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THERMAL STABILITY OF FLUOROCHLOROINDATE GLASSES

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Abstract

New fluorindate glass compositions have been investigated in order to improve optical transmission as well as thermal properties. Chloride inclusion extends transmission of a fluoride matrix to longer wavelength in infrared region. In the present work thermal parameters of an IZnBS composition, based on InF_3, ZnF_2, BaF_2 and SrF_2, with various amounts of alkaline chlorides were investigated by differential scanning calorimetry. The chloride presence decreased all characteristic temperatures and increased both thermal stability and glass forming ability up to 10% of MCl content, where *M*=Li, Na, K and Rb. The presence of NaCl promoted glass phase separation. For samples containing same concentration of NaCl, this effect is accentuated for increasing the contents of SrF_2.

Keywords: glass forming diagrams, glass stability diagrams, halide glasses

Introduction

Heavy metal fluoride glasses are promising materials with potential applications for optical and optoelectronic devices. The main advantage of fluoride glasses over silica glasses is the high transparency at infrared optical spectrum: fluoride glasses transmit light up to ≅8 μm while the silica glass transmission edge is at ≅3 μm. Telecommunications are processed at infrared wavelengths so fluoride glasses are candidate for optical fibers and optical amplifiers. Optical transparency at the infrared region is governed by phonon absorptions associated to molecular vibration amplitude increasing.

Considering a certain anion-cation pair the fundamental stretching vibration frequency can be estimated by Szigeti equation [1]:

$$\nu_0 = \frac{1}{2\pi}\sqrt{\frac{F}{\mu}} \tag{1}$$

where *F* is related to the bonding strength and μ is the reduced mass of the pair. The lower this frequency is the longer the wavelength is at which the considered pair will

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absorb photons to enhance vibration then diminishing the optical transmission. Phonon energy decreases with decreasing frequency, so in order to favor long-wavelength transparency, low phonon energy materials composed of heavy elements with weak bonding are desired. Since fluoride glasses contain heavier elements and weaker ionic bonding compared to covalent bonding of silica glasses their infrared or multiphonon edge occurs at longer wavelengths. Also their theoretical optical losses, still not achieved in experimental investigations, are lower than that of silica glasses. Among fluoride glasses these features depend on the specific composition. The most extensively studied fluoride glass has been the fluorozirconate system [2]. But new fluoride glass compositions, with required thermal stability, were investigated, generally including heavier cations that extended the multiphonon limit even more [3, 4]. The development of glasses based on indium fluoride represented a great improvement in IR transmission, since they have lower phonon energy [5, 6] than fluorozirconate glasses. A natural extrapolation of these efforts was the inclusion also of other heavier anions, such as chlorides on fluoride glass systems [7–11] with the purpose of arising the good properties of each system: the extended transmission of chlorides glasses associated with the greater moisture resistance of fluoride glasses. Besides it the increase on component number must contribute to the thermal stability improvement according to ‘confusion principle’ for fluoride glasses. Nonetheless, the possibility of industrial use, there is a lack of systematic studies on the general physical properties of the fluoride glasses containing chlorides [11, 12]. In this work the glass forming ability and thermal stability parameters of fluorindate glasses containing alkali chloride were determined by the usual techniques [13, 14] of thermal analysis and calorimetry.

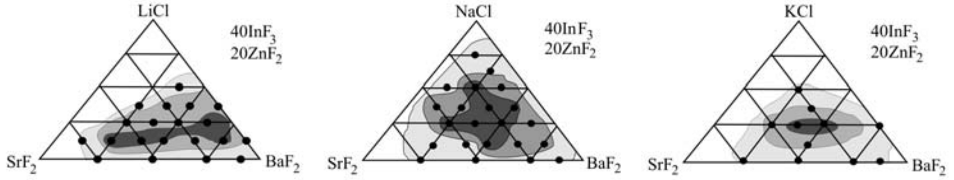

Fig. 1 Glass formation area for compositions with 40InF$_3$–20ZnF$_2$ showing comparative crystallization quantity, where black rectangle denotes glasses with no crystallization, medium black rectangle glasses with surface crystallization and grey rectangle glasses with bulk crystallization

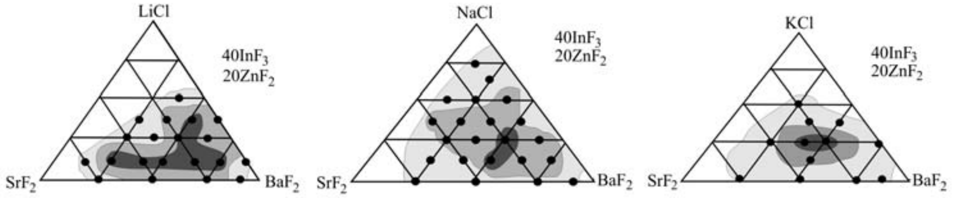

Fig. 2 Glass stability area for compositions with 40InF$_3$–20ZnF$_2$, each delimited area denotes $\Delta T=T_x-T_g$ values in the same range. Black rectangle>90°C, medium black rectangle>60°C and grey rectangle>30°C

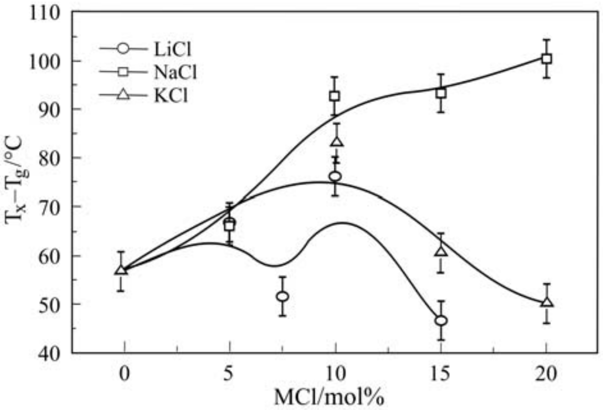

Fig. 3 Thermal stability parameter $\Delta T=T_x-T_g$ *vs*. alkaline chloride concentration

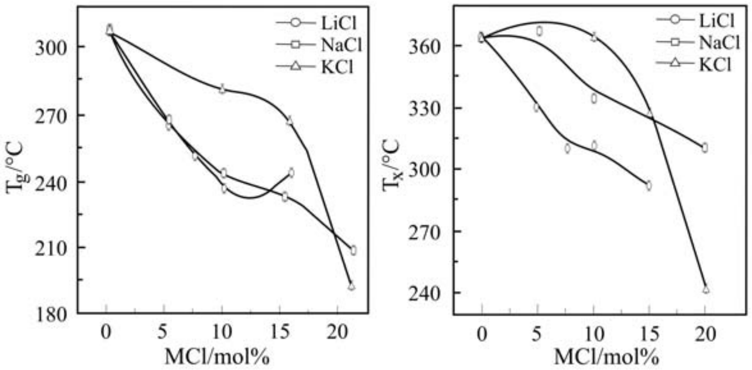

Fig. 4 Characteristic temperatures dependence on chloride concentration

Experimental

Samples were prepared by conventional fusion method. Starting materials were InF_3 (99.9%), ZnF_2 (99.9%), SrF_2 (99.9%), BaF_2 (99.9%), from BDH-Merck and MCl (99.5%) where *M*=Na, Li, K and Rb. The composition studied was $40InF_3–20ZnF_2–xBaF_2–ySrF_2–zMCl$, in mol%, with $x+y+z=40$. The glasses have been prepared in open platinum crucibles at room atmosphere. The melt temperature was held at 850°C for 30 min. Only in the last 3 min of melting process chloride was included to reduce its loss.

Samples obtained were qualitatively analyzed visually with lens of 10× amplification in order to determine glass formation diagrams. The typical sample size was of the order of 6.0×8.0×2.5 mm. Visual observation before and after sample polishing allows to differentiate superficial and bulk crystallization.

The glass transition temperature (T_g), temperature for the onset of crystallization (T_x) and the maximum of exothermic peak temperature (T_p) were determined by

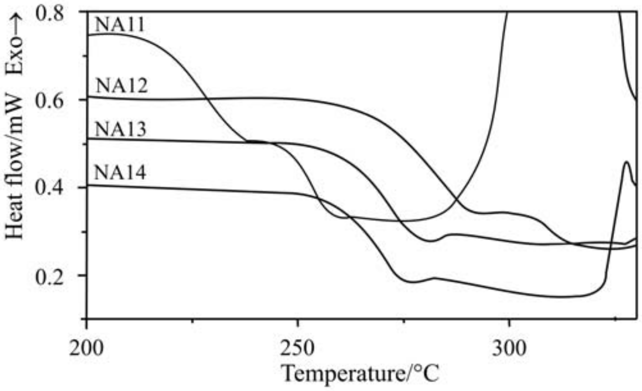

Fig. 5 DSC curves showing glass transition temperatures of glasses with 5% of NaCl and containing different concentrations of SrF_2

differential scanning calorimetry (DSC) in DSC-50H Shimadzu equipment. Glass stability was evaluated by the thermal stability parameter $\Delta T=T_x-T_g$.

Results

Current glass formation diagrams specify two regions: where there is glass formation, no matter its quality, and where there is not. In this work, glass samples were classified according to the degree of crystallization visually determined. Pseudo-ternary diagrams were established for the systems $40InF_3$, $20ZnF_2$, with varying amount of BaF_2, SrF_2 and MCl, Fig. 1. Darker regions corresponded to compositions with greater glass forming ability, these areas decreased from LiCl to KCl. No glass was obtained for RbF.

For the fabrication of special devices not only the ability of glass formation from melting is important, but also the capacity of remaining in vitreous state at posterior heating of the glass obtained allowing production of materials in certain geometry or dimension. An optical fiber, for instance, can be obtained by heating a preform composed of two glasses with different diffraction index over their softening temperatures. So thermal stability was also determined.

According to the values of thermal stability parameter $\Delta T=T_x-T_g$, pseudo-ternary diagrams were also established, Fig. 2. The compositions presented increasing stability parameters up to approximately 10% of LiCl and KCl, while kept increasing with NaCl content, Fig. 3.

So compositions with up to 10% of MCl optimize both characteristics: glass forming ability and thermal stability.

Including alkaline chloride generally decreases glass transition and crystallization onset temperatures, Fig. 4. But NaCl induces the greatest characteristic temperatures changes, arousing another glass transition for samples containing 5% or more of NaCl, an effect not observed for LiCl nor KCl inclusion.

Further analysis on samples containing 5% of NaCl, Table 1, showed that increasing the content of SrF_2 induces failure on structural homogeneity, Fig. 5. The arousing of an additional glass transition temperature, clearly observed for 15% SrF_2 or more, is related to glass phase separation. This effect brought out variations on other physical properties such as Arrhenius thermal viscosity behavior, that presented two values of activation energy for the case of two vitreous phases [15].

Table 1 Compositions of IZnBS glasses containing NaCl

NA11	$40InF_3–20ZnF_2–15BaF_2–20SrF_2–5NaCl$
NA12	$40InF_3–20ZnF_2–20BaF_2–15SrF_2–5NaCl$
NA13	$40InF_3–20ZnF_2–25BaF_2–10SrF_2–5NaCl$
NA14	$40InF_3–20ZnF_2–30BaF_2–5SrF_2–5NaCl$

Discussion

A main interest on fluoride glasses is to produce optical fiber, so their thermal characteristics are relevant:

1) Fluoride glasses fiber are drawn from preforms. The preform consists of two glasses (core and cladding) with different diffraction indexes, but similar values of thermal dilatation coefficient and viscosity. Successful preform melting, free of nucleation, requires that both compositions present reasonable glass forming ability.

2) The fiber drawing process at temperatures higher than glass transition requires both glass compositions to present good thermal stability to prevent nucleation during heating.

So there is a commitment between glass formation ability and thermal stability of fluoride glasses for optical fiber, in order to avoid crystallization in any involved process of fiber fabrication. Both glass forming ability, confirming the ‘confusion principle’, and the thermal stability increased with the inclusion of up to approximately 10% of lithium, sodium and potassium chloride content. The glass formation area, considering only the best compositions without visual traces of crystallization, diminishes as the atomic mass of the alkaline metal increases, it is higher for LiCl and there was no vitreous sample for RbCl. Samples containing LiCl and KCl presented only one glass transition in DSC curves, whilst for high contents of NaCl two glass transitions were observed at different temperatures.

The presence of at least 5% of NaCl promoted glass phase separation, an effect that is even more emphasized for higher contents of SrF_2. Glass phase separation is undesirable for optical glasses since any non-homogeneity in the composition or in the density promotes diffraction index variation that would induce light scattering. In multicomponent systems such as fluoride glasses there is a high possibility of structural or compositional non-homogeneity occurrence. This effect may occur for other fluoride systems and must contribute to the achieved performance of fluoride glass optical fiber transmission, which is still much lower than theoretical predictions. DSC then provided a primary method to select the most promising compositions for potential use in optical fibers, laser host and other optical devices. So for the glass system studied, the compositions with simultaneously higher glass formation ability and thermal stability are those with up to 10% of KCl or LiCl. The inclusion of NaCl up to 10% increases both thermal stability and glass forming ability, however it should not exceed 5% to avoid phase separation that would deteriorate optical properties.

Conclusions

In this work we have investigated the influence of chloride contents on glasses IZnBS. Glass formation and thermal stability diagrams were established. Both characteristics are improved for compositions containing up to 10% of alkaline chlorides. Glass formation area decreased with metal alkaline atomic mass and for RbF there was no vitreous composition. NaCl inclusion at contents of 5% or higher induces phase separation, a characteristic even more pronounced with increasing amounts of SrF_2. For optical purposes the good compositions were those with up to 5% of NaCl and up to 10% of KCl and LiCl.

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