GLASS FORMING ABILITY AND THERMAL STABILITY IN THE SYSTEM ZrF$_4$–BaF$_2$–PrF$_3$

J. R. J. Delben[*]*, D. R. Chaves, P. D. Candelorio and A. A. S. T. Delben*

DFI-CCET-Universidade Federal de Mato Grosso do Sul, cx. p. 549, Campo Grande-MS-Brazil, CEP 79070-900, Brazil

New glasses have been synthesized in the system ZrF$_4$–BaF$_2$–PrF$_3$. Glasses were prepared by conventional fusion method and the vitreous domain was established. For vitreous samples the thermal stability parameters were determined, so that the best compositions could be selected according to a compromise between high glass forming ability and thermal stability *vs.* crystallization.

Keywords: *fluorozirconate glasses, glass forming ability, thermal stability*

Introduction

Rare earth elements present applications in divers areas such as high dielectric constant insulator for microelectronics [1], in organic synthesis and catalysis [2, 3], as biological active ligands with antibacterial activity [4], in magnets [5], as in spectroscopic probe as surrogates for Ca(II) ions, as crystalline phase stabilizer, for instance, of zirconia [6], as diagnostic agent in clinical medicine [7–9] and as optical active doping in solid-state systems [10–15]. Some glass compositions can be used as host but the fluoride glasses present some advantages.

Fluoride glasses present high rare earth solubility; they permit great efficiency in light emission in infrared region and emission in wavelengths not allowed for rare earth doped oxide glasses. Some characteristics of fluorine ion itself contribute to luminescence effects. Due to strong ionic character of fluor bonding the lifetime of rare earth ions in excited state are higher than those verified in oxide glasses. Besides it, the low phonon energy of fluoride glasses, compared to oxide glasses, reduces the non-radiative decay of rare earth ions. These facts favor the light emission and explain the rare earth doped fluoride glasses potential use in laser, optical amplifiers for telecommunication and in infrared to visible light conversion devices [16–20]. Rare earth fluoride glasses allow light amplification in the three telecommunication windows: the first centered at 0.8 μm (for fluoride glass containing Tm), at 1.3 μm (for glasses containing Pr, the most promising, or Nd or Dy), at 1.5 μm (for Er). Since the optical fiber network already installed worldwide works predominantly at 1.3 μm there is a great interest in praseodymium doped fluoride glasses.

Recently it has been reported that glass ceramics in mixed oxy-fluoride systems containing rare earth resulted in higher fluorescent emission, mainly if the crystalline phase dimensions were of the order of nanometer [21–23]. A glass can turn into a glass ceramic by heat treatment under controlled conditions of time and temperature. Changes of glass structure network [24, 25] as well as thermal stability [26] of various types of glasses can be evaluated by differential thermal analysis (DTA) or by differential scanning calorimetry (DSC). The initial glass should exhibit high degree of homogeneity in order to result in a glass-ceramic of commercial interest, then the importance of studying the glass forming ability. In order to establish the best conditions for thermal treatment required in the glass-ceramic processing from vitreous phase, the characteristics temperatures of the resulting glasses must be determined. Fluorozirconate glasses are the most extensively studied among fluoride systems, but up to now, there is no report in the system ZBP, based on ZrF$_4$–BaF$_2$–PrF$_3$, the object of present paper. The resulting glasses can be used as precursor matrix for glass-ceramics or it can be added to other multicomponent glasses to improve optical properties. Ternary glasses on the system ZrF$_4$–BaF$_2$–LaF$_3$ were known to be stable, but the substitution of La for Pr is advantageous regarding the luminescent properties of Pr ions. The vitreous domain was determined, the characteristic temperatures and the thermal stability parameters of this vitreous system were investigated.

Experimental

Materials and methods

Samples with different contents of ZrF$_4$, BaF$_2$ and PrF$_3$ were prepared by fusion in Pt crucible at 850°C/40 min,

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in a dry box containing N_2. ZrF_4, BaF_2 and PrF_3 compounds were Fluortran Grade (fiber optic grade), from BDH-Merck. Samples were prepared by splat-cooling to evaluate their glass forming ability. They were classified as glass or crystalline materials according to visual analysis, so that a ternary diagram of vitreous domain could be determined.

The compositions that resulted in vitreous samples were analyzed by DSC in a DSC-50, Shimadzu equipment, under N_2 flux of 20 mL min^{-1}, 10°C min^{-1} heating rate, in a Pt open crucible. The characteristics temperatures T_g, the glass transition temperature, T_x, the crystallization on-set temperature and T_p, the crystallization peak temperature were determined on DSC curves. These temperatures are used in the calculation of the thermal stability parameters: the usual work range $\Delta T = T_x - T_g$ and a parameter proposed for fluoride glasses [27].

$$S = \frac{(T_x - T_g)(T_p - T_x)}{T_g + 273.15}$$

Results and discussion

Samples were classified according to the presence of crystallization. DSC measurements were done on the vitreous samples, the curves for the system $(70-x)ZrF_4$, $30BaF_2$, $xPrF_3$, $x=5–20$ mol%, are presented in Fig. 1.

The ternary diagram of PrF_3, ZrF_4 and BaF_2, Fig. 2, presents the composition range in which glass formation occurred (dark area). At least two samples of each composition were prepared in order to establish this diagram and the samples closer to the edges of the dark area sometimes presented crystalline points. The best samples were obtained around the composition $60ZrF_4–30BaF_2–10PrF_3$, in mol%, near the geometric center of glass forming area. Additional samples were prepared along the two bold lines that cross each other at this composition, in order to study the stability against
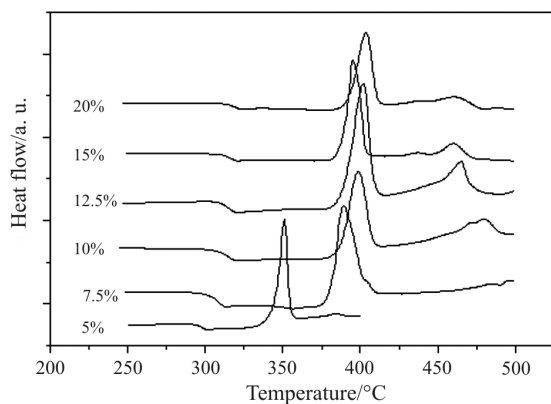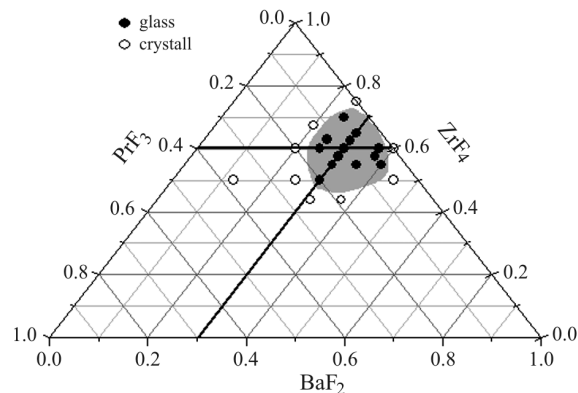

Fig. 2 Ternary diagram of glass forming ability in the system ZBP

devitrification *vs.* composition. Along one line PrF_3 replaces ZrF_4, and in the other line PrF_3 replaces BaF_2.

Great amounts of PrF_3 induce the increase of characteristic temperature, up to approximately 10% of PrF_3, Fig. 3, either replacing ZrF_4 or BaF_2. Above this content the glass transition temperature is almost constant while the crystallization on-set and crystallization peak temperatures decrease slowly.
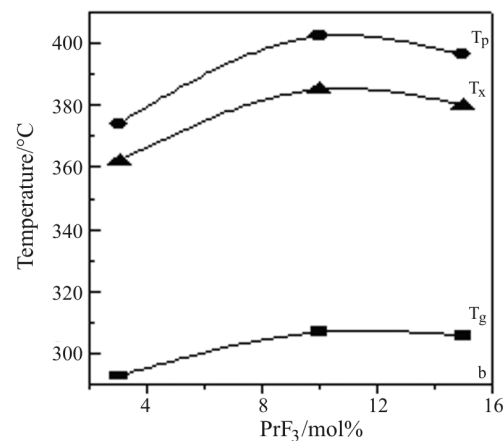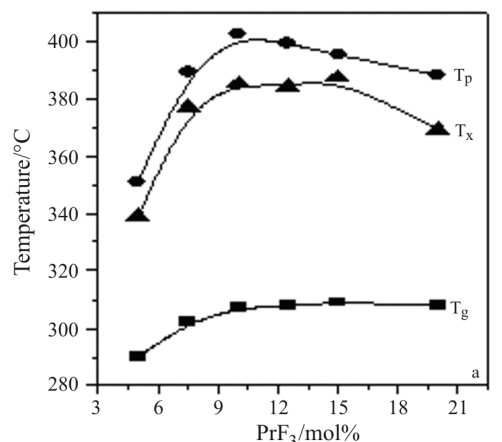

Fig. 1 DSC curves of glasses containing various PrF_3 contents replacing ZrF_4

Fig. 3 Characteristics temperatures of glasses with a – PrF_3 substituting ZrF_4, b – PrF_3 substituting BaF_2

Fig. 4 Thermal stability parameter ΔT a – for PrF$_3$ replacing ZrF$_4$, b – for PrF$_3$ replacing BaF$_2$
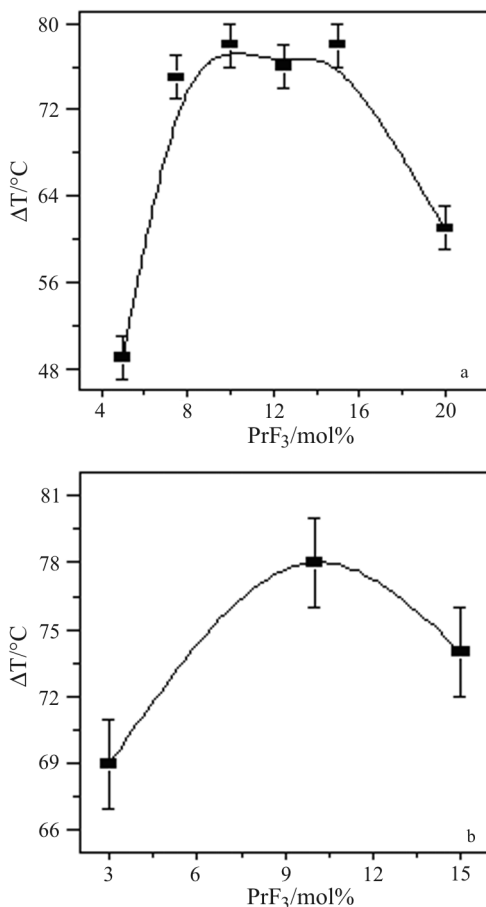
Fig. 5 Thermal stability parameters S a – for PrF$_3$ replacing ZrF$_4$, b – for PrF$_3$ replacing BaF$_2$

The stability parameter ΔT increases with PrF$_3$ replacing ZrF$_4$, keeping its maximum value almost constant in the range 7.5–15% PrF$_3$, Fig. 4a and decreases for higher content. The fact that samples with 5 and 20% presented lower stability parameter was expected, since these compositions correspond to points close to the limits of glass formation area in Fig. 2.

For samples in which PrF$_3$ replaces BaF$_2$, both stability parameter curves are quite similar, a maximum occurring for 10% of PrF$_3$, Figs 4 and 5.

The stability parameter S fluctuates when PrF$_3$ substitute ZrF$_4$, Fig. 5. Two effects must be taken in account in S determination:

- The temperature T_x is close to T_p and their difference, present in S, is only few degrees above the error in T_x and T_p determinations. These errors are indicated in Fig. 5.
- In the main crystallization peak a superposition of at least two crystallization curves could usually be observed, Fig. 1. The heating rate in DSC experiments as well as the thermal history of the samples determines which phase would predominantly
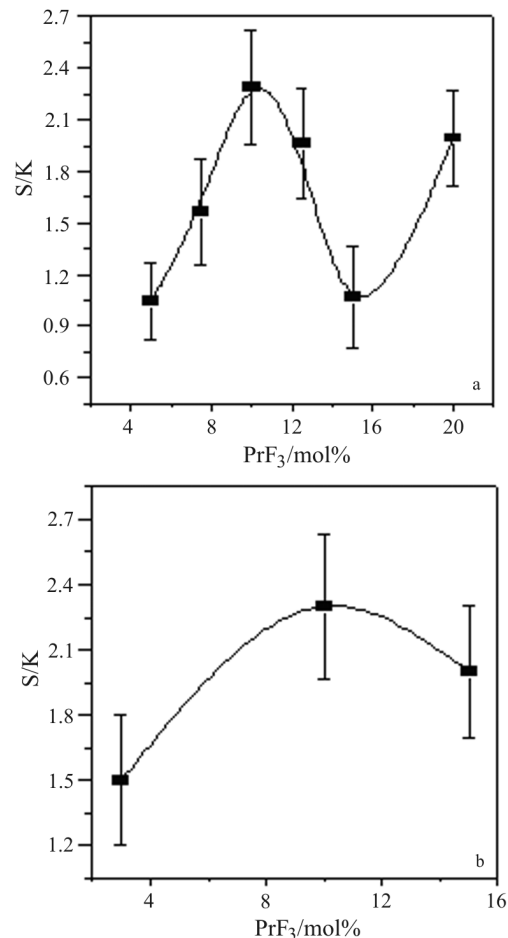
crystallize affecting strongly T_x and T_p positions. This last effect could not be completely controlled, so neither the errors in T_x and T_p determinations, then they were not taken in account in Fig. 5a, where the errors are underestimated.

Another aspect that points to stability parameter S inadequacy to describe the ZBP system is the fact that S increases at 20% of PrF$_3$, Fig. 5a, contradicting glass forming ability observations of ZBP system, since this composition in near the edge of glass formation area, Fig. 2.

Processing of many optical vitreous devices requires a commitment between glass formation ability and thermal stability.

For ZBP system glass formation occurs in the region where ZrF$_4$ varies between 50–78 mol%, BaF$_2$ varies between 20–40 mol% and PrF$_3$ between 3–20 mol%. Good glass samples could be easily reproduced near composition 60ZrF$_4$–30BaF$_2$–10PrF$_3$, in mol% and it became more difficult for samples closer to the limits of glass formation area.

Characteristics temperatures presented a maximum for PrF_3 content between 10–15 mol% either for ZrF_4 or BaF_2 replacement. Thermal stability parameter ΔT is greater than 60°C, a relative good stability among fluoride glass systems. The maximum for ΔT lied between 8–12 mol% of PrF_3, either substituting ZrF_4 as well BaF_2. The parameter S was inadequate to describe ZBP system.

So, considering both properties the glass forming ability and thermal stability, the best composition is the one containing 10% of PrF_3.

Conclusions

Numerous glass compositions have been investigated in the system ZBP, so that vitreous domain could be established. The presence of PrF_3 is desirable due to Pr ion luminescent properties. Although glass formation occurs up to 20 mol% of PrF_3, the greater thermal stability occurred for PrF_3 concentration around 10 mol%. These glasses can be used independently to prepare glass-ceramics or in addition on another multi-component glass system.

Acknowledgements

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