JOURNAL OF Materials CHEMISTRY

Composition adjustments in fluoroindate glasses

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Received 4th October 1999, Accepted 29th November 1999

New fluoroindate glasses have been synthesized by the incorporation of NaF, CdF_2 and PbF_2 in vitreous compositions based on the InF_3–YF_3–BaF_2–SrF_2 system. Systematic investigations were implemented in the different systems with a constant amount of 45% InF_3 and 5% YF_3. The corresponding vitreous areas are reported. Relative resistance to devitrification was evaluated using stability factors. The incorporation of NaF, CdF_2 and PbF_2 had only limited influence on the glass stability. Optimized glass compositions are reported. Important physical properties, including characteristic temperatures, densities and refractive indices have been measured and correlated with composition.

1 Introduction

Since their discovery,[1] the first heavy metal fluoride glasses have shown potential applications in various fields:[2,3] fibres for telecommunications[4] and medicine, sensors,[5] optical amplification, laser fibres and up-conversion devices.[6] First developments were based on fluorozirconate glasses. However, enhanced performances are expected for fluoride glasses exhibiting still higher transmission in the IR spectrum, or equivalently lower phonon energy. A particular interest focuses on radiative transitions in rare earth electronic levels which are sensitive to matrix phonon energy.[7] A classical example is praseodymium fluoride fibre amplifier for operation at 1.3 µm. For this reason, various studies have been implemented on fluoroindate glasses.[8,9] Systematic investigations have been performed by us for the InF_3–YF_3–$(Ba/Sr)F_2$ system.[10] The final aim of this work is to obtain high quality glass samples which can be cast as bulk samples or drawn into fibres without devitrification. For this purpose it is necessary to study the influence of various fluorides upon glass stability and properties.

In a first step, some new glass forming systems have been investigated. Then various substitutions and additions have been carried out, and the corresponding glasses characterized.

2 Experimental

The glasses were prepared in open crucibles at room atmosphere using ammonium bifluoride (NH_4HF_2) to prevent hydrolysis. The details of the synthesis have been described in a previous paper.[11] Starting materials are the oxides In_2O_3 (3 99.9% from Preussag), Y_2O_3 (3 99.9% from Rhone Poulenc) and the fluorides BaF_2, SrF_2, PbF_2, CdF_2 and NaF (Merck). The fluorides and oxides were preheated for 1 h with ammonium bifluoride at *ca.* 400 °C to ensure complete fluorination of the starting materials. Then the batch was gradually heated to the melting temperature before the fining, cooling and casting steps. In the final stage, glass samples were annealed at a temperature lower than glass transition temperature T_g, and cooled slowly to room temperature. For new compositions, the annealing temperature was estimated from semi-empirical criteria.

Sample size and optical quality depend on the cooling rate of the melt since large samples will crack if they are cooled too rapidly. On the other hand, glass formation requires that the melt is solidified before crystallization occurs. Therefore there is a direct correlation between maximum sample thickness, cooling rate and glass forming ability. As a practical consequence, the compositional limits for glass formation are extended when the quenching rate increases. The vitreous areas which are reported below correspond to quenching of the melt between two brass plates. The corresponding quenching rate is close to 1000 K s^{-1} and sample thickness ranges from 0.3 to 0.5 mm. Large samples may be prepared only from vitreous compositions stable enough against devitrification. Such samples are required for optical measurements and were obtained by pouring the melt onto a hot metal mould.

The characteristic temperatures of the glasses were measured by differential scanning calorimetry (DSC) with a heating rate of 10 K min^{-1} (D.S.C. 220 SEIKO Instruments). Glass forming ability was estimated using the following numerical factors: thermal stability range:[12] $\Delta T = (T_x - T_g)$ and stability criterion $S = (T_x - T_g)(T_p - T_x)/T_g$, where T_g, T_x and T_p are, respectively, the temperatures (K) for glass transition, onset of crystallization and exotherm maximum.[13] As usual, the absence of crystals is checked by visual inspection. This simple method is much more sensitive than X-ray diffraction: light scattering may be perceived when the crystalline fraction exceeds 10^{-4} and microscopic observation is still more accurate. Densities were measured using the Archemedean method. The refractive indices, n_D for the sodium D-line were determined at room temperature using an Abbe refractometer. Estimated accuracy on temperatures is 2 °C, insofar as they correspond to intersection points derived from the DSC curve. The random error is 0.0005 for refractive indices and 0.02 g cm^{-3} for densities.

3 Results

3.1 Glass forming systems and regions

Limits for glass formation have been determined in the system 45% InF_3–5% YF_3–$x$$BaF_2$–$y$$SrF_2$–$z$$MF_n$, where $x+y+z=50$ (mol%) and M = Pb, Cd or Na. These systems have been chosen because they are usual glass components in heavy metal fluoride glasses. The corresponding vitreous areas are drawn in Fig. 1. The two first diagrams exemplify the predominant role of the BaF_2 in the glass composition: it may be substituted only partly by the other difluorides (PbF_2, SrF_2, CdF_2). As expected from the so-called 'confusion principle' which states that more stable glasses are obtained when the number of components increases, thicker samples may be cast from compositions located in the middle of the pseudoternary diagrams. The incorporation of sodium fluoride has a positive effect on glass

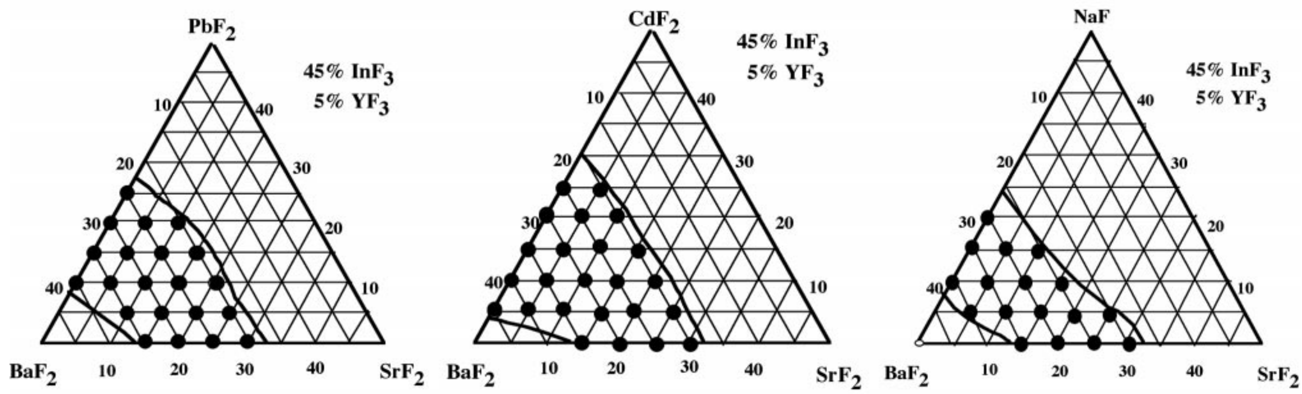

Fig. 1 Vitreous areas in fluoroindate systems $(45InF_3–5YF_3)+BaF_2–SrF_2–MF_n$ (M = Pb, Cd, Na). Compositions in mol%.

forming ability and the melt could be cooled more slowly without devitrification.

3.2 Physical properties

The characteristic temperatures for glass transition and crystallization were measured for most compositions investigated in these multicomponent systems. Glass transition temperatures are close to 300 °C, as found in low alkali content fluorozirconate glasses. Refractive indices and densities have also been measured in selected samples. Typical values are given in Table 1. Densities are *ca.* 5 g cm^{-3} with, as expected, the measured density being larger with lead and smaller with sodium. Refractive indices are close to 1.5 and IR transmission is similar to that for standard fluoroindate glasses.

3.3 Compositional dependence of physical properties

Reports from the literature show that in most fluoride glasses, the primary physical properties vary linearly *vs.* composition parameters. This is also observed with the glasses in this study when we plot the evolution of physical properties as a function of PbF_2, CdF_2 and NaF concentration.

Glass samples with different concentrations of sodium, lead and cadmium were synthesized with the general formulae:

$$45InF_3-5YF_3-30BaF_2-(20-x)SrF_2-xPbF_2 \quad (0\leq x\leq 20)$$

$$45InF_3-5YF_3-25BaF_2-(25-x)SrF_2-xCdF_2 \quad (0\leq x\leq 25)$$

$$45InF_3-5YF_3-35BaF_2-(15-x)SrF_2-xNaF \quad (0\leq x\leq 15)$$

The relative concentrations of barium and strontium fluorides are different in the three groups of samples. This results from empirical attempts to obtain thick samples in the whole composition range. As a consequence, the glass compositions are not the same when $x=0$ and the corresponding physical characteristics are not identical. However they are relatively similar, especially glass transition temperatures.

The evolution of characteristic temperatures, refractive indices and densities *vs.* composition parameter x are shown in Fig. 2–4. While a linear plot is observed for the glass transition temperature T_g, refractive index and density, the value of the crystallization temperature varies in a more random way. This is not surprising as it corresponds to a kinetic transformation which does not have a simple and predictable correlation with composition. The stability indices ΔT and S may be calculated from the values of the characteristic temperatures. Their evolution *vs.* composition is shown in Fig. 5.

Table 1 Glass transition temperatures, refractive indices and densities of glasses in this study

Glass composition (mol%)	SrF_2	NaF	CdF_2	PbF_2	T_g/°C	ρ/g cm^{-3}	n_D
$45InF_3–5YF_3–35BaF_2$	10	5			317	5.10	1.501
	5	10			289	5.03	1.492
$45InF_3–5YF_3–30BaF_2$	15		5		322	5.45	1.499
	10		10		316	5.59	1.503
$45InF_3–5YF_3–25BaF_2$	20			5	320	5.12	1.505
	15			10	305	5.31	1.515

4 Discussion

The main purpose of this study was to improve the thermal stability of the quaternary $InF_3–YF_3–BaF_2–SrF_2$ glass system. As there are no precise guidelines for predicting glass stability, we have used an empirical approach based on the systematic investigation of vitreous phases incorporating one or two additional glass components. While the concept of glass stability itself has been discussed and remains somewhat

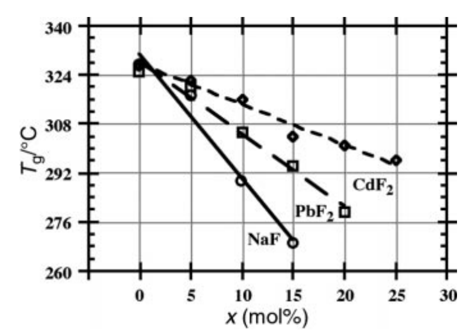

Fig. 2 Evolution of glass transition temperatures T_g *vs.* concentration parameter x (mol%) in IYBS glass. Lines are drawn as guides for the eye. Molar compositions are: $45InF_3–5YF_3–30BaF_2–(20-x)SrF_2–xPbF_2$, $45InF_3–5YF_3–25BaF_2–(25-x)SrF_2–xCdF_2$, $45InF_3–5YF_3–35BaF_2–(15-x)SrF_2–x$ NaF.

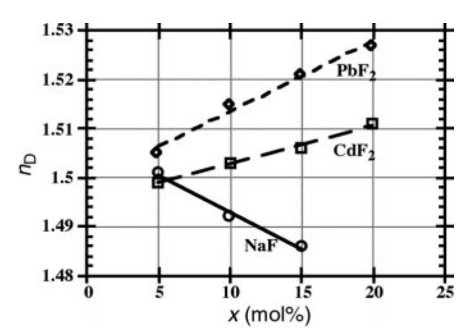

Fig. 3 Variation of refractive index, n_D, *vs.* composition parameter x (mol%). Glass compositions: (a) $45InF_3–5YF_3–30BaF_2–(20-x)SrF_2–xPbF_2$, (b) $45InF_3–5YF_3–25BaF_2–(25-x)SrF_2–xCdF_2$, (c) $45InF_3–5YF_3–35BaF_2–(15-x)SrF_2–xNaF$.

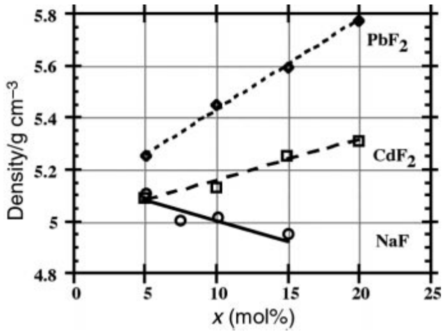

Fig. 4 Glass density *versus* composition parameter x. Glass compositions: (a) $45InF_3$–$5YF_3$–$30BaF_2$–$(20-x)SrF_2$–$xPbF_2$, (b) $45InF_3$–$5YF_3$–$25BaF_2$–$(25-x)SrF_2$–$xCdF_2$, (c) $45InF_3$–$5YF_3$–$35BaF_2$–$(15-x)SrF_2$–$xNaF$.

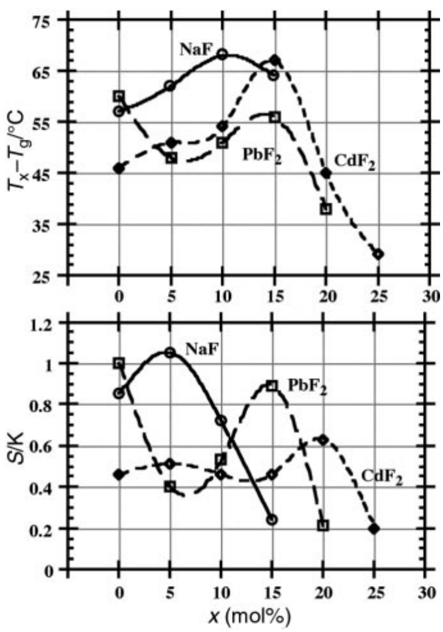

Fig. 5 Variation of stability factors ΔT and S *vs.* composition parameter x (mol%). Glass compositions: (a) $45InF_3$–$5YF_3$–$30BaF_2$–$(20-x)SrF_2$–$xPbF_2$, (b) $45InF_3$–$5YF_3$–$25BaF_2$–$(25-x)SrF_2$–$xCdF_2$, (c) $45InF_3$–$5YF_3$–$35BaF_2$–$(15-x)SrF_2$–$xNaF$.

hazy, it corresponds to an important practical parameter, because it relates closely to the maximum thickness and the optical quality of the glass samples. In this study we have used the parameters ΔT and S for stability assessment since these are easily deduced from DSC scans. As shown in Fig. 5 the evolution of these factors *vs.* composition suggests that sodium and cadmium incorporation have a stabilizing effect, while lead incorporation results in glasses which are less stable than the unmodified glass. However, this effect of lead on glass forming ability is not monotonous, and a relatively more stable vitreous phase is observed at 15 mol% PbF_2. Thus the substitution of barium fluoride, which exhibits a predominantly ionic character, by lead fluoride which is more covalent, does not increase the resistance of the glass to devitrification. In this case we must conclude that there is no obvious correlation between covalency and glass forming ability. This observation also leads to some restriction to the application of the 'confusion principle' quoted above: while the incorporation of an additional component in a glass composition is likely to induce the improvement of the glass stability in the optimum composition range; it is far from being automatic.

The evolution of physical properties with respect to sodium, lead and cadmium fluoride concentration is approximately linear, as in many other fluoride glass systems. This suggests that there is no major change in the structural behavior of the various cations in the whole composition range. It is expected that coordination numbers and ionic radii are nearly constant, which is consistent with the view that glasses are much more flexible hosts for doping elements than crystals. As a practical consequence, it becomes possible to predict the value of selected physical properties from the nominal composition.[14] Correct agreement between measured and calculated values is obtained for fluoride glass refractive indices. This method could be extended to other properties such as glass transition temperature, density and thermal expansion.

The main potential interest of these glasses relates to IR optical fibres, either passive for IR transmission, or active for laser fibres and optical amplification. Lead and cadmium tend to raise the refractive index for achieving fibres with large difference between the respective refractive indices of the core and cladding glasses. Cadmium toxicity should not be a major problem for practical uses insofar as it is located only in fibre core. However, further developments are required in order to achieve the high optical quality required for the manufacturing of optical fibres.[15,16] For such purposes, scattering which originates from nucleation must be reduced to a level below 0.1 dB km^{-1}.

5 Conclusion

New glass compositions have been prepared by substituting strontium by Na, Cd and Pb in the basic glass IYBS fluoroindate glass. The glass forming areas have been investigated. Characteristic temperatures (T_g, T_x, T_p), densities and refractive indices have been measured. Incorporation of Na, Cd and Pb increases the stability towards devitrification: both ΔT and S factors increase while thicker samples could be cast without devitrification. In a general way and in a limited composition range, physical properties such as refractive index and density are strictly correlated to the relative concentration of the glass components.

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Paper a907969f