The glass transition and crystallization kinetic studies on BaNaB$_9$O$_{15}$ glasses

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Abstract
Transparent glasses of BaNaB$_9$O$_{15}$ (BNBO) were fabricated via the conventional melt-quenching technique. The amorphous and the glassy nature of the as-quenched samples were, respectively, confirmed by x-ray powder diffraction and differential scanning calorimetry (DSC). The glass transition and crystallization parameters were evaluated under non-isothermal conditions using DSC. The correlation between the heating rate dependent glass transition and the crystallization temperatures was studied and the Kauzmann temperature was deduced for BNBO glass plates and powdered samples. The values of the Kauzmann temperature for the plates and powdered samples were 776 K and 768 K, respectively. An approximation-free method was used to evaluate the crystallization kinetic parameters for the BNBO glass samples. The effect of the sample thickness on the crystallization kinetics of BNBO glasses was also investigated.

1. Introduction

Glass–ceramics are in general composites (glasses and crystallites) obtained by the controlled crystallization of the glassy materials. The glasses subjected to a carefully regulated heat-treatment schedule result in the nucleation and growth of crystalline phases within the glass. Glass–ceramics have received considerable attention in the past few decades because of their promising applications in the fields of non-linear optics and pyroelectrics [1–3]. There are many advantages associated with glass–ceramics such as low/zero porosity and consequently high dielectric breakdown voltages, easy controllability of the properties and could be produced in a variety of sizes and shapes. Glassy dielectric materials comprising nano/micro-crystallites of polar phases have been known to exhibit interesting physical properties which include piezoelectric, pyroelectric, electrooptic and non-linear optical (NLO) [1, 4–9]. In the last two decades, researchers have investigated glass–ceramic systems containing ferroelectric crystalline phases such as Li$_2$NbO$_4$ [8], SrBi$_2$Nb$_2$O$_9$ [4] and Bi$_2$WO$_6$ [5]. In the area of photonics, glasses comprising NLO crystals have received much attention, because these materials have high potential for laser hosts, tunable waveguides, tunable fibre gratings, etc.

Borate-based compounds have attracted the attention of many researchers because of their wide transmission window, moderate melting point, high chemical and mechanical stability, which make them useful for various applications [10]. Borate-based NLO crystals, which include Li$_2$B$_4$O$_7$ [11], La$_2$CaB$_{10}$O$_{19}$ [12] and CsLiB$_6$O$_{10}$ [13], were used to obtain UV light. We have been making systematic attempts to explore the possibilities of employing borate-based glass systems comprising nano/micro-polar crystals of the same phase for pyroelectric, electrooptic and non-linear optic device applications [1, 4, 5]. Recently, it was reported that BNBO crystallizes in noncentrosymmetric space group, R3c [14]. Therefore, we thought that it was worth attempting to grow nano/micro-crystals of BNBO in their own glass matrix and visualize their NLO and polar properties. To begin with one needs to have a priori knowledge about crystallization processes and mechanisms in order to fabricate glass–ceramics of the desired microstructure, namely, transparency. We have fabricated surface crystallized BNBO glasses using ultrasonic treatment (UST) and the effect of the UST on crystallization behaviour of the glasses was demonstrated using DSC [15]. In order to further our understanding of these glasses, the relation between the glass transition and the crystallization and the crystallization kinetics of the bulk and powdered samples are investigated in this study. Differential thermal analysis (DTA) and differential scanning calorimetry (DSC)
has frequently been used to study the crystallization kinetics of glassy materials [16–21]. For determining the kinetic parameters such as activation energy of crystallization ($E_c$) and $n$ in Johnson–Mehl–Avrami (JMA) equation [22–24], for the present BNBO glasses, non-isothermal approximation-free method is employed. Also the method of Chen [25] is used to estimate the above parameters. The activation energy associated with the glass transition is determined using Kissinger [26] and Moynihan [27] methods. Heating rate dependent glass transition and crystallization temperatures are rationalized and correlated using Lasocka equation [28]. The Kauzmann temperatures [29] for the present glass system are calculated for the glass plate and powdered samples using Lasocka equation, the details of which are reported in this paper.

2. Experimental

$\text{BaNaB}_9\text{O}_{15}$ (BNBO) glasses were fabricated via the conventional melt-quenching technique. For this, $\text{BaCO}_3$ (99.95%, Aldrich), $\text{Na}_2\text{CO}_3$ (99.9%, Merck) and $\text{H}_3\text{BO}_3$ (99.9%, Merck) were mixed and melted in a platinum crucible at $1373 \text{ K}$ for 30 min. Melts were quenched by pouring onto a stainless steel plate that was maintained at 423 K and pressed with another plate to obtain 0.5–2.5 mm thick glass plates. The DSC non-isothermal experiments were carried out using power-compensated DSC (Model: Diamond DSC, Perkin Elmer). For glass transition analysis, the sample was heated and cooled from 738 to 848 K at different heating rates (5, 10, 15 and 20 K min$^{-1}$). For crystallization studies, the plates of various thicknesses (0.5, 1.5 and 2.5 mm) and powdered (5–10 $\mu$m) glass samples were heated from 673 to 973 K at the rates of 5, 10, 15 and 20 K min$^{-1}$. All the experiments were conducted in dry nitrogen ambience. As-quenched glass samples (there were no nuclei present before DSC runs) weighing 20 mg were used for each experiments.

3. Results and discussion

The x-ray powder diffraction (XRD) pattern that is obtained for the as-quenched sample confirms its amorphous nature (figure 1).

In figure 2, we show the typical DSC traces obtained for BNBO glass plates of different thicknesses and powdered samples at a heating rate of 10 K min$^{-1}$. The onsets of the glass transition ($T_g$) and the crystallization temperature ($T_c$) are identified as the temperatures corresponding to the intersections of the two linear portions of the transition (glass transition and crystallization) elbows of the DSC traces. As can be seen in figure 2, the glass transition temperature ($T_g$) is almost the same for all the samples (plates and powdered) whereas the crystallization occurs at a lower temperature for the powdered sample. The crystallization temperature is independent (within the limitations of the experimental errors) of the thickness of the glass plates under study. However, it is noticed that the width of the exothermic peaks decreases with increase in the thickness of the glass plates. It suggests that crystallization kinetic parameters of BNBO glasses are dependent on the thickness of the samples. The glass transition ($T_g$), the onset of crystallization temperature ($T_c$) and crystallization peak width at half maximum ($\Delta T_{\text{FWHM}}$) at a heating rate of 10 K min$^{-1}$ for all the samples (glass plates and powder) are summarized in table 1.

3.1. Glass transition

Glass transition studies are important from the viewpoint of understanding the mechanism of glass transformations and in evaluating the structural rigidity of the glasses. The glass transition temperature reflects the strength or rigidity of the glasses. Figure 3 shows the glass transition ranges that are obtained for BNBO glass plates (0.5 mm) at different heating rates (5, 10, 15 and 20 K min$^{-1}$). The glass transition peak ($T_g$) shifts to higher temperatures with increasing heating rate as shown in figure 3, indicating the kinetic nature of the glass transition.

The $T_g$ dependence on the heating rate ($\alpha$) has been analysed using the following three different approaches. The
empirical relation between $T_g$ and $\alpha$ according to Lasocka is

$$T_g = A_g + B_g \log \alpha. \quad (1)$$

The value of $A_g$ is equal to the glass transition temperature for the heating rate ($\alpha$) of 1 K min$^{-1}$ and $B_g$ is constant for a given glass composition. The plot of $T_g$ (K) versus log $\alpha$ (K min$^{-1}$) for BNBO glasses and a theoretical fit (solid line) are shown in figure 4. The values that are obtained for $A_g$ and $B_g$ are 795 K and 9.9, respectively, for BNBO glasses. Therefore, the above relation can be written as

$$T_g (K) = 795 + 9.9 \log \alpha. \quad (2)$$

Equation (2) is an excellent description of the dependence of $T_g$ on heating rate for BNBO glasses.

The second approach for analysing $T_g$ or $T_{gp}$ is based on Kissinger’s formula, in which the $T_{gp}$ has a linear dependence on the heating rate, according to which

$$\ln \left( \frac{\alpha}{T_{gp}^2} \right) = \text{const} - \frac{E_g}{RT_{gp}}, \quad (3)$$

where $E_g$ is an activation energy for the glass transition which involves the molecular motion and rearrangement of atoms around the glass transition temperature and $R$ is the universal gas constant.

A plot of $\ln(\alpha/T_{gp}^2)$ versus (1000/$T_{gp}$) gives a linear relation, which is depicted in figure 5. The value of the activation energy $E_g$ obtained from the above plot is 656 ± 5 kJ mol$^{-1}$.

The activation energy for the glass transition $E_g$ could be calculated using the following formula, suggested by Moynihan,

$$\ln \alpha = \text{const} - \frac{E_g}{RT_{gp}}. \quad (4)$$

For equation (4), the necessary constraint is that prior to reheating, the glass must be cooled from above to well below
the glass transition region at a rate, which is either equal to or proportional to the reheating rate.

In the present experiments, samples are heated and cooled around the glass transition region in such a way that the cooling rate is equal to the reheating rate. A plot of ln(α) versus (1000/T<sub>gp</sub>) is shown in figure 5. The value obtained for E<sub>g</sub> from figure 5 is 648±5kJ mol<sup>-1</sup>, which is close to that obtained by Kissinger’s method.

3.2. Glass transition and crystallization correlation

Non-isothermal methods are useful in obtaining kinetic parameters associated with the crystallization of the glasses. This would be obtained by monitoring the shift in the position of an exotherm as a function of the heating rate. The non-isothermal crystallization process of BNBO glass powdered sample at different heating rates (5, 10, 15 and 20 K min<sup>-1</sup>) exhibits a single symmetric exothermic peak in the DSC studies, as shown in figure 6. Similar trends were observed for BNBO glass plates of different thicknesses under study, which are not shown in figure 6.

We notice a systematic shift in the crystallization temperature to higher temperatures with an increase in the heating rate. For rationalizing heating rate dependent crystallization temperature, the Lasocka equation can be invoked, which is as follows:

\[ T_c = A_c + B_c \log \alpha, \]

where A<sub>c</sub> is the crystallization temperature at the heating rate of 1 K min<sup>-1</sup> and B<sub>c</sub> is a constant. Figure 7 shows the plots of T<sub>c</sub> (K) versus log α (K min<sup>-1</sup>) for both the samples (plate and powdered). The experimental points for this work along with the theoretical fit (solid line) to the above relation suggest its validity.

The above relation for BNBO plate shaped sample can be written as

\[ T_c(K) = 865 + 54.3 \log \alpha. \]  (6)

It is to be noted that the above relation is valid for the BNBO glass plates of various thicknesses, since T<sub>c</sub> is invariant with the thickness of the samples. While for the powdered sample

\[ T_c(K) = 858 + 32.7 \log \alpha. \]  (7)

To correlate the glass transition and crystallization temperatures of BNBO glasses, one could derive the relation (using equations (1) and (5)) in the form

\[ T_g = \left( \frac{B_c A_g - A_c B_g}{B_c - B_g} \right) T_c + \left( \frac{B_g}{B_c} \right) T_c. \]  (8)

Therefore, for BNBO glass plates, the above relation can be expressed as

\[ T_g(K) = 636 + 0.18T_c(K) \]  (9)

while for BNBO glass powder, one would write

\[ T_g(K) = 538 + 0.3T_c(K). \]  (10)

Equations (9) and (10) show that the glass transition and the crystallization temperatures are dependent parameters. Indeed similar correlation was reported for amorphous alloys by Yao et al [30]. The Lasocka equations for the glass transition and the crystallization temperatures could be used to evaluate Kauzmann temperature. The Kauzmann temperature (T<sub>k</sub>) is an important parameter to characterize glassy materials from a thermodynamic viewpoint. T<sub>k</sub> is the temperature at which the entropy of liquid becomes equal to that of crystal. It denotes a lower boundary for the glass transition temperature from thermodynamic aspects and existence of an under-cooled liquid below this temperature would violate thermodynamic law [29]. Equation (8) could be used to determine the Kauzmann temperature (T<sub>k</sub>) for the present glass system. The Kauzmann temperature is the lowest theoretical boundary for the glass transformation. One can assume that T<sub>k</sub> = T<sub>c</sub> = T<sub>g</sub> [31] at a heating rate α<sub>k</sub>.

After solving equation (8) for T<sub>k</sub> (which is equal to T<sub>g</sub> or T<sub>c</sub>) and α<sub>k</sub>, one would arrive at

\[ T_k = \frac{B_c A_g - A_c B_g}{B_c - B_g} \]  (11)

and

\[ \alpha_k = 10^{(A_c A_g)/(B_g - B_c)} \]  (12)
The values obtained for $T_i$ from equation (11) are around 776 K and 768 K for BNBO plate and powdered samples, respectively, and the corresponding heating rates (from equation (12)) to reach these temperatures are 0.027 and 0.002 K min$^{-1}$. Due to very low heating rates, it is extremely difficult to observe this ideal glass transition experimentally.

3.3. Crystallization kinetics

The isothermal crystallization process of the glass is described by the JMA equation [22–24]

$$x = 1 - \exp[-(kt)^n], \quad (13)$$

where $k$ is a rate constant which is a function of the temperature and depends on the nucleation rate and on the speed of growth of the crystallites, $n$ is the Avrami exponent which reflects the characteristics of nucleation and growth process, $t$ is the transformation time and $x$ is the volume fraction that is crystallized at time $t$. The constant $k$ is related to the crystallization activation energy, $E_c$, for the process, and its Arrhenius temperature dependence is given by

$$k = k_o \exp(-E_c/RT), \quad (14)$$

where $k_o$ is the frequency factor, $R$ is the universal gas constant and $T$ is the absolute temperature.

There are various methods that are derived based on the JMA equation for non-isothermal crystallization process [32]. All the methods assume a constant heating rate, $\alpha$, in the DSC or DTA experiments, wherein

$$T = T_i + \alpha t, \quad (15)$$

where $T_i$ is the temperature at which the crystallization begins and $T$ is the temperature after time $t$. For non-isothermal crystallization, the JMA equation can be written as

$$x = 1 - \exp[-(k_o \exp(-E_c/RT))^n \times ((T - T_i)/\alpha)^n] \quad (16)$$

on rearranging and taking logarithm,

$$-\ln(1-x) = \left[ (k_o \exp(-E_c/RT))^n \times \left( T - T_i \right) / \alpha \right]^n \quad (17)$$

for $-\ln(1-x) = 1$ or $x = 0.63$, equation (17) can be written as

$$k_o \left[ \exp \left( -\frac{E_c}{RT_{0.63}} \right) \times \left( \frac{T_{0.63} - T_i}{\alpha} \right) \right] = 1, \quad (18)$$

where $T_{0.63}$ is the temperature at which 63% glass is crystallized.

When one expresses the above equation in logarithmic form, one obtains

$$\ln \left( \frac{\alpha}{T_{0.63} - T_i} \right) = \ln k_o - \frac{E_c}{RT_{0.63}}. \quad (19)$$

Thus the plot of $\ln[\alpha/(T_{0.63} - T_i)]$ versus $1/T_{0.63}$ yields a straight line. The values of crystallization activation energy and frequency constant are obtained from the slope and intercept of the above plot, respectively. This method is approximation free and is applied to extract the crystallization kinetic parameters for the present glasses.

Equation (17) could be used for calculating the Avrami exponent. For fractions of crystallization $x_1$ and $x_2$ at different temperatures $T_1$ and $T_2$ at a heating rate of $\alpha$, one obtains

$$\frac{\ln(1-x_1)}{\ln(1-x_2)} = \left[ \frac{\exp(-E_c/RT_1)}{\exp(-E_c/RT_2)} \times \frac{(T_1 - T_i)}{(T_2 - T_i)} \right]^n \quad (20)$$

on taking the logarithm of the above equation,

$$\ln \left[ \frac{\ln(1-x_1)}{\ln(1-x_2)} \right] = n \left[ \frac{E_c}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) + \ln \left( \frac{T_1 - T_i}{T_2 - T_i} \right) \right] \quad (21)$$

The Avrami exponent ($n$) could be obtained using the above relation. The crystallized fraction $x$ at any temperature $T$ is $x = A_T/A$, where $A$ is the total area of the exotherm, $A_T$ is the area under exotherm from $T_i$ to temperature $T$ as shown in figure 8. The crystallized fraction $x$ as a function of temperature at all the heating rates under study for BNBO glass plates (0.5 mm) and powdered samples are shown in figures 9 and 10.

The crystallization activation energies, $E_c$, and the frequency constants for BNBO glass plates and powdered samples, could be calculated using equation (19). Plots of $\ln[\alpha/(T_{0.63} - T_i)]$ versus $1000/T_{0.63}$ for BNBO glass plates (0.5 mm) and powdered samples are shown in figures 11 and 12, respectively. The values of $E_c$ obtained from the above plots are 279 ± 10 kJ mol$^{-1}$ and 424 ± 10 kJ mol$^{-1}$ for glass plates and powdered samples, respectively.

It is seen that BNBO glass powder has higher activation energy for the crystallization than that of the plate shape samples. Since the specific area is higher in the case of powdered samples, more energy is required to relieve the surface strain and hence larger activation energy for crystallization. The values for the frequency constant are about $2 \times 10^{15}$ s$^{-1}$ and $2 \times 10^{24}$ s$^{-1}$ for BNBO plate and powdered samples, respectively. A large difference between the values of frequency constant for the plate and the powdered samples is due to a large difference in the activation energy [33]. It
Figure 9. Fraction of crystallization versus temperature curves at various heating rates for 0.5 mm thick BNBO glass plates.

Figure 10. Fraction of crystallization versus temperature at various heating rates for BNBO glass powder.

is worth mentioning that the frequency constant indicates the number of attempts per second made by the nuclei to overcome the energy barrier. However, higher value of frequency constant obtained for the powdered sample evidently suggests that the fit and model is not satisfactory as the value of frequency constant is expected to be much lower and to be within the range of frequencies of atomic vibrations of the order of $10^{13}\text{ s}^{-1}$ for a simple diffusion process. Chen [25] developed a method, which could be used commonly for analysing the crystallization data in non-isothermal DSC or DTA experiments, according to which

$$\ln\left(\frac{\alpha}{T_{2\text{cr}}}\right) = -\frac{E_c}{RT_{\text{cr}}} + \text{const.} \quad (22)$$

The plots of $\ln(\alpha/T_{2\text{cr}})$ versus $1000/T_{\text{cr}}$ for both the samples (BNBO glass plates and powdered) are shown in figures 11 and 12, respectively.

Figure 11. $\ln(\alpha/(T_{0.63} - T_i))$ versus 1000/$T_{0.63}$ and $\ln(\alpha/T_{2\text{cr}}^2)$ versus 1000/$T_{\text{cr}}$ plots for BNBO glass plates (0.5 mm).

The values that are obtained for $E_c$ are $283 \pm 10\text{ kJ mol}^{-1}$ and $432 \pm 10\text{ kJ mol}^{-1}$ for the plate and powdered samples, respectively. These values are in good agreement with that obtained by the approximation-free method (equation (19)). It is clear from equation (22) that the values for the activation energy would not be different for different thicknesses of samples as $T_{\text{cr}}$ is found to be independent of the thickness of the samples (figure 3). The Avrami exponents for BNBO plate (0.5 mm thick) and powdered samples were determined using equation (21). The values for the Avrami exponent ($n$) are $2.5 \pm 0.1$ and $2 \pm 0.1$ for the 0.5 mm thick plate and powdered BNBO glass samples, respectively. Augis and Bennett [34] pointed out that the crystallization with the same $E_c$ but different values of $n$ would exhibit crystallization peaks at the same temperature. The value of $n$ determines the shape of the crystallization peak; the higher the value of $n$, the narrower
the peak. According to equation (23), a sharp peak (small $\Delta T_{\text{FWHM}}$, large $n$) implies bulk crystallization while a broad peak (large $\Delta T_{\text{FWHM}}$, small $n$) signifies surface crystallization. The following expression could be used for estimating the value of $n$:

$$n = \frac{2.5 \cdot T_p^2}{\Delta T_{\text{FWHM}}(E_c/R)}$$

(23)

where $\Delta T_{\text{FWHM}}$ is the width of the crystallization peak at half-maximum. In this study, peak crystallization temperature ($T_p$) and activation energy associated with crystallization, $E_c$, were insensitive to the thickness of the BNBO glass plates. For the glass plates of different thicknesses, the above relation (equation (23)) can be written as

$$n \cdot \Delta T_{\text{FWHM}} = \text{constant.}$$

(24)

It suggests that the product of $n$ and $\Delta T_{\text{FWHM}}$ is constant for glass plates of different thicknesses and can be stated as

$$(n \cdot \Delta T_{\text{FWHM}})_{1} = (n \cdot \Delta T_{\text{FWHM}})_{2}.$$  

(25)

We have calculated the values of $n$ for 1.5 and 2.5 mm thick BNBO glass plates using the values of $\Delta T_{\text{FWHM}}$ for all the glass plates along with the value of $n$ obtained for the 0.5 mm thick glass plates. The obtained values for $n$ are reported in table 1. The value of $n$ generally indicates the mode of crystallization. It is suggested that $n = 4$, 3 and 2 correspond to the volume nucleation, three-, two- and one-dimensional growth, respectively and $n = 1$ suggests surface nucleation, and one-dimensional growth. In this study, the $n$ values for the glass plates indicate volume nucleation accompanied by one-, two- and three-dimensional growth depending on the thickness of the samples, while for the powdered sample, one-dimensional bulk growth is dominant.

4. Conclusions

The glass transition and crystallization behaviour are rationalized in terms of Lasocka formulae. Linear correlations are found between the glass transition and crystallization temperatures and are given as $T_g(K) = 636 + 0.18T_m(K)$ and $T_s(K) = 538 + 0.3T_m(K)$ for BNBO glass plates and powdered samples, respectively. The values of Kauzmann temperature are calculated using the above relations representing the lower bound for the kinetically observed glass transition. The crystallization parameters for BNBO glasses, which are scientifically important, have been analysed using a new approximation-free method derived for non-isothermal experiments. The average value for the crystallization activation energy is $281 \pm 10 \text{kJ mol}^{-1}$ for BNBO glass plates and $424 \pm 10 \text{kJ mol}^{-1}$ for powdered samples. Crystallization temperature and activation energy were found to be independent of the thickness of the BNBO glass plates. However, the value obtained for the Avrami exponent increases with increase in thickness, indicating that the thickness of the samples has a strong influence on the crystallization mechanisms. These thermal parameters are crucial for the fabrication of glass nano/micro-crystal composites.

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