DR. TANMOY PAUL (Orcid ID : 0000-0002-2258-3951)

Thermal and structural investigations of xLi$_2$O-(1-x)Bi$_2$O$_3$ (0.25 ≤ x ≤ 0.35) glasses

T. Paul[a,b*], G. Mountjoy[a] and A. Ghosh[b]

[a]School of Physical Sciences, Ingram Building, University of Kent, Canterbury, CT2 7NH, U. K.

[b]Department of Solid State Physics, Indian Association for the Cultivation of Science, Jadavpur,

Kolkata, 700032, India

Abstract

In this paper we have studied the non-isothermal and isothermal crystallization kinetics

of xLi$_2$O-(1-x)Bi$_2$O$_3$ (0.25 ≤ x ≤ 0.35) glasses using differential scanning calorimetry. Both the

energies of glass transition and crystallization are estimated using the Ozawa and Kissinger

methods for non-isothermal crystallization. The modified Johnson-Mehl-Avrami (JMA) equation

is used to estimate the nature of nucleation and crystal growth during the non-isothermal

crystallization. The nature of nucleation and crystal growth is also determined by the Sestak-

Berggren model for the non-isothermal crystallization. On the other hand the JMA equation

describes the diffusion controlled growth of crystallites for isothermal crystallization. Nature of crystal growth is identified by scanning electron micrographs both non-isothermally and isothermally. In-situ low frequency Raman spectra are analyzed to determine the degree of amorphous naturebelow onset of crystallization temperature for the glasses. Transition from local ordering to high range ordering of Bi-O octahedral units after crystallization is also identified using Raman susceptibility spectra.

Keywords: glasses, quenching, microstructure, thermal analysis, scanning electron microscopy, Raman spectroscopy

*E-mail: paultanmoy00@gmail.com

1. INTRODUCTION

Heavy-metal oxide based glasses such as Bi_2O_3 have applications in the field of optical, opto-electronic devices, thermo-mechanical windows, etc.[1] Eventually, in most of the studies the bismuthate glasses are multicomponent and also are used as precursor for high-T_c superconductors.[2,3] The search on binary glasses especially based on Bi_2O_3 as unique network former is very limited, because Bi_2O_3 does not form glass alone. Studies confirm that for binary glasses the network is built up of $[BiO_3]$ pyramidal units but multicomponent based bismuth glasses are built up of both $[BiO_3]$ and $[BiO_6]$ units.[4,5] Among Bi_2O_3 based binary glasses lithium bismuthate is most interesting in terms of structure as well as Li ion conductivity. X-ray diffraction and scanning electron microscopy (SEM) have shown that the glasses can be made as xLi_2O-$(1-x)Bi_2O_3$ in the range of x = 20 – 35 mol%.[5] A study on optical property has confirmed that Li ion incorporates inside the glass matrix with increasing Li content in the glass.[5] The

enhanced Li ion conductivity in lithium bismuthate glasses proves its applicability as electrolyte in solid state battery.[6] The high thermal stability and mechanical stability and good knowledge of physical property of amorphous nature are necessary for successful application of these glasses in a battery.

It is well known that differential scanning calorimetry (DSC) or differential thermal analyses (DTA) can probe the thermal properties of glasses. These techniques provide quantitative information regarding the nucleation and crystal growth both isothermally and non-isothermally. For isothermal crystallization heat is applied to the glass above the glass transition temperature and the heat absorbed during this process is measured as a function of time.[7] Whereas in non-isothermal crystallization glass is heated at a fixed rate and the change in enthalpy is recorded as a function of temperature.[8,9] Various theoretical models[10-13] have been suggested to obtain the kinetic parameters and the activation energies of crystallization from the isothermal and non-isothermal thermograms. These theoretical models also explain their applicability at different stages of crystallization of glasses.[14-15] To the best of our knowledge the effect of both isothermal and non-isothermal heat treatment on the microstructure of this lithium bismuthate glasses coupled with theoretical models is not investigated before.

Among many quantitative procedures to study the degree of amorphous nature of glasses FT-Raman, infrared, solid state NMR, neutron and synchrotron studies are widely accepted. Both high frequency Raman and neutron studies have confirmed the presence of broad Raman active bands and bismuth-oxygen local structures.[16,17] Recent studies especially on amorphous materials of pharmaceutical importance have shown that low frequency Raman spectrum

(LFRS) is very much sensitive on degree of amorphous nature.[18] This analysis has been also applied in the intriguing glacial state for glass forming liquids.[19] LFRS detects the long range order of crystalline nature confined in the nano-domains and gives sharp peaks in contrary to the high frequency Raman active bands. It seems interesting to analyze the structure using LFRS.

The first objective is to study the kinetics of crystallization both non-isothermally and isothermally in xLi_2O-$(1-x)Bi_2O_3$ glasses of compositions x = 0.25, 0.30 and 0.35 using DSC technique. The activation energy of glass transition and crystallization are obtained by Ozawa and Kissinger equations. The applicability of different models of crystallization is also studied both in non-isothermal and isothermal crystallization cases. SEM is also used to investigate the nucleation and crystallization nature both non-isothermal and isothermal crystallization to validate the theoretical results. Secondly, the LFRS technique is used to determine the degree of amorphous nature by analyzing the *in-situ* Raman active modes. The technique is also applied to find the correlation between the thermal property and Raman spectroscopy.

2. EXPERIMENTAL PROCEDURE

Glass samples of compositions xLi_2O-$(1-x)Bi_2O_3$ (0.25 ≤ x ≤ 0.35) were prepared by melt quenching method. Appropriate amounts of Li_2CO_3 (99.99%, Sigma Aldrich) and Bi_2O_3 (Reagent Plus 99.9%, Sigma Aldrich) in their mole fractions were mixed and pre-heated in alumina crucible at 723 K for 2 h. The mixture was then melted inside an alumina crucible at 1223 K and equilibrated for 30 min. The melt was then quenched rapidly between two copper plates to obtain the desired glass sample. The contamination between the crucible and the glass was

checked in an energy dispersive X-ray fluorescence spectrometer (Panalytical Epsilon 3[X]). The X-ray fluorescence spectrum for all the glasses confirmed the presence of Bi without any contamination of Al (not shown).

The DSC measurements of the powdered glass samples were performed using a differential scanning calorimeter (Netzsch DSC 200 PC) in a constant N_2 gas flow (20 ml min^{-1}). For non-isothermal DSC measurement the glass flakes weighing 20 mg were crushed in powder and poured into an alumina pan and the heat flow difference was measured with respect to an empty reference pan of alumina. This non-isothermal data were collected with a wide range of temperatures at different heating rates (10, 15, 20, 25 and 30 K min^{-1}). In Figure 1 we have represented A as the area under curve between the onset of crystallization temperature (T_X) at T_{on} and completion of crystallization (T_{end}) and A_T as a partial area as shown by hatched region under the curve between the t_{on} and at a particular temperature T. The crystallization volume fraction at T is defined by $\alpha_T = A_T/A$. The onset crystallization temperature T_X is defined as the intersection of the tangent and below the initial change in the baseline slope of each thermogram as shown in Figure 1.

The isothermal DSC measurements for all the compositions were performed by heating the powder glass samples of 20 mg weight in an alumina pan from 580 K to 590 K with a heating rate of 80 K min^{-1} and holding for 20 min. A similar experimental process is also followed by Ref. 10. This temperature range is chosen because it is in the vicinity of the onset of crystallization and also depends on the compositions.

The crystalline nature was checked using a scanning electron microscope (Hitachi S-3400N) after both non-isothermal and isothermal measurements. For microstructure evaluation after non-isothermal crystallization the powder glass samples were heated at different heating rates (10 - 30 K min^{-1}) at various onset crystallization temperatures (T_X) in alumina pan in the calorimeter and then extracted from the alumina pan for SEM analysis after cooling down from T_X. For isothermal heat treated glasses the powder glass samples were studied for isothermal DSC measurements (as stated before) and then extracted from alumina pan.

Raman spectra were recorded in a Raman spectrometer (Jobin Yvon HR 640) attached to Olympus (BX40) microscope in range 100 – 1000 cm^{-1} from RT to 773 K with heating rate 10 K min^{-1}. A HeNe laser with wavelength 632.8 nm and 0.5 mW energy were used to avoid local heating. The accumulation time was typically 10 s and the spectral resolution was better than 1 cm^{-1}. As the Raman scattering is sensitive to micro-crystals we also checked at least 40 glass flakes under Raman microscope to confirm the uniformity of amorphous nature in glasses. The glass samples beyond (0.25 ≤ x ≤ 0.35) exhibit crystallinity in Raman spectra (see Figure S1). This restricts our studies to x = 0.25, 0.30 and 0.35 compositions.

3. THEORETICAL CONSIDERATIONS

A. Non-isothermal crystallization

Non-isothermal crystallization is studied to estimate the activation energies for both glass transition and crystallization peaks. The activation energy is obtained by inspecting the shift in the crystallization peak at different heating rates. Actual determination of the activation energy

can be obtained by DSC using Ozawa[11,12] and Kissinger[8] methods. The activation energy for glass transition (E_{Og}) as obtained from the Ozawa method[12] is given by

$$\ln(\beta) = -\frac{E_{Og}}{RT_g} + \text{constant} \tag{1}$$

, where β is the heating rate and R is the universal gas constant. Generally the value of E_{Og} is calculated from the slope of linear least square fit between $\ln(\beta)$ and $1000/T_g$. The estimation of activation energy for glass transition (E_{Kg}) is also obtained from Kissinger method[8] as

$$\ln\left(\frac{\beta}{T_g^2}\right) = -\frac{E_{Kg}}{RT_g} + \text{constant}$$

$$\tag{2}.$$

The activation energy for crystallization in non-isothermal process is also obtained using the heating rate dependence of T_c. Using the Ozawa method we can write[12]

$$\ln(\beta) = -\frac{E_{Oc}}{RT_c} + \text{constant} \tag{3}$$

and using the Kissinger method we can also write [8]

$$\ln\left(\frac{\beta}{T_c^2}\right) = -\frac{E_{Kc}}{RT_c} + \text{constant}$$

$$\tag{4}.$$

Here E_{Oc} and E_{Kc} are the activation energies of crystallization determined using Ozawa and Kissinger methods respectively. Some authors[13,20] have applied the Johnson-Mehl-Avrami (JMA) equation for the non-isothermal crystallization to estimate the nature of crystallization. However JMA equation is derived for the isothermal crystallization previously (see Section B

below). Matusita *et al.* [21,22] have shown a technique to analyze the non-isothermal crystallization on the basis of nucleation and crystal growth as

$$\ln[-\ln(1-\alpha)]=-n\ln\beta-1.052m\left(\frac{E_c}{RT}\right)+\text{constant}$$

(5)

, where m is related to crystal nucleation. The numerical factor (1.052) comes during integral approximation [9]. Eqn. (5) is called modified JMA equation. A typical plot can be obtained between $\ln[-\ln(1-\alpha)]$ against $\ln(\beta)$ at different crystallization temperatures. The slope of the plot gives the value of the Avrami exponent n signifying the nature of crystal nucleation and growth.[22-26] For equal values of m an n it indicates the surface crystallization in two dimension. When the bulk crystallization predominants then m = 3, n = 4 suggesting three dimension crystal growth.[22]

Occassionally, the kinetic equation of DSC curve is also described by the following equation[25]

$$\Phi=\Delta H\cdot\Gamma\cdot e^{-\frac{E}{RT}}\cdot f(\alpha)$$

(6),

where Φ is the measured heat flow, ΔH is the crystallization enthalpy, Γ is the pre-exponential factor, E is the activation energy of the process and $f(\alpha)$ is the expression of a kinetic model with α is the conversion or volume fraction factor. Using JMA model we can also write[24]

$$f(\alpha)=-m'(1-\alpha)[\ln(1-\alpha)]^{1-\frac{1}{n'}}$$

(7)

, where m′ and n′ describe the nucleation and crystal growth mechanism. Previously this law has been used only for isothermal conditions, but Henderson[26,27] has extended the applicability of this model to the non-isothermal cases. According to Henderson for non-isothermal crystallization the nucleation starts first and finishes after the crystal growth. Nevertheless Malek has defined the characteristic functions say, y(α) and z(α)[28,29] as

$$y(\alpha) = \frac{d\alpha}{dT} e^{\frac{E}{RT}}$$

(8)

$$z(\alpha) = \beta \frac{d\alpha}{dT} T^2$$

(9).

Both functions depend on the crystallization observed in the glassy system and with these two functions the applicability of JMA model can be checked.[28,29] Here E is the apparent activation energy and can be obtained from the Kissinger plot of the crystallization peak (T_c) more accurately.

We have extended our studies using the Sestak-Berggren (SB) model[30] to check its applicability for the non-isothermal crystallization. The SB model can be written as

$$\frac{d\alpha}{dt} = k\alpha^{m''}(1-\alpha)^{n''}[-\ln(1-\alpha)]^{p''}$$

(10),

where dα/dt is the rate of reaction, k is the rate constant and m″, n″, p″ are the shape parameters to determine the shape of the non-isothermal DSC thermogram. The values of n″ and p″ signify the occurrence of some complex transformation processes regarding nucleation and growth of crystal.

B. Isothermal crystallization

It is interesting to analyze the isothermal crystallization for the present system using the

JMA equation[31-35]

$$\alpha = 1 - \exp\left[-(\kappa t)^{\ell} \right] \qquad (11)$$

, where κ is the rate constant and depends on both nucleation rate and crystal growth, and

ℓ is the Avrami exponent signifying the morphology of nucleation and crystal growth. κ is

related to the effective activation energy (E_{JMA}). The temperature dependence of κ is given by

$$\kappa = \kappa_0 \exp\left(-\frac{E_{JMA}}{RT} \right) \qquad (12),$$

where κ_0 is the pre-exponential factor and is related to the number of nuclei per unit volume.

As the number of nuclei is constant during the isothermal process κ_0 can be taken as constant.

C. Raman spectroscopy

The intensity of low frequency Raman spectrum for disordered materials can be converted to

reduced intensity [18] by

$$I_r(\nu) = \frac{I^R(\nu)}{[\nu(n(\nu)+1)]} \qquad (13a)$$

,where $\qquad n(\nu) = \frac{1}{e^{\frac{h\nu}{\kappa T}} - 1} \qquad (13b).$

n(v) is the Bose occupation number. $I^R(v)$ is the experimental Raman intensity and v is the Raman shift in cm^{-1}. The quasi-elastic component of the Raman intensity ($I_q(v)$) is also determined by curve fitting as described in Ref. 18. Generlly, $I_q(v)$ is obtained by peak fitting of Lorentzian shape of $I^R(v)$ which is centered at zero. In this occasion the Raman succeptibility can also be calculated as

$$\chi''(v) = \left[I_r(v) - I_q(v) \right] v \tag{14}.$$

The Raman succeptibility is also correlated with the vibrational density of states (VDOS) $G(v)$ as

$$\chi''(v) = \frac{C(v)}{v} G(v) \tag{15}.$$

$C(v)$ is known as light-vibration coupling coefficient. Most important of these mathematical expressions is the determination of VDOS from Raman spectra.

4. EXPERIMENTAL RESULTS

A.   Non-isothermal crystallization

The non-isothermal DSC thermograms at different heating rates for all the compositions are shown in Figure 2. The curves show an endothermic baseline shift (exotherm: ↑) signifying the glass transition (T_g) followed by the exothermic onset (T_X) and exothermic peak (T_c) which represents the maximum crystallization. There is no thermal "overshoot" observed between T_g and T_c which differentiates oxide glasses from bulk metallic glasses. It is observed that with increasing heating rate the glass transition and the peak for crystallization both shift towards higher temperatures. The shift in T_g with different heating rate reflects the kinetic nature of

glass transition. Additionally the shift in T_c depends on the induction time associated with the nucleation process.[36] As the heating rate increases this induction time increases from zero to further time leading to shift in crystallization temperature. Since the crystallization increases with increasing heating rates, the volume fraction of crystalline nature increases at a greater rate in shorter time and as a result peak height increases.

B.   Isothermal crystallization

For studying the isothermal crystallization a typical thermogram at 587 K is shown in Figure 3 for x = 0.25. The experimental volume fraction α is plotted as a function of time t in the inset of Figure 3. The initial stage of the curve corresponds to the start of the nucleation. The increase of α in the intermediate time signifies the increase of the nucleation and crystal growth. The final stage shows the saturation of the nucleation and growth of crystal as observed earlier for non-isothermal crystallization. Similar nature is also obtained for other glasses.[37,38]

C.   Raman study

Figure 4 shows the in-situ Raman spectra for all the compositions. Below onset of T_c the glasses mainly consist of broad peaks. The broad peaks below onset of T_c indicate the disordered nature of the glass structure.[16] These broad peaks are deconvoluted to obtain the exact band position as described later. The spectra look similar for all compositions below the onset of T_c. Inspecting the composition dependence of the Raman spectra one observes the intense and sharp peak ca. 125 cm^{-1} which remains at the same position after crystallization.

Interestingly at 300 cm^{-1} a sharp peak is observed after crystallization which is due to Bi-O vibration. Whereas the shoulder peak ca. 500 cm^{-1} has similarity for all the compositions below onset of T_c but shifts towards lower frequency side after crystallization. A different intensity profile is obtained for x = 0.35 in Figure 4(c) above onset of T_c.

5. DISCUSSION

A.   Non-Isothermal crystallization

In this section we describe the parameters obtained from fitting for non-isothermal crystallization. One of the most important parameters for the stabilization of the glass is the activation energy for glass transition. This energy is needed to relax atoms from the amorphous state. The value of E_{Og} is calculated from the slope of linear least square fit between ln(β) and 1000/T_g as shown in Figure 5. The Kissinger plot is shown in the inset of Figure 5. The calculated E_{Og} and E_{Kg} are obtained as 429 kJ mol^{-1} and 420 kJ mol^{-1} respectively for the composition x = 0.25. The values of E_{Og} and E_{Kg} for all compositions are presented in the supporting information (Table S1). It is found that both the values are close to each other indicating the applicability of both methods. Please note that T_g depends on the heating rate varying from 540 – 546 K, or 1.1% and similarly T_c depends on the heating rate varying from 601 – 611 K, or 1.7%. Since the variation of T is very small as compared to that of heating rate, then after expanding the logarithm part of eqns. (2 and 4) they correspond to eqns. (1 and 3). This may be possible reason for similar activation energies.

The activation energy of crystallization is also obtained using the heating rate dependence of T_c. Figure 6 shows the estimation of E_{Oc} using ln(β) plotted against 1000/T_c.

Similarly the plot of $\ln(\beta/T_c^2)$ vs $1000/T_c$ is also shown in the inset of Figure 6. The estimation of

E_{Oc} and E_{Kc} are 93 kJ mol^{-1} and 98 kJ mol^{-1} respectively for the composition x = 0.25 and the

values for all compositions are also listed in Table S1. Similar values of the activation energy

indicate the validity of both Ozawa and Kissinger approaches. It is further obtained that the

activation energy for crystallization is lower than that of glass transition except for x = 0.35

composition which has complex exothermic peak (see Figure 2(c)). For sodium bismuthate

glasses[14] and bulk metallic glass[39] two closely spaced crystallization peaks are obtained which

indicate faster kinetics of two different phases. It is thus quite conceivable that for present

system the crystallization has single phase. On the other hand, above T_g the glass system has a

tendency to shift either to a stable equilibrium state (crystalline state) or a metastable state

(supercooled liquid).[40] Eventually for most of the oxide glasses including our system the shift

occurs towards the crystalline state. For metallic glasses the shift towards metastability

employing structural relaxation coupled with physical aging.[40] It is also found that the glass

transition corresponds to primary electrical relaxation for bulk metallic and oxide glasses due to

presence of traditional glass former.[41] The electrical relaxation for the present system shows

strong temperature dependence.[6] As a result the glass transition may be connected with

electrical relaxation although Bi_2O_3 is not a glass former by itself. In general, the activation

energy for glass transition is related to the molecular motion around glass transition so that

higher value for energy of glass transition is needed than that of the energy for crystallization.

This is in agreement with that of previous study.[6] The higher activation energy for glass

transition also indicates slower grain growth than the nucleation process.[42] Addintionally, for bismuthate glasses with lower Li_2O content the Li occupies intersticial sites of BiO_6 octahedral units to compensate the excessive negative charge and thus the ionic conductvity is shown to be low.[6] However, in the current composition range the Li ions acts as charge compensator and as a result the relatively strong bonds Bi-O are replaced by weak ionic Li-O bonds in the network. This manifests as the decrease of the activation energy with increasing Li content.[6,43] This analysis proves the incorporation of Li ions in glass matrix.

The volume fraction (α) of crystallization during the non-isothermal crystallization at different heating rates is shown in Figure 7(a). The curves in Figure 7(a) look like sigmoidal type. The initial shape represents the beginning of nucleation, the intermediate rise indicates the increased nucleation rate and the final stage shows the saturation of nucleation and growth of crystal as shown in Figure 7(a). Figure 7(b) shows the plot of ln[-ln(1-α)] against ln(β) at different crystallization temperatures using eqn. (5). The slope of the plot gives the value of the Avrami exponent n signifying the nature of crystal nucleation and growth.[23,24] The value of n obtained for all the glass samples is listed in the supporting information (Table S2). It has been found that with increasing crystallization temperature the dimensionality of nucleation and crystal growth decreases for all the compositions. At low temperatures three dimensional or spherical growth of particles is observed whereas it reduces to two dimensional or disc like as temperature increases thereafter.

Figure 8(a) shows the spherical crystal growth in SEM image at 600 K whereas at 614 K Figure 8(b) represents the attached-disc like crystal growth for the composition x = 0.25. A similar result is also obtained for other compositions. The surface morphology in Figure 8(a) suggests the lithium incorporation in the glass matrix and spherical growth (3 dimensional) at a constant rate. As temperature increases the growth process is predominantly over the surface and two dimensionally it resembles an attachment of discs. The surface morphology of glasses is also studied using SEM for GeS_2-Ga_2S_3 glass ceramics .[44] Different types of crystallinity are obtained due to phase segregation in the glass matrix.[44] Consequently, for our system one type of crystal signifies a single phase.

The analysis on non-isothermal crystallization is extended further by calculating two nonlinear parameters say, y(α) and z(α). The y(α) and z(α) functions for the glass compositions are presented in Fig. 9. The data are normalized on both axes for clarity. Both functions are sensitive to the heating rates as observed in Figure 9. In Figure 9(a) and (c), y(α) initially increases rapidly but decreases monotonically for x = 0.25 and 0.30 respectively, whereas the shape changes for the composition x = 0.35 due to the different shape of the crystallization peak (See Figure 3(c) and Figure 9(e)). This information indicates more complex phenomenon of crystallization kinetics for x = 0.35. As observed in Figures 8(b), (d) and (f) the maximum of z(α) function for all the heating rates are around 0.50 which is far away from the expected value [$\alpha_{max,z}$ = 0.632 (theoretically)] and this indicates the insufficiency of the JMA equation.[30] This notable difference from 0.632 may be due to preparation of fine powder (< 1 μm).[45] As

previously stated that JMA equation describes the isothermal crystallization but the approach is unclear when the nucleation gets completeness prior to the growth of the crystalline nature. But present system may have the situation where the nucleation process and the growth of tiny crystallites occur together after the adsorbed water is removed from the glass upon heating. This deviation further indicates increasing complexity in crystallization process and there may chances of mutual overlapping of nucleation and crystal growth.[46] It is interesting to say that Figure 7(b) describes the outcome of modified JMA equation and it is unclear whether the nucleation and crystal growth occurs simultaneously or not. However, SEM studies confirm that for x = 0.25 at 600 K which is actually in an increased zone of nucleation (say for 10 K min^{-1} in Figure 7(a)) it has crystal growth. Thus it is concluded that there is mutual overlapping in nucleation and crystal growth.

Figure 10 shows dependence of dα/dt on the volume fraction α at different heating rates. The solid line represents the fit using eqn. (10). The fitting also confirms the validation of the SB model. The fitting parameters are also listed in the supporting information (Table S3) are inferring the faster kinetic processes. The values of n″ and p″ signify the occurrence of some complex transformation processes regarding nucleation and growth of crystals. The consistency of values over the temperature range for both n″ and p″ indicates the same type of transformation processes and also justifies homogeneous nucleation and controlled growth of crystals simultaneously.[30] This analysis also confirms the homogeneous crystal growth as identified by SEM studies.

B.   Isothermal

In this section we describe the applicability of JMA equation. The fitting of eqn. (11) using JMA equation is shown in the inset of Figure 3. The value of ℓ = 2.00 ± 0.02 indicates the crystallization process via diffusion controlled growth with constant nucleation rate.[24] A similar type of two dimensional growth is also obtained for $Ti_{16.7}Zr_{16.7}Hf_{16.7}Cu_{16.7}Ni_{16.7}Be_{16.7}$ type high entropy bulk metallic glass and $Zr_{60}Al_{15}Ni_{25}$ bulk amorphous alloy.[42,47] Interestingly for $Ca_{65}Mg_{15}Zn_{20}$ bulk metallic glass the Avrami exponent decreases from 3 to 2 with raising the annealing temperature.[39] The impingement effect and heterogeneous distribution of nuclei plays an important role apart from the diffusion controlled crystal growth for the decreasing nature of the dimensionality.[39] In an auxiliary experiment for Li_2O-$2SiO_2$ glass it is shown that with change in T_X the Avrami exponent does not change.[48] We have extended this idea by examining the crystallinity after isothermal crystallization for different compositions and at different T_X's. In order to check the transformation from the amorphous to crystalline state the sample is also studied by scanning electron microscope. Figure 11shows the change in the morphology under isothermal crystallization; (a) for the x = 0.25 at 587 K (b) for x = 0.30 at 608 K and (c) for x = 0.35 at 587 K. The particle size is observed to be composition dependent. This is because of different shape of the crystallization peak (see Fig. 2). It is evident that the crystalline morphology is random and covers the specimen surface completely. In addition, the small crystallites represent the laminar or two-dimensional morphology. This characteristic phenomenon of two dimensional crystalline nature is observed by the isothermal study using the JMA equation. It is to be noted that for isothermal crystallization the shape of crystalline

peak describes the three stages of crystal growth. However, the present theoretical support does not allow them to be separated out. On the other hand both the theoretical and experimental analysis for non-isothermal crystallization describe the whole process as stated in this paper.

C.   Raman spectra

To get exact positions of Raman active bands we have deconvoluted each spectrum with Gaussian peaks for all temperatures. After deconvolution main Raman active bands below the onset of T_c are obtained at ca. 125, 169, 380, 492 and 592 cm^{-1} . The deconvoluted spectrum at room temperature for x = 0.25 is shown in Figure 12(a). Main Raman active bands due to Bi-O are obtained in the spectrum. The low frequency band ca. 125 cm^{-1} and the shoulder band ca. 169 cm^{-1} are due to vibration of Bi-O.[16,49] The band ca. 125 cm^{-1} becomes sharper with increasing Li content without any noticeable shift. The broad bands at 380 and 493 cm^{-1} are due to Bi-O-Bi stretching vibration of BiO_6 octadedra.[16] The band at 592 cm^{-1} can be ascribed due to vibrations of the Bi-O-Bi in the distorted BiO_6 octahedra.[49]

The composition dependence of the full width at half maximum for all the Raman active modes are presented in Figure 12(b) at room temperature. It is observed that the FWHM for the band ca. 125 cm^{-1} is small and the FWHM remains constant for all compositions. The composition dependence of FWHM for bands ca. 380, 592 and 169 cm^{-1} have small changes. Since with increasing Li content there is no extra peak arising, we can confirm that the Li ion modifies the Bi-O structure without any Li enriched secondary phases. The FWHM variation at

different temperatures below onset of T_c is not shown as they are similar to that of Figure 12(b).

In this connection the reduced intensity profiles for all the compositions are shown in Figure 13. All the spectra look similar with that of Figure 4 below onset of T_c. The broad band at 493 cm^{-1} has reduced sharpness in this plot which is the characteristic nature of reduced intensity plot. The similar intensity profile below onset of T_c confirms temperature independent nature of the β type relaxation process.[18] On the other hand the reduced intensity profiles above onset of T_c are similar to each other in Figure 13. The difference in intensity profile below and above onset of T_c suggests the structural anomaly with change in β type relaxation process.[18] It is to be noted that the non-isothermal heat treatment corresponds to the primary electrical relaxation. As stated earlier the sharp peak at ca. 300 cm^{-1} above the onset of T_c for all compositions also corresponds to Bi-O vibrational mode of Bi_2O_3.[50] This peak also signifies the crystallinity in bismuth oxide compound. Thus the transition from glassy state to crystalline state makes the strong bond between Bi and O and then the vibrations due to BiO_6 polyhedra become obvious.

Using the mathematical expressions the Raman susceptibility for all the compositions is presented in Figure 14. We have presented data up to 150 cm^{-1} as our interest is only on the structural arrangements in the short range. The vibrational spectra are found to be superimposed for x = 0.25 and 0.30 above onset of T_c in Figures 14(a) and (b). The non-superimposed spectra below onset of T_c for Figures 14(a) and (b) and that for x = 0.35 in Figure 14(c) at all temperatures indicate the small temperature dependence of quasi-elastic vibrations

of Bi-O units. The change in shape of the spectra is also due to difference in quasi-elastic component and as a result the local ordering is different from liquid like phase (below onset of T_c) to solid phase (above onset of T_c). Also for x = 0.35 the local ordering in liquid phase is also temperature dependent. This is the reason for why the glass cannot be formed with further doping of Li. The Raman susceptibility is considered as representative of VDOS and here the VDOS is temperature dependent as well as composition dependent. The variation in shape of the spectra with temperature above onset of T_c indicates different phonon vibrational modes of different crystalline forms.[18] The absence of sharp peaks and broadness of humps below onset of T_c in Figure 14 indicate the highest degree of disordered nature of glass. Higher number of phonon modes or broad bands above onset of T_c indicates long range ordering in crystalline state as observed in Figure 14. Since only phonon mode of Bi-O is detected at low wavenumbers it can be concluded that Bi plays important role in formation of glass structure. With increasing temperature the broadness of humps changes irregularly. The only conclusion that can be drawn that this low frequency range is most sensitive in detecting crystalline phase and transformation from liquid state to solid state happens only when the local structure around Bi changes. Nevertheless, the increasing concentration of Li only helps to distort BiO_6 polyhedra. So VDOS can be used to analyze the structure when the Intensity profiles of experimental Raman spectra look similar. Our approach can be extended further for other glasses.

Regarding the present analysis we can say that the appropriate model to analyze the kinetics data is not simple. Despite the simplicity of exotherms at crystallization peaks, obtained both non-isothermally and isothermally, the best parametric approach has to be chosen. As

demonstrated here the well-known JMA model may not be suitable for describing the non-isothermal kinetics although it fits nicely with isothermal kinetics. The reverse can also be true and may be studied for some other glasses in the future. The non-applicability of a model may be due to microstructure (bulk, coarse powder (< 100 μm), or fine powder (< 1 μm)), heating rate for non-isothermal process, and isotherm obtained at the onset of T_x. In this point of view, we recommend to fit the experimental data on the basis of the model which has largest parameters. It is also helpful to monitor the model based prediction by other auxiliary experiments (say, SEM, Raman etc).

6. CONCLUSIONS

Crystallization kinetics have been studied for the glass system $xLi_2O-(1-x)Bi_2O_3$ using the DSC technique. The values of activation energies for both glass transition and crystallization have been determined using Ozawa and Kissinger methods for non-isothermal crystallization respectively. The Sestak-Berggren model is found to be appropriate to describe the non-isothermal crystallization. The values of the shape parameters obtained from Sestak-Berggren model fitting describe the complex transformations during the simultaneous nucleation to growth of crystallization processes. Spherical to disc like crystal growth is obtained from SEM analysis for non-isothermal crystallization. The Johnson-Mehl-Avrami equation is found to agree with the isothermal crystallization process. Raman spectroscopy is also used to find the degree of disorder and formation of crystalline phases after crossing the crystallization temperature. Both the primary and secondary relaxations are confirmed through the thermal and vibrational analyses.

ACKNOWLEDGEMENT

References

1.   Hall DW., Newhouse MA, Borrelli NF, Dumbaugh WH. Nonlinear optical susceptibilities of high-index glasses. *App. Phys. Lett*. 1989;54:1293.

2.   Komatsu T, Sato R, Imai K, Matusita K, Yamashita T. Preparation of High-Tc Superconducting Bi-Pb-Sr-Ca-Cu-O Ceramics by the Melt Quenching Method. *Jpn. J. Appl. Phys. Part 1*, 1988;27:L550.

3.   Minami T, Akamatsu Y, Tatsumisago M, Tohge N, Kowada Y. Glass Formation of High-Tc Compound BiCaSrCu2Ox by Rapid Quenching. *Jpn. J. Appl. Phys. Part 1*, 1988; 27: L777.

4.   Zheng H, Xu R, Mackenzie JD. Glass formation and glass structure of BiO1.5–CuO–Ca0.5Sr0.5O system. *J. Mater. Res*. 1989;4:911-915.

5.   Hazra S, Mandal S, Ghosh A. Properties of unconventional lithium bismuthate glasses, *Phys. Rev. B* 1997;56**:** 8021.

6.   Pan A, Ghosh A. Dynamics of lithium ions in bismuthate glasses. *J. Chem. Phys*. 2000;112:1503.

7.   Avrami M. Kinetics of Phase Change. I General Theory. *J. Chem. Phys*. 1939;7:1103.

8.   Kissinger HE. Reaction Kinetics in Differential Thermal Analysis. *Anal. Chem*. 1957;29:1702-1706.

9.   Matusita K, Komatsu T, Yokota R. Kinetics of non-isothermal crystallization process and activation energy for crystal growth in amorphous materials. *J. Mater. Sci.* 1984;19:291-296.

10.   Xia X, Dutta I, Mauro JC, Aitken BG, Kelton KF, Temperature dependence of crystal nucleation in BaO·2SiO2 and $5BaO·8SiO_2$ glasses using differential thermal analysis. *J. Non-Cryst. Solids* 2017;459:45-50.

11.   Taniguchi A, Tatsumisago M, Minami T., Crystallization Kinetics of α-AgI in Ag I-Based Silver Orthoborate Glasses. *J. Am. Ceram. Soc*. 1995;78:460-464.

12.   Ozawa T. Kinetic analysis of derivative curves in thermal analysis. *J. Therm. Anal.* 1970;2:301-324.

13.   Kizilaslan O, Kirat G, Ali AM. Thermal and structural characterization of the $Bi_{2-x}Sm_xSr_2Ca_2Cu_3O_{10+\delta}$ glass-ceramic system. *Int. J. Appl. Glass Sci*. 2016;00:1-8.

14.   Al-Assiri MS, Tashtoush NM, Ragab HS, El-Desoky MM. Physical properties of unconventional binary sodium bismuthate glasses. *Phys. Stat. Sol. A*. 2008;205:1540-1545.

15.   Shaaban ER, Mohamed SH. Thermal stability and crystallization kinetics of Pb and Bi borate-based glasses. *J. Therm. Anal. Calorim.* 2012;107:617-624.

16.   Pan A, Ghosh A. Structural and optical properties of lithium bismuthate glasses. *J. Mater. Res.* 2002;17:1941-1944.

17.   Watanabe T, Nanba T, Miura Y. X-ray and neutron scattering study of the structure of lithium bismuth oxide glass. *J. Non Cryst. Solids* 2002;297:73-83.

18.   Hedoux A, Paccou L, Guinet Y, Willart JF, Descamps M. Using the low-frequency Raman spectroscopy to analyze the crystallization of amorphous indomethacin. *Euro. J. Pharm. Sci.* 2009;38:156-164.

19.   Hedoux A, Guinet Y, Descamps M. Size dependence of the Raman spectra in an amorphous–nanocrystalline mixed phase: the glacial state of triphenyl phosphite. *J. Raman Spectrosc.*, 2001;32**:**677-688.

20.   Marseglia EM*. Kinetic theory of crystallization of amorphous materials. J. Non-Cryst. Solids* 1980;41**:**31-36.

21.   Matusita K, Sakka S. Kinetic study of crystallization of glass by differential thermal analysis—criterion on application of Kissinger plot. *J. Non-Cryst. Solids*, 1980;38&39:741-746.

22.   Matusita K, Komatsu T, Yokota R. Kinetics of non-isothermal crystallization process and activation energy for crystal growth in amorphous materials. *J. Mater. Sci.* 1984;19:291.

23.   Avrami M. Granulation, Phase Change, and Microstructure Kinetics of Phase Change. III. *J. Chem. Phys*. 1941;9:177.

24.   Málek J. The applicability of Johnson-Mehl-Avrami model in the thermal analysis of the crystallization kinetics of glasses. *Thermochim. Acta*, 1995;267:61-73.

25.   Málek J, Klikorka J. Crystallization Kinetics of Glassy GeS_2. *J. Therm. Anal.,* 1987;32:1883-1893.

26.   Henderson DW. Thermal analysis of non-isothermal crystallization kinetics in glass forming liquids. *J. Non Cryst Solids*, 1979;30:301-315.

27.   Henderson DW. Experimental analysis of non-isothermal transformations involving nucleation and growth. *J. Therm. Anal* Calorim. 1979;15:325-331.

28.   Brown ME, Maciejewski M, Vyazovkin S, Nomen R, Sempere J, et al, Computational aspects of kinetic analysis: Part A: The ICTAC kinetics project-data, methods and results. *Thermochim. Acta,* 2000; 355:125-143.

29.   Málek J, Matsuda S, Watanabe A, Ikegami T, Mitsuhashi T. Crystallization kinetics of zirconia-yttria gels. *Thermochim. Acta*, 1995;267:181-194.

30.   Šesták J, Berggren G. Study of the kinetics of the mechanism of solid-state reactions at increasing temperatures. *Thermochim. Acta*, 1971;3:1-12.

31.   Leal JLC, Vazquez J, Barreda DGG, Palma RG, Alemany PLL, Villares P. Analysis of the glass–crystal transformation kinetics by means of the theoretical method developed (TMD) under both non-isothermal and isothermal regimes. Application to the crystallization of the $Ag_{0.16}As_{0.34}Se_{0.50}$ glassy alloy. *J. Alloy. Compd*. 2015;622:610-617.

32.   Taghvaei AH, Eckert J. A comparative study on the isochronal and isothermal crystallization kinetics of $Co_{46.45}Fe_{25.55}Ta_8B_{20}$ soft magnetic metallic glass with high thermal stability. *J. Alloy. Compd*. 2016;675:223-230.

33.   Akhtar D, Mathur RP. Isothermal crystallization kinetics of $Ni_{60}Nb_{40-x}Cr_x$ glasses. *J. Mater. Sci*. 1987;22:2509-2514.

34.   Lu K, Wang JT. Crystallization kinetics of Ni-P glass — activation energies for nucleation and growth of nuclei. *J. Mater. Sci*. 1988;23:3001-3005.

35.   Cheng K. Determining crystallization kinetic parameters of $Li_2O–Al_2O_3–SiO_2$ glass from derivative differential thermal analysis curves. *Mater. Sci. Eng. B* 1999;60:194-199.

36.   Khan ZH, Khan SA, Alvi MA. Study of Glass Transition and Crystallization Behavior in $Ga_{15}Se_{85-x}Pb_x$ (0 ≤ x ≤ 6) Chalcogenide Glasses. *Acta Phys. Pol A* 2013;123:80-86.

37.   Prasad NS, Varma KBR. Crystallization Kinetics of the $LiBO_2–Nb_2O_5$ Glass Using Differential Thermal Analysis. *J. Am. Ceram. Soc.* 2005;88:357-361.

38.   Deb B, Ghosh A. Kinetics of crystallization in selenium molybdate glass. *J. Non Cryst. Solids* 2014;385:30-33.

39.   Hu L, Ye F. Crystallization kinetics of Ca65Mg15Zn20 bulk metallic glass. *J. Alloy. Compd*. 2013;557:160-165.

40.   Qiao JC, Pelletier JM. Dynamic mechanical relaxation in bulk metallic glasses: a review. *J. Mater. Sci. Technol.* 2014; 30:523-545.

41.   Lunkenheimer P, Schneider U, Brand R, Loid A. Glassy dynamics. *Contemp. Phys*. 2000;41:15-36.

42.   Gong P, Yao KF, Ding HY. Crystallization kinetics of TiZrHfCuNiBe high entropy bulk metallic glass. *Mater. Lett*. 2015; 156:146-149.

43.   Fu J. Lithium alkaline earth bismuthate glasses. *Phys. Chem. Glasses* 1996;37:84.

44.   Qu G, Zhai S, Xu Y, Dai S, Tao H. et al. The Effect of PbS on Crystallization Behavior of GeS2-Ga2S3-Based Chalcogenide Glasses. *J. Am. Ceram. Soc*. 2014;97:3469-3474.

45.   Málek J. Kinetic analysis of crystallization processes in amorphous materials. *Thermochim. Acta*. 2000;355:239-253.

46.   Chrissafis K, Kyratsi T, Paraskevopoulos KM, Kanatzidis MG. Crystal/Glass Phase Change in KSb5S8 Studied through Thermal Analysis Techniques. *Chem. Mater*. 2004;16:1932-1937.

47.   Yan Z, Dang S, Wang X, Lian PX. Applicability of Johnson-Mehl-Avrami model to crystallization kinetics of Zr60Al15Ni25 bulk amorphous alloy. *Trans. Nonferrous Met. Soc. China* 2008; 18:138-144. 48.   Ray CS, Zhang T, Reis ST, Brow RK. Determining kinetic parameters for isothermal crystallization of glasses. *J. Am. Ceram. Soc*. 2007;90:769-773.

.   .

.

49. Kharlamov AA, Almeida RM, Heo J. Vibrational spectra and structure of heavy metal oxide glasses. *J. Non-Cryst. Solids* 1996;202**:**233-240.

50. Udovic M, Thomas P, Mirgorodsky A, Durand O, Soulis M, Masson O, M-Mejean T. C-Mesjard JC. Thermal characteristics, Raman spectra and structural properties of new tellurite glasses within the Bi_2O_3–TiO_2–TeO_2 system. *J. Solid State Chem*. 2006;179:3252-3259.

Figure captions:

FIGURE 1. A schematic diagram of a DSC curve is shown for evaluating α_T.

FIGURE 2. (Color online) The non-isothermal DSC curves for the sample of xLi_2O-$(1-x)Bi_2O_3$ at several heating rates. Exotherms are in upward direction.

FIGURE 3. (Color online) The isothermal DSC curve under the crystallization region for the composition x = 0.25 at 587 K. The dotted line represents the base line. In the inset the time dependence of α is shown. The solid line is the fit using Eq. (11).

FIGURE 4. (Color online) Raman spectra for (a) x = 0.25; (b) x = 0.30 and (c) x = 0.35 at different temperatures.

FIGURE 5. (Color online) The Ozawa plot for glass transition for the composition x = 0.25. The Kissinger plot for glass transition is shown in the inset. The solid line represent the linear least square fit for determining the activation energies of glass transition.

FIGURE 6. (Color online) The Ozawa plot for crystallization process for the composition x = 0.25. The Kissinger plot for crystallization is shown in the inset. The solid line represents the linear least square fit to determine the activation energies of crystallization.

FIGURE 7. (Color online) (a) The variation of crystallization volume fraction α with temperature at different heating rates for the composition x = 0.25. (b) Matusita plot at different temperatures of crystallization for the composition x = 0.25. The solid lines are the linear least square fits.

FIGURE 8. The SEM images at (a) 600 K and (b) at 614 K indicate the spherical and disc like crystal growth respectively for the composition x = 0.25.

FIGURE 9. (Color online) Normalized y(α) in (a) and z(α) in (b) for x = 0.25 respectively; y(α) in (c) and z(α) in (d) for x = 0.30 respectively; y(α) in (e) and z(α) in (f) for x = 0.35 respectively at different heating rates.

FIGURE 10. (Color online) Normalised dα/dt plot for the composition x = 0.25 at different heating rates. The solid line represents the fitting of Sestak-Berggren method.

FIGURE 11. (Color online) (a), (b) and (c) show the surface crystallization for the composition x = 0.25, x = 0.30 and x = 0.35 respectively. The isothermal heat treatment was at 587 K, 608 K and 587 K for x = 0.25, 0.30 and 0.35 respectively.

FIGURE 12. (Color online) (a) Deconvoluted Raman spectrum for x = 0.25 at room temperature. The overall fitting profile is shown by dotted line. (b) The composition dependence of FWHM for different vibrational modes at room temperature.

FIGURE 13. (Color online) Reduced intensity plot at different temperatures for (a) x = 0.25; (b) x

= 0.30 and (c) x = 0.35.

FIGURE 14. (Color online) Raman susceptibility plot at different temperatures for (a) x = 0.25;

(b) x = 0.30 and (c) x = 0.35.

(a)

200 nm

(b)

200 nm

(a) 100 µm

(b) 100 µm

(c) 100 µm