NUCLEATION AND CRYSTALLIZATION IN FLUOROINDATE GLASSES

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ABSTRACT

Devitrification of fluoride glasses of ZBSI and ZBCdSI composition has been studied by non isothermal differential thermal analysis .For all compositions the Avrami exponent n varies between 3 and 4 suggesting a tridimensional interface controlled growth process with a decreasing nucleation rate. For ZBSI glasses, the curves of activation energy and stability parameters versus InF_3 concentration show an anomaly for x=35% InF_3. No anomaly has been observed for ZBCdSI glasses composition. Mechanisms of nucleation and crystal growth are discussed.

1.INTRODUCTION

Fluoroindate glasses are receiving increasing interest as they exhibit extended infrared transmittivity with low optical loss (1). Although they show enhanced thermal stability compared to the standard fluorozirconate (ZBLAN) glasses, the fabrication of bulk samples for optical applications requires slow cooling rates to achieve suitable size. Therefore the crystallization rate of the melt must be as low as possible and it is necessary to understand the crystallization phenomena in this new glass family for their technological development.
The kinetics of crystallization of ZBSI(ZnF_2-BaF_2-SrF_2-InF_3) and ZBCdSI(ZnF_2-BaF_2-CdF_2-SrF_2-InF_3) glass compositions has been studied following the same approach utilized to investigate the devitrification process of zirconate based glasses (2). Possible mechanisms of nucleation and crystal growth are discussed.

2.EXPERIMENTAL

Starting materials were ZnF_2 from Merck,SrF_2 and BaF_2 from B.D.H., CdF_2 from Fluka, and In_2O_3 supplied by Prussag. Batches of 10g were mixed with 7g of ammonium bifluoride(NH_4F,HF) in platinum crucible and heated in air at 400°C for 1.5 hour. After fluorination, the mixture was heated to 700°C for melting and then to 800°C for fining. The glasses were cast by pouring the melts on open brass mold. Glass crystallization was studied by differential scanning calorimetry technique using a Dupont 1090 equipment.

3.NON ISOTHERMAL DSC STUDIES

The kinetics of crystallization of a glass can be described by the empirical Avrami law (3):

$$x=1-\exp(-(kt)^n) \quad (1)$$

where x is the crystalline fraction, t is the time, n is an exponent which depends on crystallization mechanism and k is the reaction rate constant expressed by the Arrhenius equation:

$$k=k_o\exp(-E/RT) \quad (2)$$

where E is the activation energy for nucleation and crystal growth, R the perfect gas constant and T is the temperature in Kelvin..
In order to determine the Avrami exponent, Ozawa (4) and Augis and Bennett (5) proposed a relation for non-isothermal treatment expressed as:

$$Ln(-Ln(1-x))= nLn(k(T-T_0))- nLn\alpha \quad (3)$$

Experimentally, DSC scans were carried out at different heating rate in order to calculate the crystalline fraction x at temperature T and n from relation (3). The values of n found under various transformation conditions are given in reference.
The activation energy was determined from linear plots of the following reactions given by Chen (7) and Mac Farlane (8):

$$Ln(T_p^2/\alpha)=E/RT_p + Ln(E/R) - Ln(k_0) + Ln(-Ln(1-x)) \quad (4)$$

$$Ln\alpha =-E/RT_p + Ln(Nk')- Ln(-Ln(1-x)) \quad (5)$$

where T_p is the exotherm peak temperature.The instrument was calibrated at different heating rates and the sample temperature gradients were minimized by using small samples.

4.EXPERIMENTAL RESULTS

4.1.Evolution of the activation energy versus composition

The evolution of the activation energy E as a function of InF_3 content is shown in figure 1a for ZBSI glasses of composition $(60-x)ZnF_2$-$20BaF_2$-$20SrF_2$-$xInF_3$. The overall behavior passes through a minimum, 53 kcal/mole, at around 38% InF_3 corresponding to a more stable composition (9) with a larger difference T_x- T_g and a viscosity profile more favorable for glass formation.However an anomaly, confirmed by 3 measurements with 3 different samples, is found at x=35% InF_3.

The behavior of the stability parameters(T_x-T_g) and $S=(T_x-T_g)(T_p-T_x)/T_g$ as a function of InF_3 content also presents an anomaly at the same x=35% value.The values of T_x-T_g and S first increase with x, passes through a maximum around x = 40 % and then decrease. However a sharp drop is observed around x = 35 %. It is known that in glasses the energy decreases as the temperature increases from T_g to the liquidus temperature (10,11). Therefore,the sharp increase of E observed at 35% InF_3 signifies that the exotherm peak temperature T_p should shift to lower temperature at this value. This is confirmed experimentally (figure 2).For these compositions the Avrami exponent lies between 3 and 4 and is independent of the InF_3 content.This suggests a tridimensional interface controlled growth process with a decreasing nucleation rate (6). Therefore, it is not sure that relation (1) describes adequately the process occuring in these multicomponent glasses. In order to get more information a ZBSI composition with a smaller ZnF_2 content has

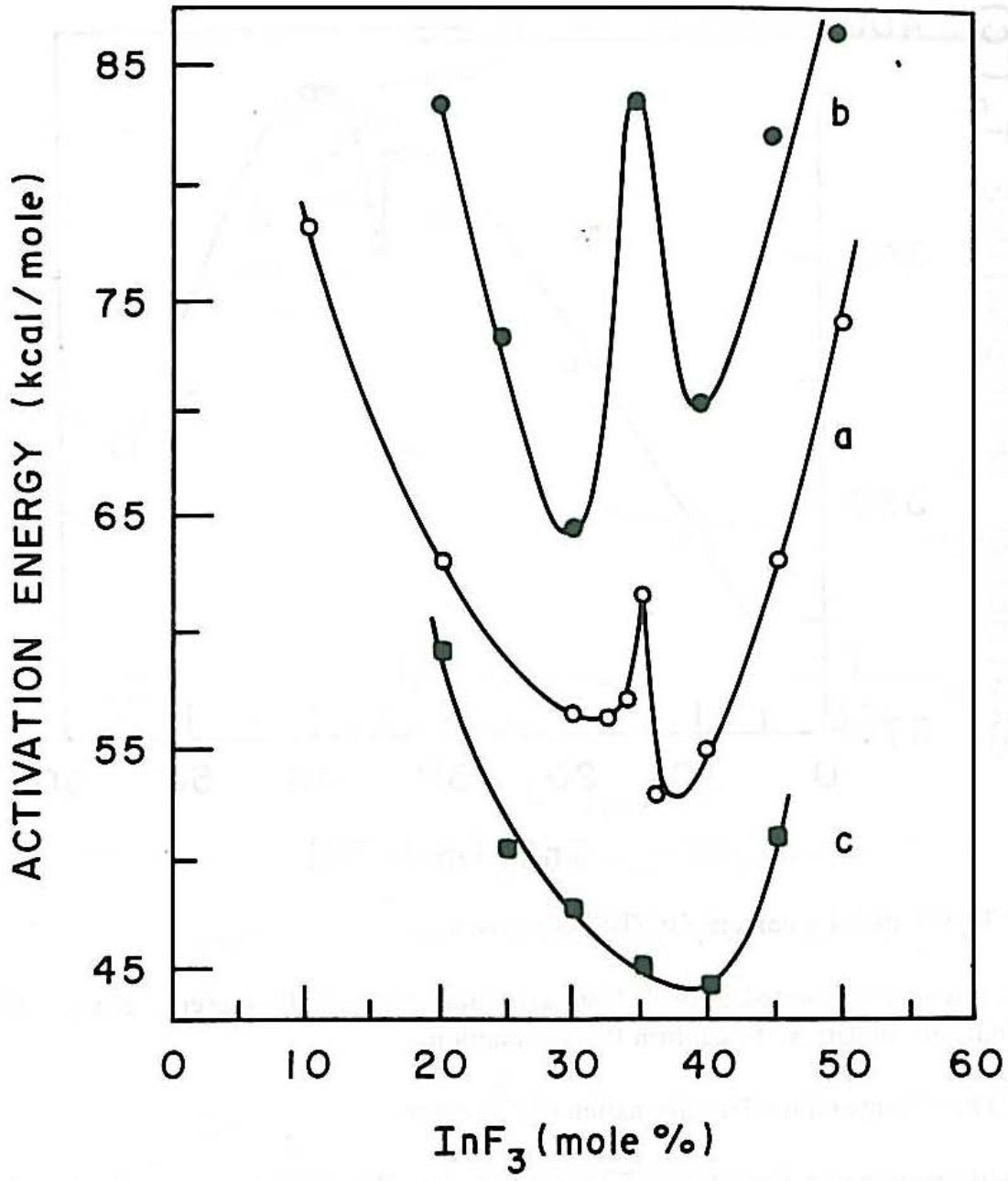

Figure 1: E versus InF_3 content (mol %) for a) and b) ZBSI c) ZBCdSI (see text for composition).

been studied: $(50-x)ZnF_2$-$25BaF_2$-$25SrF_2$-$xInF_3$.The evolution of the activation energy versus InF_3 concentration also presents the same anomaly at 35% InF_3 (Figure 1b). The overall values of E are however larger than those of the first ZBSI compositions and the anomaly is more pronounced These compositions are therefore less stable than the previous one.The anomaly is independent of the ZnF_2 concentration and seems solely related to the presence of InF_3.
On the other hand glasses produced by substituting 5% of BaF_2 by CdF_2 in the first composition do not present such an anomaly (figure 1 c). The activation energies are always smaller than those of ZBSI compositions; E passes through a minimum at 44 Kcal/mole at around x = 40 % . These compositions are therefore more stable. The observation of the anomaly is clearly related to the stability of the glasses. However we do not have yet a clear answer to explain it. Another

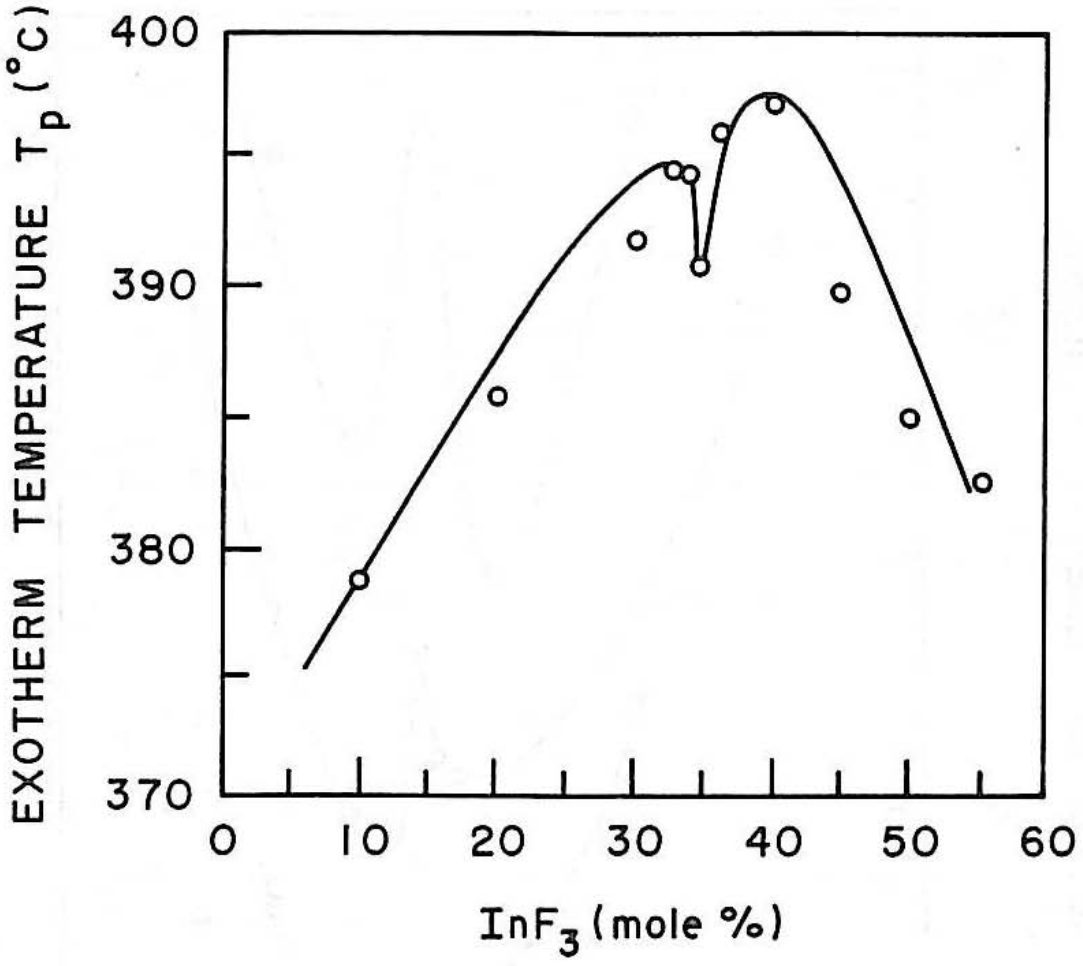

Figure 2: T_p versus InF_3 content for ZBSI composition.

crystalline phase, not detected through DSC measurements, may be present. X-ray diffraction measurements are underway to confirm this assumption.

4.2.Time-Temperature-Transformation (TTT) curve

The time-temperature-transformation (TTT) curve of one ZBCdSI composition $20ZnF_2$-$20SrF_2$-$15BaF_2$-$5CdF_2$-$40InF_3$ has been determined experimentally using DSC technique. Glass samples were first melted in an open pan outside the calorimeter. The pan was then placed in the DSC unit preheated at temperature $T_x<T<T_l$. The maximum of the exotherm temperature which corresponds to a constant crystallization fraction (around 45%), defines both the temperature and the time required to obtain the TTT curve (Figure 3).

The curve presents 3 noses at 517,494 and 484°C. The nose at 517°C is probably related to heterogeneous nucleation, enhanced by water and oxygen from the atmosphere, which may contribute to the formation of In_2O_3. The two lower temperature noses correspond to two different crystalline phases. Evidence for that is given by thermal analysis which shows two glass transition temperatures at 285 and 310°C and by the evolution of the crystallization temperature T_p determined during nucleation study with annealing stages performed during 20 min at each temperature (Figure 4). The vitreous fraction, defined as the ratio of the crystallization enthalpies of untreated and treated glasses, was determined form DSC data (Figure 5). A small fraction of the glass (~10%) crystallizes at 310°C and the remaining part at ~350°C. This is also evidence

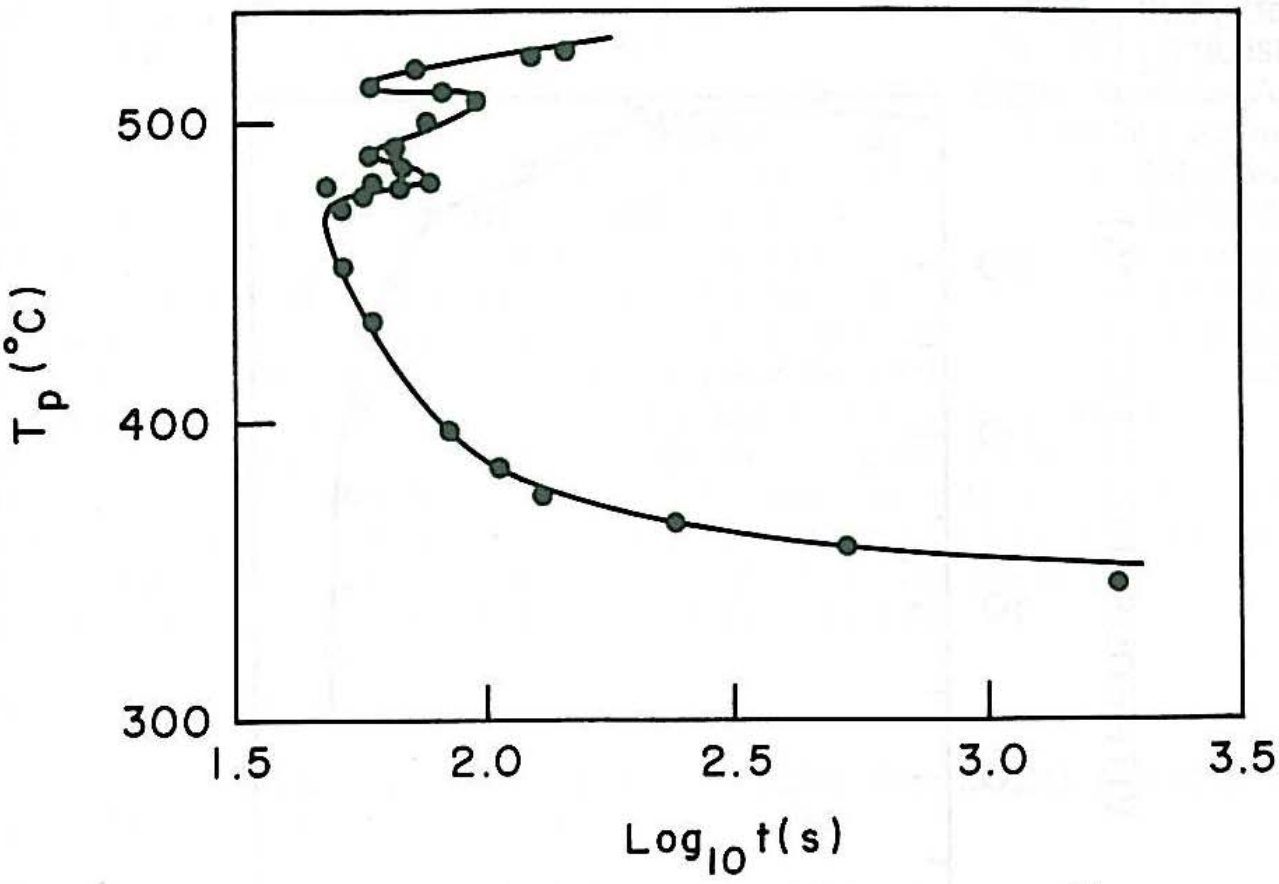

Figure 3: TTT curve of $20ZnF_2$-$20SrF_2$-$15BaF_2$-$5CdF_2$-$40InF_3$ glass composition.

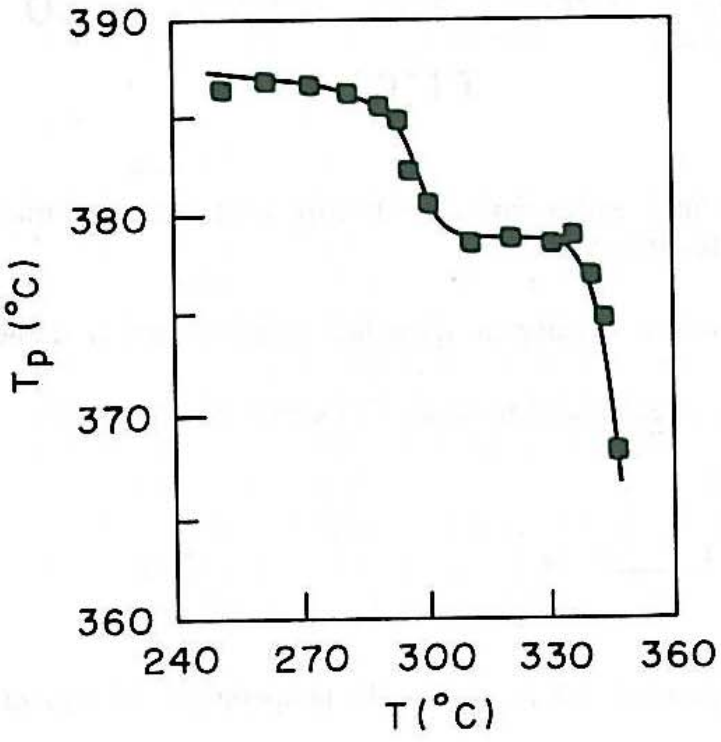

Figure 4: Crystallization temperature as a fuction of isothermal annealing temperature maintained during 20 mn. Glass composition: 40In-20Sr-15Ba-20Zn-5Cd.

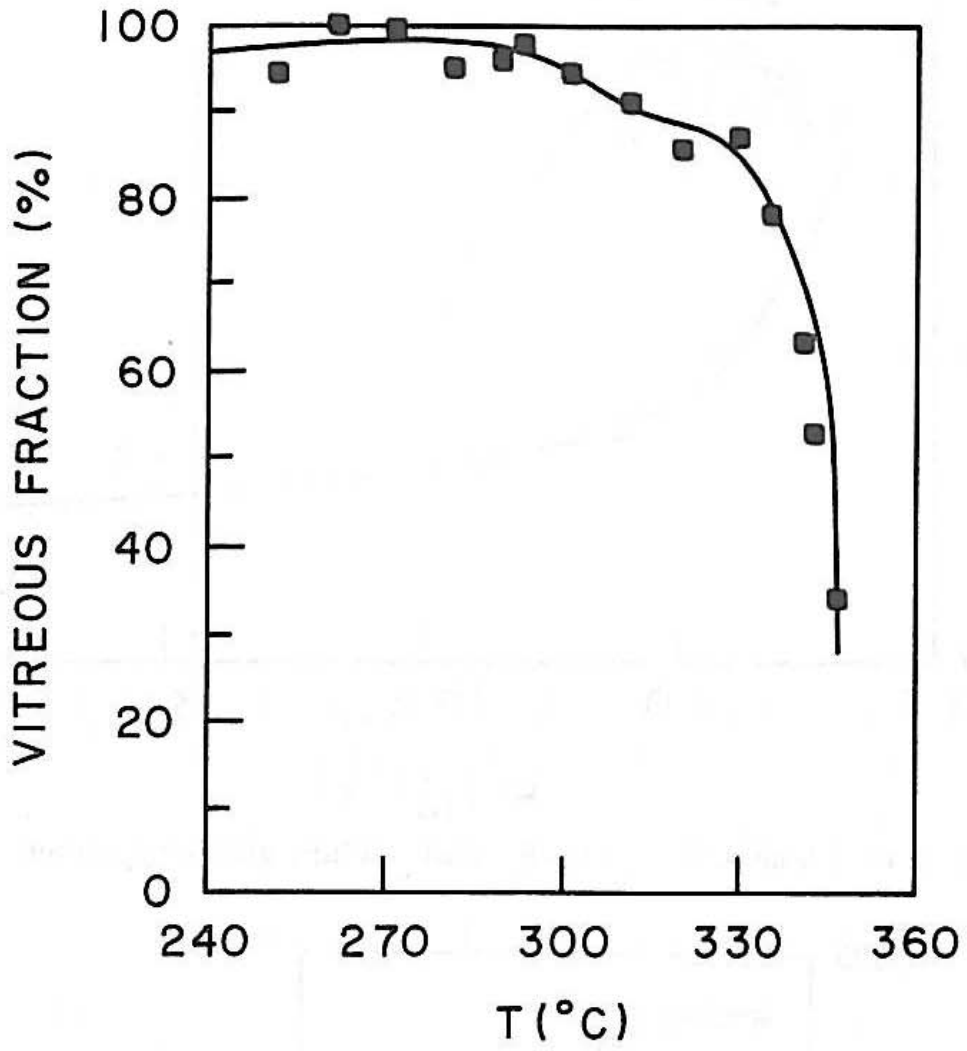

Figure 5: Vitreous fraction in samples annealed specific temperatures during 20 mn. Glass composition: 40-In-20Sr-15Ba-20Zn-5Cd

that it exists two vitreous phases coexisting in quenched samples. Further studies are needed to confirm them.

The critical cooling rate R_c was calculated from the TTT curve using a relation given by Ovorato and Uhlmann (12):

$$R_c = \frac{T_f - T_N}{t_N} \qquad (6)$$

where T_f is the melting temperature and T_N, t_N are the temperature and time of the peak of the curve, respectively.

The critical cooling rate is approximately 1.6 K/s. It is higher than those found for ZBLA (0.28 K/s) (13) and ZBLAN (0.13 K/s) (14), indicating that this particular composition is less stable than the others.

5. CONCLUSION

The devitrification of fluoroindate glasses of composition (60-x) ZnF_2-20BaF_2-20SrF_2-XInF_3, (50-x) $ZnF_2$25-BaF_2-25SrF_2-xInF_3 (ZBSI) and (60-x) ZnF_2-20SrF_2-15BaF_2-5CdF_2-xInF_3 (ZBCdSI) with 10< x 50 (mole %) has been studied by non-isothermal method using a DSC apparatus. For all compositions the Avrami exponent n lies between 3 and 4, independent of the InF_3 content. This value suggests that the crystallization follow a tridimensional interface controlled growth process with a decreasing nucleation rate. The results are difficult to interpret near and above the exotherm temperature(T_p), when the number of crystalline nuclei changes with time and temperature. These cases have been already observed in fluorochloride glasses (15) for which several mechanisms occur simultaneously when the temperature increases. The activation energy depends on the InF_3 content and passes through a minimum. For ZBSI compositions an anomaly (sharp increase) is observed for x = 35%. It is independent of the ZnF_2 content and solely related to the presence of InF_3. A similar anomaly is also observed in the behavior of the stability parameters. However no anomaly was found in ZBSCdI compositions.The critical cooling rate determined for a ZBCdSI composition with x = 40 mole % and is 1.6 K/s indicating a lower stability of this composition compared to ZBLA and ZBLAN. Recently, new compositions have been investigated with lower value of R_c (16) allowing fiber drawing.

6. ACKNOWLEDGMENTS

This research was financially supported by Telebrás, CNPq and the Program RHAE, New Materials (Brazil), MRT and the program EUREKA EU 113 (England).

7. REFERENCES

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