

# Structural relaxation due to sub- $T_g$ annealing in Se-Te-Zn chalcogenide glasses

S. FAHEEM NAQVI\*, N. S. SAXENA

*Semi-conductor & Polymer Science Laboratory, 5-6, Vigyan Bhawan, University of Rajasthan, Jaipur- 302055, India.*

Structural relaxation during sub- $T_g$  annealing of  $\text{Se}_{80-x}\text{Te}_{20}\text{Zn}_x$  ( $x = 2, 4, 6, 8$  and  $10$ ) glassy alloys was investigated using differential scanning calorimetry (DSC). On annealing the glasses at a temperature of  $333\text{K}$ , for different annealing times, the glass transition temperature increases and attains a constant value for higher annealing times. The recovery of excess enthalpy  $\Delta H_{\text{excess}}$  as obtained from the knowledge of excess specific heat  $\Delta C_p$ , has been plotted as a function of annealing time  $t_a$ . It is found that the excess enthalpy released  $\Delta H_{\text{excess}}$  increases with increase in annealing time ( $t_a$ ). The so obtained values of  $T_g$  and  $\Delta H_{\text{excess}}$  indicate that the relaxation process of  $\text{Se}_{80-x}\text{Te}_{20}\text{Zn}_x$  ( $x = 2, 4, 6, 8$  and  $10$ ) glasses is almost completed and the glasses reach a stable equilibrium state.

(Received August 25, 2011; accepted October 20, 2011)

*Keywords:* Differential scanning calorimetry (DSC), Annealing, Excess specific heat, Excess enthalpy

## 1. Introduction

Zn as an additive in chalcogenide glasses (CGs) has attracted widespread interest in glass science [1-3]. The interest stems in part from light induced effects relevant to optical recording and information processing [4]. It also stems from the drastically increased electrical conductivity [5] of Zn- CGs. Glass forming compositions [6], and particularly the composition variation [7] of  $T_g$  in network glasses contain vital clues on the connectivity of the backbone. Binary  $\text{Se}_{1-x}\text{Te}_x$  glasses are the rather well studied [8-9], and it thus appeared attractive to closely examine the chemical role of Zn as an additive in such glasses. Like silver, Zn can also be used for photo doping of chalcogenide glassy semiconductors [10-12] and the development of light emitting diodes and lasers. Development of  $\text{ZnSe}_x\text{Te}_{1-x}$  p-type contacts for high efficiency tandem structures is also reported [10] for the tandem solar cell devices, which have been under development in various configurations.

Besides other obvious advantages, the glassy state of these materials has an advantage of long-term change in the fundamental properties of the glasses. The as-prepared is in a highly unstable state and slowly changes its properties (volume, enthalpy etc) towards the equilibrium state represented by undercooled liquid at a given temperature. This process is called structural relaxation and is often classified after the property that is being observed, i.e. the volume relaxation or enthalpy relaxation. Structural relaxation is a very complex process that can last from minutes to years, depending on the initial state of the glass at the beginning of the relaxation, as well as the annealing temperature of the glass [13-14]. when a glass is annealed isothermally well below its glass transition temperature. Any changes seen in the physical properties are the effects of structural relaxation. As a supercooled

liquid is cooled to lower temperatures, its viscosity increases and the molecules which comprise it move more and more slowly. At some temperature, the molecules will be moving so slowly that they do not have a chance to rearrange significantly before the temperature is lowered further i.e. the time required to establish the equilibrium configuration of the liquid increases and eventually the structural change cannot keep pace with the rate of cooling. As the structure falls out of equilibrium, the liquid is said to enter the glass transition region. Continuous cooling at the rate  $q = dT/dt$  can be regarded as a series of temperature jumps of magnitude  $\Delta T$  followed by isothermal hold of duration  $\Delta t = dT/q$ ; slower the cooling rate, the longer the isothermal hold of duration [15]. The more slowly the liquid is cooled, the lower the temperature at which the equilibrium structure can be achieved, because more time is available for relaxation at a given temperature. The structure is frozen in a temperature range characterized by the fictive temperature  $T_f$  which is defined as that specific temperature obtained as the intersection of the extrapolated liquid and glass curves.  $T_f$  begins to depart from  $T$  as the liquid enters the transition range, and reaches the limiting value  $T_g$  as the relaxation is fully arrested. Upon reheating, the structure responds sluggishly to the increase in temperature, and the enthalpy falls below the equilibrium value [15]. Eventually, the atomic mobility becomes great enough to allow the relaxation rate to catch up with the heating rate, and enthalpy converges on an equilibrium value.

Hence if a glass is used as an active component, in a certain application, in an environment where the temperature is close or even below the glass transition temperature of that glass than the glassy atoms will acquire thermal energy which may be large enough to change the physical properties of the glass [16-18]. Therefore, the study of structural relaxation of these

glasses becomes important to get an overview of the structural changes occurring in the material.

In view of this, the main aim of this paper is to study the relaxation behavior of  $\text{Se}_{80-x}\text{Te}_{20}\text{Zn}_x$  ( $x = 2, 4, 6, 8$  and  $10$ ) glassy alloys by annealing the samples at a temperature below glass transition temperatures for different time intervals. In this regard the enthalpy released, when a glass was annealed at a temperature  $T_a$ , with time interval  $t_a$  has been evaluated from the knowledge of the excess specific heat,  $\Delta C_p$ , between annealed and as-prepared glass using differential scanning calorimetry (DSC).

## 2. Experimental details

$\text{Se}_{80-x}\text{Te}_{20}\text{Zn}_x$  ( $x = 2, 4, 6, 8$  and  $10$ ) glassy systems have been prepared by melt quenching technique. The materials of high purity (99.999%) were weighed according to their atomic weight percentages into a quartz ampoule. The content of the ampoule was sealed in the vacuum of  $10^{-6}$  Torr and heated in a furnace. The temperature of the furnace was raised at a rate of  $3\text{--}4 \text{ K min}^{-1}$  up to  $925^\circ\text{C}$  and kept around that temperature for 12 hours.

The ampoule was frequently rocked to ensure the homogeneity of the sample. The molten sample was then rapidly quenched in the ice-cooled water to obtain glassy state. The thermal behavior of the samples has been investigated using Rigaku 8230 differential scanning calorimetry (DSC). The accuracy of heat flow measurement is  $\pm 0.01 \text{ mW}$  and the temperature precision as determined by the microprocessor of the thermal analyzer is  $\pm 0.1 \text{ K}$ . DSC runs have been taken at a heating rate of  $10 \text{ K/min}$  on accurately weighed (10–15 mg) samples taken in aluminum (Al) pans under non-isothermal conditions. The temperature range covered in DSC was from room temperature (294K) to 450 K.

To investigate the relaxation behavior of Se-Te-Zn glasses, the samples were annealed at a temperature  $T_a = 333 \text{ K}$  for different annealing times (i.e. 8, 12, 16, 20, 24 and 28h).

## 3. Results and discussion

Typical DSC thermograms of as-prepared  $\text{Se}_{80-x}\text{Te}_{20}\text{Zn}_x$  ( $x = 2, 4, 6, 8$  and  $10$ ) glassy system at a heating rate of  $10 \text{ K/min}$  are shown in Fig.1. It is clear from the Fig.1 that each DSC thermogram exhibits well-defined endothermic and exothermic peaks.

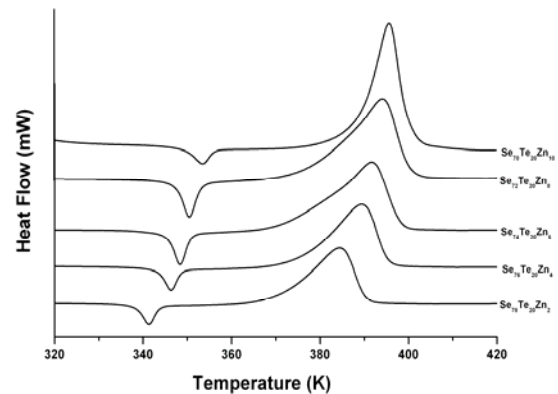


Fig. 1. DSC thermograms of  $\text{Se}_{80-x}\text{Te}_{20}\text{Zn}_x$  ( $x = 2, 4, 6, 8$  and  $10$ ) glassy system at a heating rate of  $10 \text{ K/min}$ .

From Fig. 1 it is observed that the glass transition temperatures of these samples increase with the increasing concentration of Zn. The reasons of such a behavior have been discussed by the authors elsewhere [19].

The effect of annealing of  $\text{Se}_{80-x}\text{Te}_{20}\text{Zn}_x$  ( $x = 2$  and  $10$ ) glasses on peak glass transition temperatures ( $T_{\text{max}}$ ) annealed at a temperature of  $333 \text{ K}$  with different annealing times i.e. 8h, 12h, 16h, 20h, 24h and 28h at a heating rate of  $10 \text{ K/min}$  is shown in Figs. 2 & 3 as representative cases respectively of the whole system  $\text{Se}_{80-x}\text{Te}_{20}\text{Zn}_x$  ( $x = 2, 4, 6, 8$  and  $10$ ) of glassy alloys.

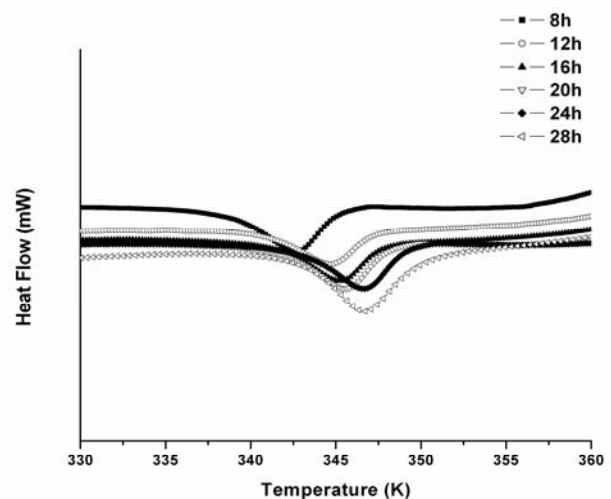


Fig. 2. DSC thermogram of  $\text{Se}_{78}\text{Te}_{20}\text{Zn}_2$  glass at a heating rate of  $10 \text{ K/min}$  annealed at  $333 \text{ K}$  for various times

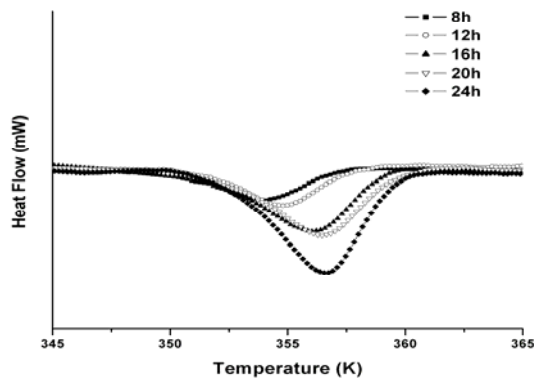


Fig. 3. DSC thermogram of  $Se_{70}Te_{20}Zn_{10}$  glass at a heating rate of 10 K/min annealed at 333 K for various times.

Fig. 4 shows that of peak glass transition temperatures ( $T_{max}$ ) with annealing time ( $t_a$ ) for  $Se_{80-x}Te_{20}Zn_x$  ( $x = 2, 4, 6, 8$  and 10) glasses.

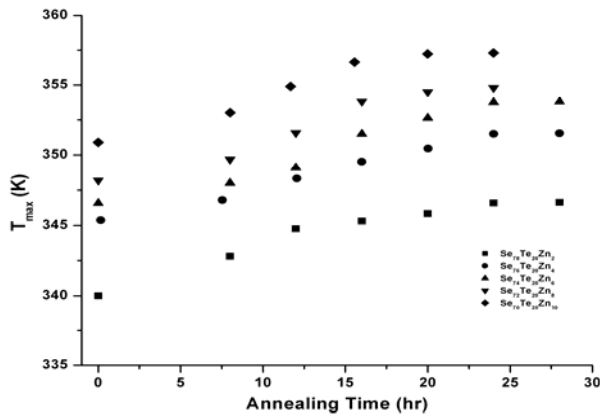


Fig. 4. Variation of peak glass transition temperatures ( $T_{max}$ ) with annealing time ( $t_a$ ) for  $Se_{80-x}Te_{20}Zn_x$  ( $x = 2, 4, 6, 8$  and 10) glasses.

From Fig 4, it is observed that peak glass transition temperatures ( $T_{max}$ ) of these glasses increase with increase in annealing time and attain a constant value for a particular higher annealing time (which is different for different glasses). This is due to the fact that annealing of the samples for a longer period causes the glass to relax to an equilibrium value and therefore no change in  $T_{max}$  is observed at higher annealing time.

The specific heat of  $Se_{80-x}Te_{20}Zn_x$  ( $x = 2, 4, 6, 8$  and 10) glasses, which is an important thermodynamic quantity has been determined using the heat flow data of glassy samples and reference material employing DSC with a standard procedure reported elsewhere [20]. This basic quantity has been used to study the structural relaxation of these glasses on Sub- $T_g$  annealing. Fig 5-6 shows the  $C_p$  versus temperature curves of as prepared and the glasses annealed at 333 K at different annealing times.

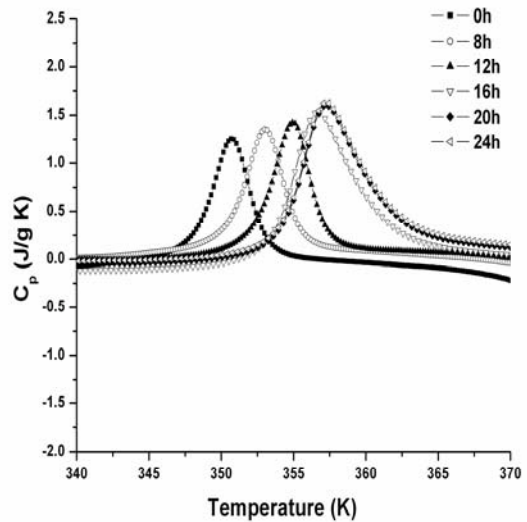


Fig. 5. Plot of  $C_p$  against temperature of  $Se_{78}Te_{20}Zn_2$  at a heating rate of 10 K/min annealed at 333 K for different times.

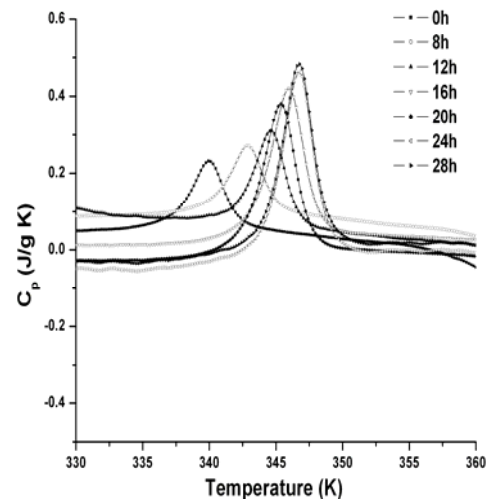


Fig. 6. Plot of  $C_p$  against temperature of  $Se_{70}Te_{20}Zn_{10}$  at a heating rate of 10 K/min annealed at 333 K for different times.

The sudden jump in the value of specific heat,  $C_p$ , at the upper end of the “ $C_p$  jump” at glass transition is due to the relaxation effects. The time scale of structure relaxation is highly dependent both on temperature and the instantaneous structure itself. In glass transition region, this time scale becomes of the order of  $10^2$  s. The jump in  $C_p$  is due to the fact that the structural relaxation times of these glasses are of the same order as the time scale of the experiment. The area of peak also increases with the increase in annealing time. The increase in area suggest that the sub- $T_g$  annealing of the samples results in release of excess specific heat that was trapped in the system during preparation. The excess specific heat  $\Delta C_p$ , which is

the difference between the specific heat of the annealed and the un-annealed samples, from rigid glasses to the equilibrium under-cooled liquid state have been calculated and plots of the same as a function of temperature have been shown in the Figs 7-8 as representative cases respectively.

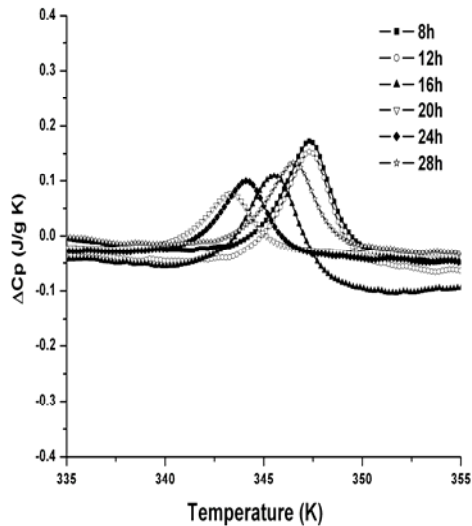


Fig. 7. Variation of excess specific heats ( $\Delta C_p$ ) with temperature for  $Se_{78}Te_{20}Zn_2$  for different times annealed at temperature 333 K.

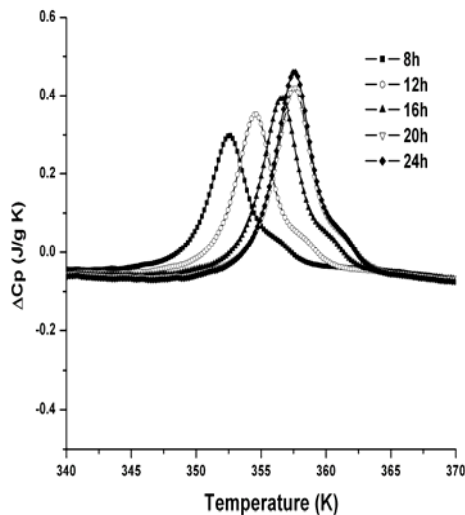


Fig. 8: Variation of excess specific heats ( $\Delta C_p$ ) with temperature for  $Se_{78}Te_{20}Zn_{10}$  for different times annealed at temperature 333 K.

From Figs. 7-8 it is interesting to note that the annealed samples show an excess endothermic specific heat over the as-prepared samples. This implies that specific heat in the annealed samples consists of

configurational contributions in addition of those arising from purely thermal vibrations [21-22].

It is well known [23] that once the undercooled liquid is in equilibrium, then the enthalpy difference between each glass and the undercooled liquid gives the measurement of the relaxation inherent to the formation of that particular glass. The relaxation enthalpy, however, is the thermal energy released during annealing of the glass which will again be re-absorbed during reheating process to each under-cooled liquid state and is usually calculated from knowledge of area under the excess specific heat versus temperature curve, i.e.

$$\Delta H_{\text{excess}} = \int_{T_1}^{T_2} C_p dT \quad (3)$$

where  $T_2$  is taken sufficiently above the glass transition temperature to ensure that the sample is the equilibrium liquid.  $T_1$  is taken below the glass transition temperature where the difference in the specific heat, of the annealed and the as-prepared sample, for different annealing times is almost negligible. Figs.9 shows the values of  $\Delta H_{\text{excess}}$  as a function of annealing time  $t_a$  of  $Se_{80-x}Te_{20}Zn_x$  ( $x = 2, 4, 6, 8$  and 10) glasses annealed at a different temperatures.

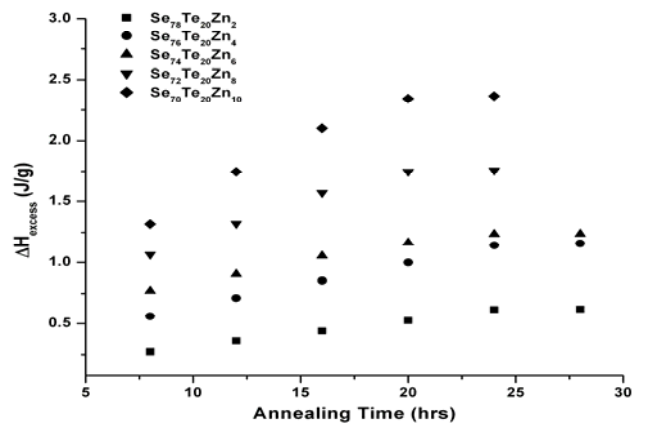


Fig. 9. Variation of  $\Delta H_{\text{excess}}$  with annealing time ( $t_a$ ) of  $Se_{80-x}Te_{20}Zn_x$  ( $x = 2, 4, 6, 8$  and 10) annealed at 333 K for annealing different times.

It is clear from Fig. 9 that at lower annealing times  $\Delta H_{\text{excess}}$  vary linearly with  $t_a$ . Moreover, at higher annealing time the excess enthalpy levels off with a very small change in the value of  $\Delta H_{\text{excess}}$  indicating that the glass has reached the state of equilibrium and the initial excess enthalpy is recovered. This is due to the reason that a glass prepared by melt quenching contains a number of liquid-like regions with un-relaxed atomic configuration, which are isolated from each other and embedded in solid like matrix [24]. As the glass is annealed at  $T_a < T_g$  some liquid like regions, with relaxation times less than the duration of annealing, will undergo local relaxation towards the local equilibrium states. Upon heating the

annealed glass in DSC furnace each of these liquid-like regions regains the initial structure and contributes to the excess endothermic specific heat and to the excess enthalpy, as it is evident from Figs 7-9. From Fig. 9 it is also observed that the excess enthalpy released is more in the case of  $\text{Se}_{20}\text{Te}_{20}\text{Zn}_{10}$  glass as compared to other investigated glasses in the series, which again suggests the higher stability of  $\text{Se}_{20}\text{Te}_{20}\text{Zn}_{10}$  glass.

#### 4. Conclusions

The structural relaxation study of  $\text{Se}_{80-x}\text{Te}_{20}\text{Zn}_x$  ( $x = 2, 4, 6, 8$  and  $10$ ) glasses leads to the following conclusion:

1. The peak glass transition temperature ( $T_{\text{max}}$ ) and  $\Delta H_{\text{excess}}$  of the annealed samples increases with increase in annealing time and attains constant values at a particular higher annealing time for particular temperature, indicating that the glass is approximately fully relaxed and reach a stable equilibrium state.
2. The excess specific heat ( $\Delta C_p$ ) curves indicate that the specific heat in the annealed samples consists of configurational contribution in addition to those arising from purely thermal vibrations.

#### Acknowledgements

Authors are thankful to Deepika for her help during the course of this work. FIST programme in the Department of Physics, University of Rajasthan for using DSC is gratefully acknowledged.

#### References

- [1] K. A. Aly, N. Afify, A. M. Aboushly, *Physica B* **405**, 1846 (2010).
- [2] M.B. El-Den, *Egypt. J. Sol.* **24**,171 (2001).
- [3] S. Yadav, R.K. Pal, S.K. Sharma, A. Kumar, *Physica B* **404**, 2225 (2009).
- [4] S. Srivastavaa, V. Pandey, S. K. Tripathi, R. K. Shukla, A. Kumar *J. Ovonic Research* **4**, 83 (2008).
- [5] R. S. Kundu, K. L. Bhatia, N. Kishore, *Phil. Mag.* **B 72**, 513 (1995).
- [6] A. Ahmad, S. A. Khan, A. A. Al-Ghamdi, F. A. Al-Agel, K. Sinha, M. Zulfequar, M. Husain, *J. Alloys. Comp.* **497**, 215 (2010).
- [7] S. Srivastavaa, M. Zulfequarb, A. Kumar, *J. Ovonic Research.* **4**, 1 (2008).
- [8] G Carini, M Cutroni, M Federico, G Galli, *J. Non-Cryst. Solids* **64**, 29 (1984).
- [9] A. El-Korashy, H. El-Zahed, H. A. Zayed, M. A. Kenawy, *Solid State Comm.* **64**, 291 (1984).
- [10] S. Vakkalanka, C. S. Ferekided, D. L. Morel, *Thin Solid Films* **515**, 6132 (2007).
- [11] V. Lyubin, M. Klebanov, A. Arsh, N. Froumin, A. V. Kolobov, *J. Non-Cryst.Solids* **326-327**, 189 (2003).
- [12] V. M. Lyubin, A. V. Kolobov, *J. Non-Cryst. Solids* **90**, 489 (1987).
- [13] P. G. Debenedetti, F. H. Stillinger, *Nature* **410**, 259 (2001).
- [14] G. W. Scherer, *Relaxation in glass composites*, John Wiley and sons, New York, 1986 (chapter 9).
- [15] C.T. Moynihan, A.J. Easteal, J. Wilder, *J. Phys. Chem.* **78**, 2673 (1974).
- [16] R. K. Pan, H. Z. Tao, H. C. Zang, T. J. Zhang, X. J. Zhao, *Physica B* **404**, 3397 (2009) .
- [17] Y. Wang, M. Nkamura, O. Matsuda, K. Murase, *J. Non-Cryst. Solids* **266**, 872 (2000).
- [18] J. M. Saiter, J. Ledru, A. Hamou, A. Zumailan, *Mater. Lett.* **33**, 91 (1997).
- [19] S. F. Naqvi, N. S. Saxena, *J. Non-Cryst. Solids* **357**, 1804 (2011).
- [20] S. F. Naqvi, N. S. Saxena, Deepika, D. Bhandari, *J. Amer. Cerem. Soc.* **94**(2), 462 (2011).
- [21] H. S. Chen, E. Coleman, *Appl. Phys. Lett.* **28**, 245 (1976).
- [22] H. S. Chen, T. T. Wang, *J. Appl. Phys.* **52**, 5898 (1981).
- [23] N. Clavagurera, M. T. Clavauera-Mora, S. Surinach, M. D. Baro. *J. Non-Cryst. Solids* **104**, 283 (1988).
- [24] R. P. Mathur, D. Akhtar, *Trans. Indian Inst. Met.* **40**(6), 529 (1987).

\*Corresponding author: faheem.spsl@gmail.com,