along join 3, within 0–40 and 70–100 mol % $CsPbBr_3$. The compositions of the most stable glasses along joins 1–3 were near the eutectic compositions, which confirmed the relation of the liquidus temperature with the glass-forming tendency in systems.

To restrict the glass formation region in the $HgBr_2$–$PbBr_2$–CsBr ternary system, in this work, we additionally studied three joins, namely, the polythermal isoconcentration join with 40 mol % $HgBr_2$ (4), $HgBr_2$–$CsPbBr_3$ (5), and $CsHgBr_3$–$PbBr_2$ (6), as well as some samples of the ternary system.

EXPERIMENTAL

To investigate glass formation in the $HgBr_2$–$PbBr_2$–CsBr system, as starting substances, we used $HgBr_2$ synthesized as in [5], high-purity grade $PbBr_2$, and chemically pure grade CsBr dried at 100°C to remove trace water. The melting points of $HgBr_2$, $PbBr_2$, and CsBr determined by DTA were 245, 360, and 640°C, respectively. The $CsPbBr_3$ and $CsHgBr_3$ compounds necessary for the investigation of glass formation along joins 5 and 6 were prepared from dried mercury, lead, and cesium bromides in silica cells evacuated to a residual pressure of 10^{-3} Pa at 640°C for 1 day under stirring, annealed for 3 days at 200°C, and then cooled in the

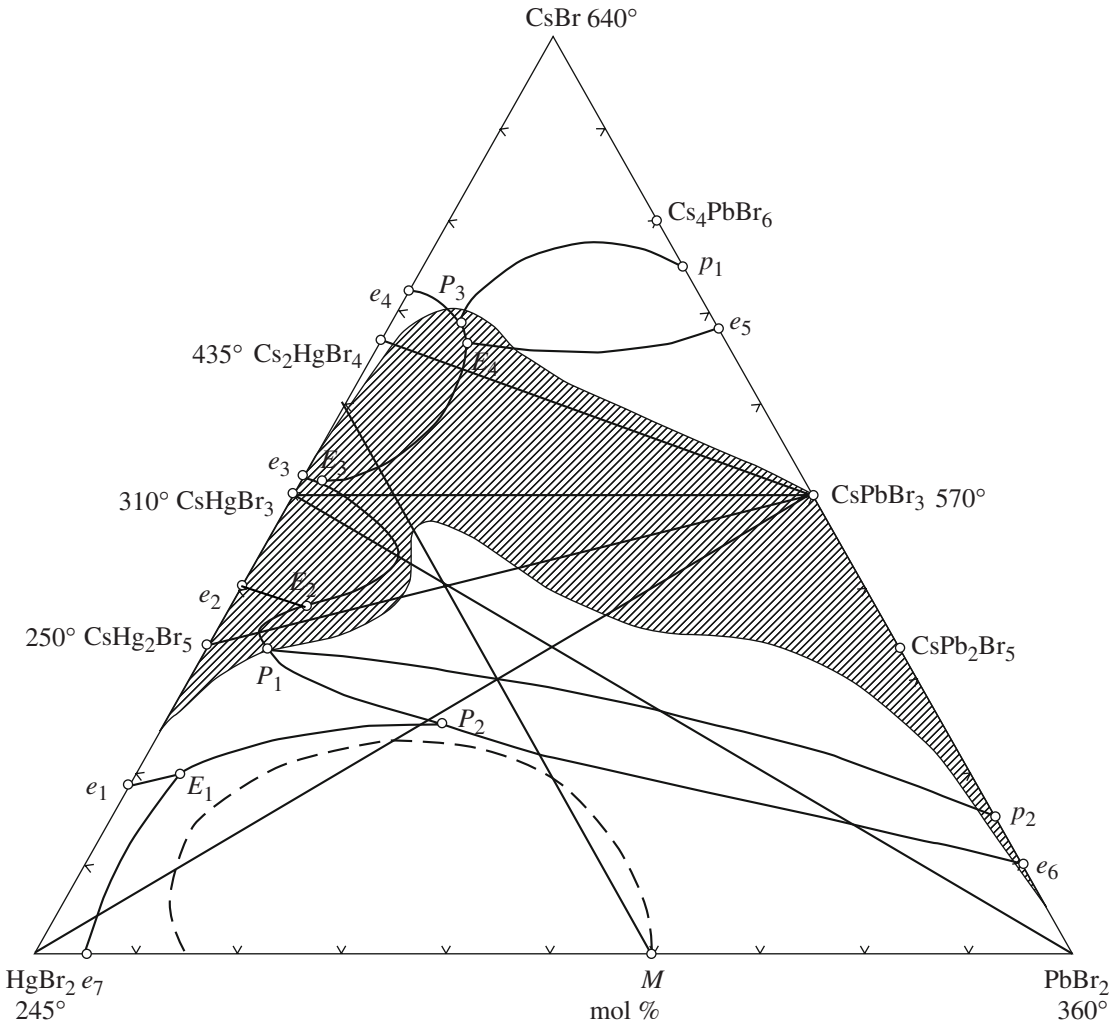

Fig. 1. Phase diagram of the $HgBr_2$–$PbBr_2$–CsBr ternary system in equilibrium and nonequilibrium states (glass-formation region is hatched).

switched off furnace. The melting points of $CsPbBr_3$ and $CsHgBr_3$ determined by DTA were 570 and 310°C, respectively. The synthesis of samples along joins 4–6 and other samples situated in different parts of the $HgBr_2$–$PbBr_2$–CsBr phase diagram, was performed in Stepanov vessels evacuated to a residual pressure of 10^{-3} Pa by the above-described procedure. The sample weight was 1 g. Glasses in the bulk were prepared via heating the synthesized samples to a temperature exceeding the melting point by 50–70°C, held at this temperature for 30 min, and quenched in iced water mixture with NaCl at about –10°C. The quenching rate was ~100–150 K/s. Quenched samples were often yellow with color intensity depending on the composition. Some samples were obtained in the vitreous state, and some in the crystalline state. Glass formation was detected both visually (as transparency and conchoidal fracture) and by DTA via determining the characteristic temperatures t_g, t_c, and t_m (°C), which are the glass-transition temperature, crystallization temperature, and melting point, respectively. DTA was performed on a pyrometer with Pt–Pt/Rh thermocouples, the reference was Al_2O_3, the heating rate was 8–10 K/min, and temperature was determined accurate to ±5°C.

RESULTS AND DISCUSSION

To determine the glass-formation regions in the $HgBr_2$–$PbBr_2$–CsBr system, we investigated three nonquasi-binary joins: polythermal isoconcentration join containing 40 mol % $HgBr_2$ (4), $HgBr_2$–$CsPbBr_3$ (5), $CsHgBr_3$–$PbBr_2$ (6), as well as some other samples with the compositions in various parts of the $HgBr_2$–$PbBr_2$–CsBr ternary phase diagram. Let us consider the results obtained along each of joins.

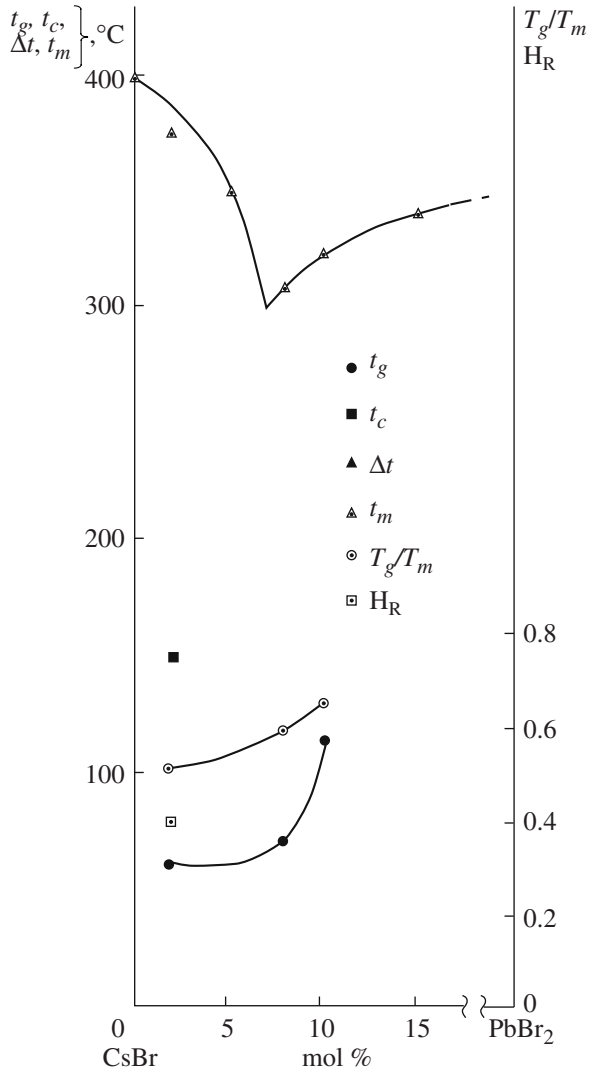

Fig. 2. t_g, t_c, Δt, t_m, T_g/T_m, and H_R vs. $PbBr_2$ percentage along the 40 mol % $HgBr_2$ join (4).

Isoconcentration join at 40 mol % $HgBr_2$ (4) was investigated over the whole concentration range. In the mentioned quenching mode, glass formation was detected in samples containing 2 to 10 mol % $PbBr_2$. Samples containing 15 and 20 mol % $PbBr_2$ were mixture of crystals and glass. The glass-forming ability of materials and stability of glasses can be characterized by variuos methods. We used the method taking into account the values of characteristic temperatures (t_g, t_c, t_m), $\Delta t = t_c - t_g$, the ratio T_g/T_m, and the Hruby factor $H_R = (t_c - t_g)/(t_m - t_c)$, and studied the appearance of samples. The results obtained for glass along join 4 are presented in Fig. 2 as the composition dependences of characteristic temperatures t_g, t_c, t_m, and Δt and the ratio T_g/T_m and H_R. t_g initially somewhat increases from 60 to 70°C with $PbBr_2$ percentage increasing from 2 to 8 mol %; for 10 mol % $PbBr_2$, t_g increases to 115°C. The ratio T_g/T_m gradually increases from 0.51 at 2 mol % $PbBr_2$ to 0.65 at 10 mol % $PbBr_2$. We succeeded to obtain the values of t_c, Δt, and H_R only for the sample with a composition of 2 mol % $PbBr_2$ (Δt = 90°C, H_R = 0.4). The values of Δt and H_R, which are considered as characteristics of devitrification, indicate that glass is moderately stable to crystallization.

Join $HgBr_2$–$CsPbBr_3$ (5) was investigated over the entire concentration range. Glasses were prepared in the range from 60 to 100 mol % $CsPbBr_3$ (Fig. 3). For the samples with 60 and 90 mol % $CsPbBr_3$, t_g is virtually constant and equals 75–80°C. A maximum value of t_g = 175°C corresponds to the $CsPbBr_3$ compound. The abrupt increase in t_g for $CsPbBr_3$ is possibly associated with the structural rearrangement of glass. The ratio T_g/T_m in the range of 60–90 mol % $CsPbBr_3$ initially decreases from 0.5 to 0.42; then, at 100 mol % $CsPbBr_3$, its value increases to 0.54. We succeeded to obtain the values of t_c, Δt, and H_R only for the sample with the composition of 60 mol % $CsPbBr_3$. Low values of Δt and H_R (45°C and 0.14) indicate that this glass in the used quenching mode is formed, but can easily crystallize.

Join $CsHgBr_3$–$PbBr_2$ (6) was also investigated over the entire concentration range. Glasses were prepared in the concentration range from 0 to 25 mol % $PbBr_2$. After quenching, the samples of compositions of 29 and 33.3 mol % $PbBr_2$ were mixtures of glass and a crystalline phase, and with more than 33.3 mol % $PbBr_2$, quenched samples were crystalline. The results obtained for glasses along join 6 are presented in Fig. 4. The value of t_g has a minimum for 5 mol % $PbBr_2$ 5 (t_g = 50°C). In the concentration range of 10–25 mol % $PbBr_2$ t_g, is almost invariable and equals 80–75°C. The drop of t_g in the range from 0 to 10 mol % $PbBr_2$ can be explained by the phase transition α-$CsHgBr_3$ $\rightleftharpoons$ β-$CsHgBr_3$. The ratio T_g/T_m varies insignificantly, in the limits of 0.57–0.67. The minimum of T_g/T_m (0.57) is also apparently associated with the phase transition in $PbBr_2$. The values of t_c, Δt, and H_R (155°C, 105°C, and 0.75) are maximal for the sample with 5 mol % $PbBr_2$. This can be explained by the fact that CsHgBr is obtained in a vitreous state upon cooling, while the addition of a small amount of $PbBr_2$ exerts the stabilizing effect on glass, which is expressed in a large value of Δt and especially H_R (0.75). As a result, two factors compete, namely, the stabilizing effect of $PbBr_2$ on $CsHgBr_3$, which enhances glass formation and facilitates the preparation of glasses more stable to crystallization, and the existance of the phase transition inhibiting the glass formation in this concentration region.

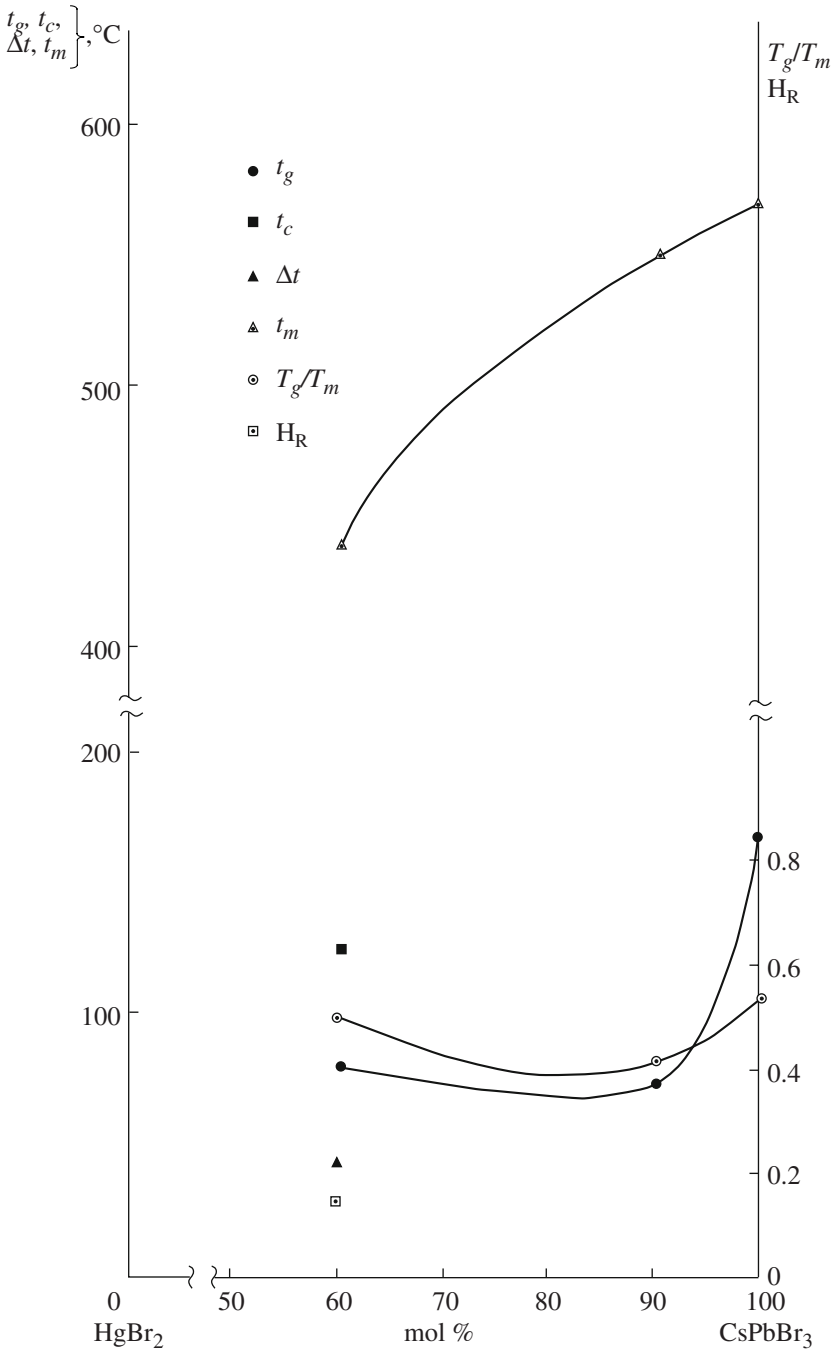

Fig. 3. t_g, t_c, Δt, t_m, T_g/T_m, and H_R $CsPbBr_3$ percentage along the $HgBr_2$–$CsPbBr_3$ join (5).

In addition to the six investigated joins of the $HgBr_2$–$PbBr_2$–CsBr ternary system, the possibility of glass formation was investigated for the samples of compositions presented in the table. However, all quenched samples, except for one, were crystals. The compositions and DTA results for quenched samples are presented in the table.

For the sample obtained in the form of glass, we determined $\Delta t = 75°C$, $T_g/T_m = 0.54$, and $H_R = 0.33$.

In Fig. 1, along with the phase diagram of the $HgBr_2$–$PbBr_2$–CsBr system in the equilibrium state (lines of univariant equilibria and invariant points), we present the generalized results of the investigation of glass formation along the joins studied in [3, 4] and in

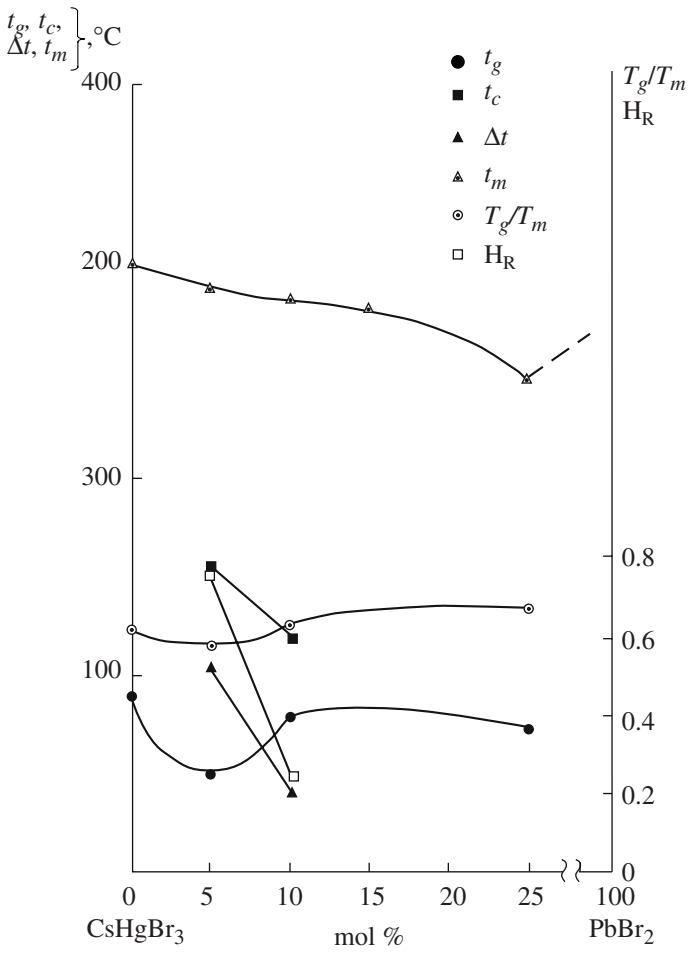

Fig. 4. t_g, t_c, Δt, t_m, T_g/T_m, and H_R vs. $PbBr_2$ percentage along the $CsHgBr_3$–$PbBr_2$ join (6).

DTA results for quenched samples of the $HgBr_2$–$PbBr_2$–CsBr ternary system

Composition, mol %			Characteristic temperatures, °C			State
$HgBr_2$	$PbBr_2$	CsBr	t_g	t_c	t_m	
27	4	69	85	160	390	Glass
17	15	68	–	–	415	Crystal
8	30	62	–	–	530	"
10	58	32	–	–	450	"
10	67	23	–	–	375	"
63	5.5	31.5	–	–	240	"
58.5	12.5	29	–	–	230	"
23	65.5	11.5	–	–	290	"

this work. The glass-formation region (hatched in Fig. 1) is considerable, is arranged along joins $CsHgBr_3$–$CsPbBr_3$ (1), Cs_2HgBr_4–$CsPbBr_3$ (2), and $CsHg_2Br_5$–$CsPbBr_3$ (3) (its boundary passes near the line of joint isolation of these phases), and includes three ternary eutectic points (E_2, E_3, and E_4). The large extent of the glass-formation region in the $HgBr_2$–$PbBr_2$–CsBr ternary system is possibly associated with a large field of primary separation of the $CsPbBr_3$ compound, which plays the role of glass former. The $CsHgBr_3$, Cs_2HgBr_4, and $CsHg_2Br_5$ compounds most probably play the role of modifiers. The presence of binary and ternary eutectics is the factor that promotes the glass formation.

As the most promising samples for preparing glasses, we can mention the samples of compositions 48.7 mol % $HgBr_2$–2.6 mol % $PbBr_2$–48.7 mol % CsBr (Δt = 105°C, T_g/T_m = 0.57, H_R = 0.75), 59.6 mol % $HgBr_2$–5.3 mol % $PbBr_2$–35.1 mol % CsBr (Δt = 105°C, T_g/T_m = 0.63, H_R = 1.24), 62.1 mol % $HgBr_2$–3.4 mol % $PbBr_2$–34.5 mol % CsBr (Δt = 90°C, T_g/T_m = 0.67, H_R = 1.125), and 51.9 mol % $HgBr_2$–11.1 mol % $PbBr_2$–37.0 mol % CsBr (Δt = 75°C, T_g/T_m = 0.64, H_R = 0.625).

Therefore, glass formation has been investigated for the $HgBr_2$–$PbBr_2$–CsBr ternary system for the first time, and the extensive glass-formation region is found. Complicating the composition via introduction of chlorides and iodides, it is possible to obtain stable glasses with high optical properties.

REFERENCES

1. K. Kadono and M. Nogami, J. Non-Cryst. Solids **95–96** Part 1, 473 (1988).
2. I. Ya. Zaitseva, I. S. Kovaleva, and V. A. Fedorov, Zh. Neorg. Khim. **52** (6), 1012 (2007) [Russ. J. Inorg. Chem. **52** (6), 940 (2007)].
3. I. Ya. Zaitseva, I. S. Kovaleva, and V. A. Fedorov, Zh. Neorg. Khim. **52** (12), 2085 (2007) [Russ. J. Inorg. Chem. **52** (12), 1968 (2007)].
4. I. Ya. Zaitseva, I. S. Kovaleva, and V. A. Fedorov, Zh. Neorg. Khim. **53** (8), 1394 (2008) [Russ. J. Inorg. Chem. **53** (8), 1300 (2008)].
5. *Handbuch der praeparativen anorganischen Chemie*, Ed. by G. Brauer (Ferdinand Enke, Stuttgart, 1975–1981; Mir, Moscow, 1985).