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Effect of addition of chloride on the crystallization behaviour of fluoride glasses in ZrF_4–BaF_2–CsF system

J. QIU
New Glass Research Center, Yamamura Glass Co. Ltd., 2-1-18, Naruohama, Nishinomiya, Hyogo 633, Japan

Fluoride glasses based on ZrF_4–BaF_2–CsF doped with $BaCl_2$ up to 10 mol % have been prepared. Crystallization behaviour of these glasses has been investigated by means of DTA and XRD. Addition of 5 mol % $BaCl_2$ into the fluoride glass of the ZrF_4–BaF_2–CsF system enhances the glass forming ability and the thermal stability against crystallization, but the glass forming ability is decreased for glass containing 10 mol % of $BaCl_2$. The results have been discussed from the view point of thermodynamics and the dynamics of glass formation.

1. Introduction

Heavy metal fluoride glasses based on ZrF_4–BaF_2 were first synthesized around 1974 by Poulain *et al.* [1]. Since then, fluoride glasses have been studied extensively. Most effort [2–4] has been made to minimize losses associated with scattering of light from crystallites, in attempting to obtain a minimal attenuation of 10^{-2}dB km^{-1} at 2.5 μm predicted in the ZrF_4–BaF_2–LaF_3–AlF_3–NaF (ZBLAN) system. Recently, Carter *et al.* [5] have achieved 0.65 dB km^{-1} at 2.5 μm with the ZBLAN composition. This is similar to the present minimum loss of silica fibre. Extrinsic defects of ZBLAN glasses are depressed to near their limits, and intrinsic loss may become the barrier for future applications. Therefore, it is important to develop new kinds of stable glasses having more desirable characteristics and lower intrinsic defects. The results reported by Jordan *et al.* [6] showed that the substitution of CsF for NaF in ZrF_4–BaF_2 based glasses could extend the infrared (i.r.) transmission region and consequently lower the minimum intrinsic loss. On the other hand, it was shown that the introduction of a small amount of chlorides into fluoride glasses in ZBLAN [7, 8] or the AlF_3–ZrF_4 system [9] resulted in an increase of the refractive index and enhancement of the thermal stability against crystallization, as well as a shift of the i.r. multiphonon absorption edge toward lower energy. The intrinsic loss in the near i.r. region was thus considered to be reduced. To clarify the possible potential of Cl-doped fluoride glasses in the ZrF_4–BaF_2–CsF system, it is necessary to understand their crystallization behaviour. However, there has been little systematic study on the crystallization behaviour of Cl-doped fluoride glasses to the author's knowledge. This investigation is focused on understanding the influence of introduced chloride on the crystallization behaviour of ZrF_4–BaF_2–CsF based glasses.

2. Experimental details

Compositions with a formula $x BaCl_2 \cdot (28 - x) BaF_2 \cdot 2InF_3 \cdot 2LaF_3 \cdot 10CsF \cdot 58ZrF_4$ were chosen in which 5 and 10 mol % of BaF_2 is replaced by $BaCl_2$, respectively. High purity fluorides and chloride were used as starting materials. 10 g batches were fully mixed and then melted in a covered Pt crucible under a dry Ar atmosphere at 950 °C for about 30 min. The melt was quenched between two preheated brass plates, and a transparent glass specimen with a thickness of 2 mm was obtained. Glass formation was also confirmed by X-ray diffraction. Differential thermal analysis (DTA) measurements were carried out under Ar or N_2 atmosphere. In the heating mode, a heating rate of 10 °C min^{-1} was used. In the cooling mode, 50 mg of the glass specimen was heated rapidly to 600 °C and held at this temperature for 5 min, then the glass melt was cooled to room temperature at various cooling rates.

3. Results and discussion

Fig. 1 shows the DTA curves of glasses in the heating mode. The glass transition temperature, T_g, decreases with the substitution of $BaCl_2$. Compared with the glass without $BaCl_2$, the top temperature of the exothermal peak, T_c, which originates from the occurrence of crystallites, exhibits little change for the glass containing 5 mol % $BaCl_2$, but it shifted slightly to a lower temperature in glass containing 10 mol % $BaCl_2$. The gap between onset temperature, T_x, of crystallization and glass transition temperature reflects the stability of the glass against crystallization. The gaps $T_x - T_g$ are 66, 81 and 86 °C for glasses without $BaCl_2$, containing 5 and 10 mol % of $BaCl_2$, respectively. Thus, at least the introduction of $BaCl_2$ can be inferred to increase the thermal stability when the concentration of $BaCl_2$ is smaller than 10 mol %.

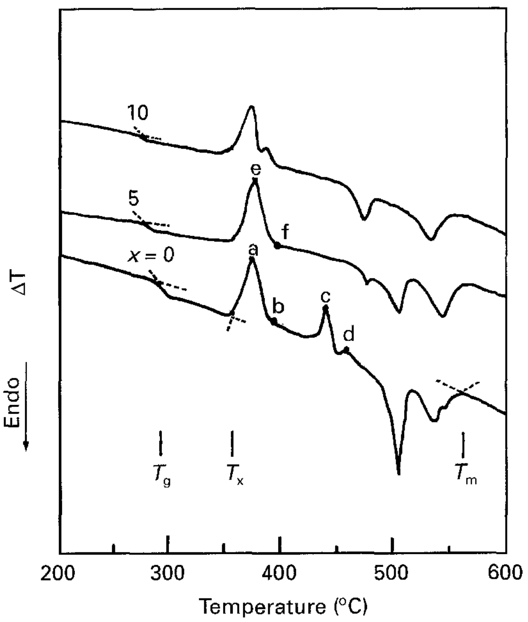

Figure 1 DTA curves of $x\mathrm{BaCl_2}\cdot(28-x)\mathrm{BaF_2}\cdot 2\mathrm{InF_3}\cdot 2\mathrm{LaF_3}\cdot 10\mathrm{CsF}\cdot 58\mathrm{ZrF_4}$ glasses.

Fig. 2 shows the X-ray diffraction patterns of the glass sample without $BaCl_2$ quenched from temperatures at points a, b, c and d as illustrated in Fig. 1 during the DTA measuring process. The results from glass containing 5 mol % $BaCl_2$ are shown in Fig. 3. Although the possible crystal phases cannot yet be identified, it is clear that a phase, denoted by α, did not appear in the glass sample containing 5 mol % $BaCl_2$, while both α and other phases occurred in the glass sample without $BaCl_2$ during the heating process. In Fig. 2, it can be inferred that the α-phase formed transforms to other ones during the heating process. In glass containing 5 mol % $BaCl_2$, these crystallites were avoided or restrained.

Fig. 4 shows the DTA curves of glass melts in the cooling mode, which were cooled from 600 °C at a cooling rate of 50 °C min^{-1}. All DTA curves exhibit complicated features and there are two or three exothermal peaks in each DTA curve. The onset temperature, T_x^*, of crystallization shifted to a lower temperature in the glass containing 5 mol % $BaCl_2$, but it shifted to a higher temperature for the glass containing 10 mol % $BaCl_2$. The dependence of the top temperature, T_c^*, and onset temperature, T_x^*, of the first peak due to the occurrence of crystallization at various cooling rates are plotted as a function of $BaCl_2$ concentration in Figs 5 and 6, respectively. Glass containing 5 mol % $BaCl_2$ exhibits the lowest crystallization temperature, at cooling rates ranging from 25 to 200 °C min^{-1}.

The critical cooling rate can be obtained from Equation 1:

$$\ln R = \ln R_c - b/(\delta T_x^*)^2 \qquad (1)$$

where R (°C min^{-1}) is the cooling rate, b is a constant and δT_x is the difference between the liquid temperature T_l and the crystallization temperature T_x^* upon cooling. The plots of $\ln R$ versus $10^4/(\delta T_x^*)^2$ for these glasses are shown in Fig. 7. The critical cooling rates R_c thus obtained are 500, 324, and 665 °C min^{-1} for glasses without $BaCl_2$, containing 5 and 10 mol % of $BaCl_2$, respectively. Therefore, among the three compositions, the composition containing 5 mol % $BaCl_2$ exhibits the most favourable glass forming ability.

The effect of the addition of chloride to glasses of the ZBLAN system on the thermal stability of these

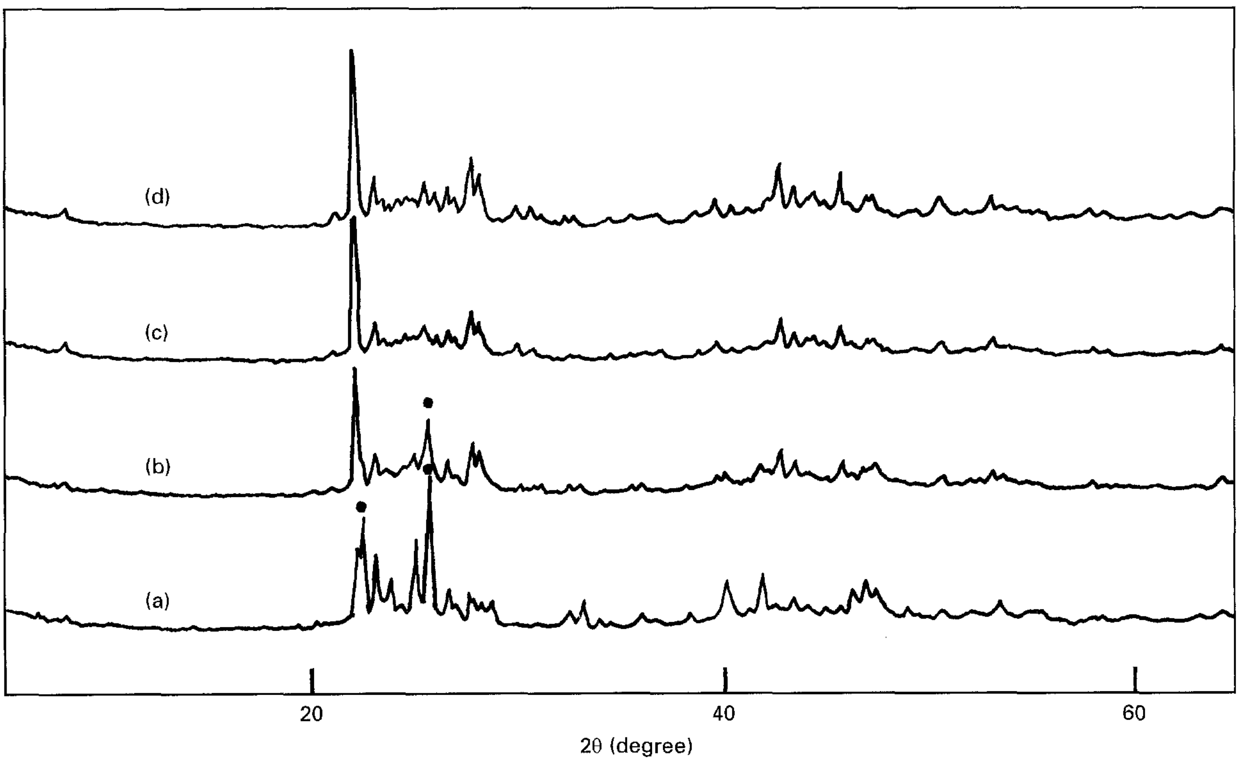

Figure 2 X-ray diffraction patterns of glass without $BaCl_2$ quenched from temperatures at points a, b, c and d as illustrated in figure 1, during the DTA measuring process. ● represents the α-phase.

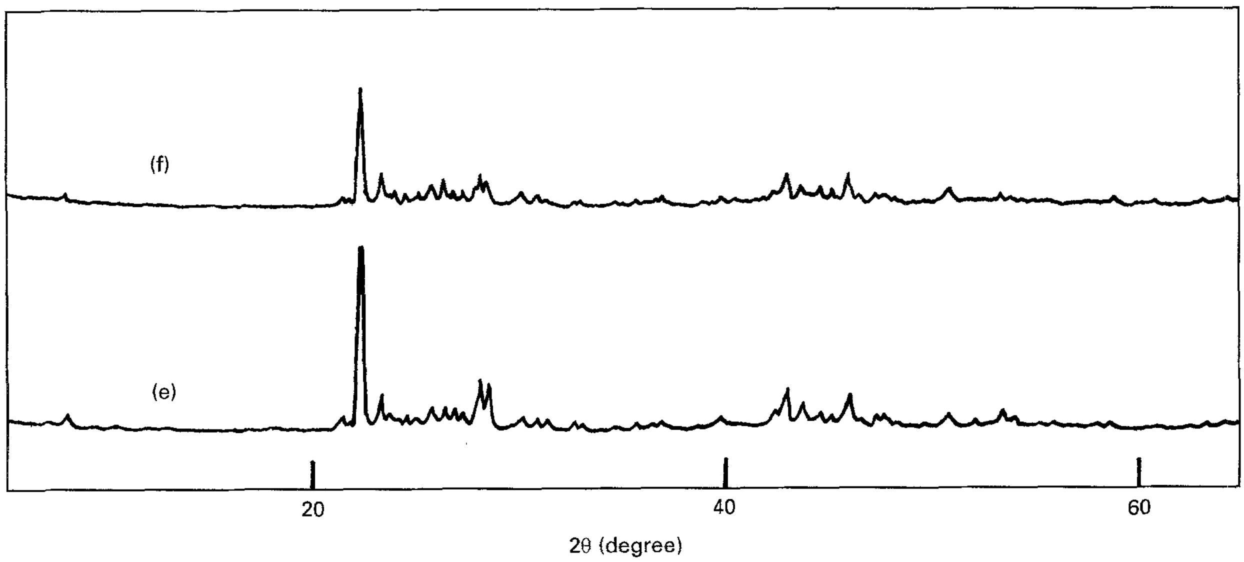

Figure 3 X-ray diffraction patterns of glass containing 5 mol % $BaCl_2$ quenched from temperatures at points e and f as illustrated in figure 2, during the DTA measuring process.

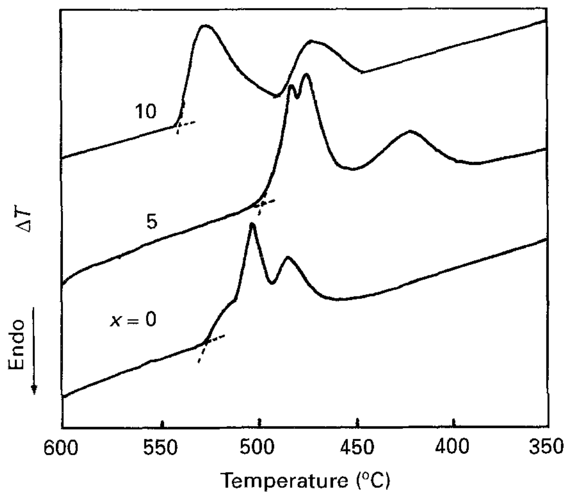

Figure 4 DTA curves of $x\mathrm{BaCl_2} \cdot (28 - x)\mathrm{BaF_2} \cdot 2\mathrm{InF_3} \cdot 2\mathrm{LaF_3} \cdot 10\mathrm{CsF} \cdot 58\mathrm{ZrF_4}$ glasses cooled from 600 °C at a cooling rate of 50 °C min^{-1}.

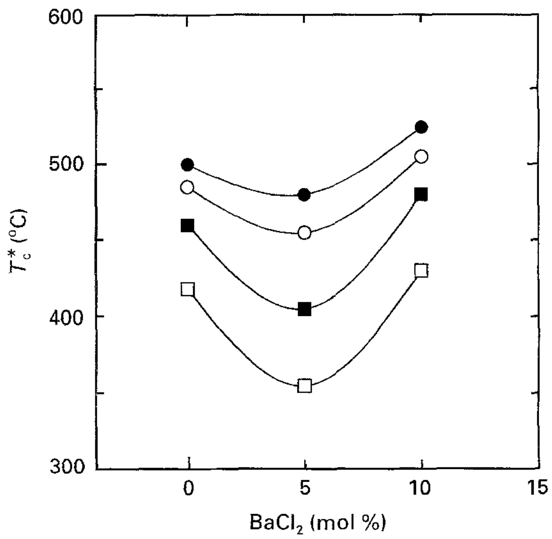

Figure 5 Dependence of top temperature T_c^* of the first crystallization peak and cooling rates versus $BaCl_2$ concentration. Key: ● 25 °C min^{-1}; ○ 50 °C min^{-1}; ■ 100 °C min^{-1}; □ 200 °C min^{-1}.

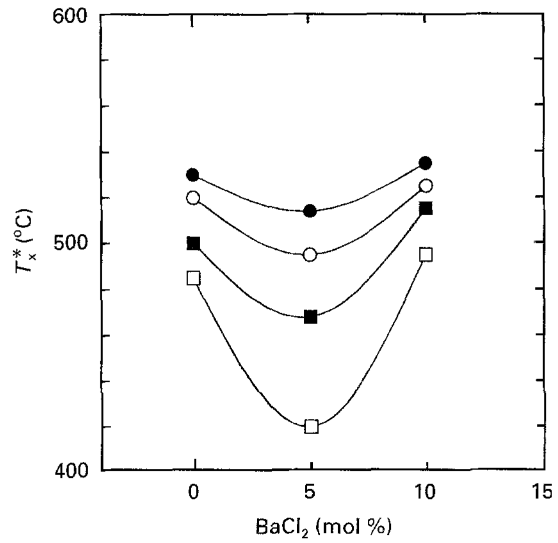

Figure 6 Dependence of onset temperature T_x^* of the first crystallization peak and cooling rates versus $BaCl_2$ concentration. Key: ● 25 °C min^{-1}; ○ 50 °C min^{-1}; ■ 100 °C min^{-1}; □ 200 °C min^{-1}.

glasses has been studied by Parker *et al.* [7]. A similar investigation was made by Miura *et al.* [9] on the AlF_3–ZrF_4 based glasses. Considering the thermal stability against crystallization, both the present and the previous results show that there exists an optimum amount of chloride in the low chloride region. But, with a further addition of chloride, the glass tends to become unstable and crystallize easily.

The above phenomenon can be classified as a "mixed anion effect", which was first proposed by Zarzicky [10] and recently reviewed by Zhang and Zhang [11]. Until now, such a phenomenon has been difficult to explain quantitatively. However, it can be explained qualitatively. Devitrification can be ascribed to either a thermodynamic phenomenon or a dynamic one. Introduction of chloride into fluoride glass decreases the diffusion coefficient of various ions in glass or glass melts, because of the obstructing effect

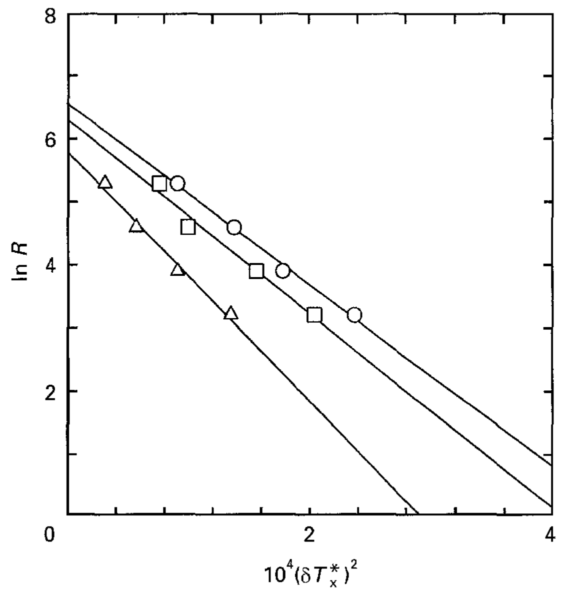

Figure 7 Dependence of ln*R* versus $10^4/(\delta T_x^*)^2$ for $x BaCl_2 \cdot (28 - x) BaF_2 \cdot 2InF_3 \cdot 2LaF_3 \cdot 10CsF \cdot 58ZrF_4$ glasses. Key: △ $x = 5$; □ $x = 0$; ○ $x = 10$.

of the chlorine ions, and so decreases the probability of ions forming an orderly structure. However, further addition of chloride into fluoride glass will weaken the strength of the glass framework because of low bonding strength between chlorine and metal ions, and this decreases the viscosity of the glass seriously, thus promoting the formation of crystallites.

4. Conclusion

From the above results, it can be concluded that the addition of a small amount of chloride into ZrF_4–BaF_2–CsF based glass increases the glass forming ability and thermal stability against crystallization. Such phenomena can be explained qualitatively from a thermodynamic and dynamic view of glass formation.

Acknowledgement

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