

STUDY OF CRYSTALLIZATION KINETICS OF $\text{Te}_5(\text{In}_x\text{Se}_{100-x})_{95}$ GLASSY ALLOYS

A. S. Maan*, D. R. Goyal,
Department of Physics, Maharshi Dayanand University, Rohtak – 124 001, India

Results of Differential Scanning Calorimetric (DSC) study carried out in $\text{Te}_5(\text{In}_x\text{Se}_{100-x})_{95}$ ($x = 10, 15, 20$ and 25) glasses are presented in this paper. The DSC runs were obtained at different heating rates and well-defined endothermic and exothermic peaks corresponding to glass transition (T_g) and crystallization temperatures (T_c) respectively are observed in all glasses. The activation energy of crystallization (E_c) has been evaluated by employing three different methods. T_c values have been found to increase with In%. The compositional dependence of (E_c) in ternary alloys shows a reversal in the trend at $x = 20$ glass which is explained in terms of mechanically stabilized structure at this composition and a replacement of homopolar Se-Se bonds by polar In-Se bond with the introduction of indium. This behavior may be explained in terms of mean atomic masses of ternary alloys.

(Received August 22, 2007; accepted August 30, 2007)

Keywords: DSC technique, activation energy, crystallization

1. Introduction

Chalcogenide glasses have been quite attractive due to suitability of peculiar properties exhibited by these materials for processing of devices for electrical and opto-electronic applications. Optical data storage based on laser induced amorphous to crystalline (a-c) phase transformation of chalcogenide glasses is an area with on-going research activity [1-7]. Chalcogenide glasses are expected to have many potential applications in optics and optoelectronics such as photo doping, optical imaging, photo lithography and phase change optical recording [8-16]. These glasses are known to exhibit single glass transition and single crystallization temperatures, which is an important condition for rewritable disks. Several chalcogenide alloys have been developed as recording layer and their good practical performance has been reported [13-16]. In phase change technology (PC), the laser pulse of duration several hundred nanoseconds is used to erase a written spot. The a-c phase transformation in PC recording layer material must be very fast so as to enable erasing in such a short time. Hence, the study of a-c phase transformation is of utmost importance for the development of some new chalcogenide glasses as better PC recording materials.

Selenium in particular has been reported to exhibit a unique property of reversible transformation, which makes these glasses useful as optical memory devices. It is reported [17,18] that addition of Te into a-Se results in dissociation of long polymeric chains and eight member rings of amorphous selenium [19]. As a result Se-Te alloys are more important as compared to a-Se due to distinct advantages (greater hardness, better photosensitivity, lesser ageing effects etc.) and hence find applications as recording layer material in optical phase change technique [20]. However, limited reversibility [21] and low glass transition and crystallization temperatures in these alloys are serious problems. These problems can be overcome by addition of third element as a chemical modifier as it is reported to expand the glass forming region and also creates compositional and configurational disorder [22]. The addition of dopant [In] can modify the lattice perfection and optical properties, which play a major role in device preparation. As such the

*Corresponding author: asmaan66@rediffmail.com

analysis of crystallization kinetics of $a\text{-Te}_5(\text{In}_x\text{Se}_{100-x})_{95}$ alloys is important from basic as well as application point of view.

The crystallization kinetics in chalcogenide glasses can be studied using isothermal and non-isothermal methods. In isothermal method, the sample is brought near to crystallization temperature very quickly and then any physical quantity which changes drastically is measured as a function of time. In non-isothermal method, the sample is heated at a fixed rate and the physical parameter is recorded as a function of temperature. Isothermal method is disadvantageous due to impossibility of reaching a test temperature instantaneously and during the time which the system needs to stabilize, no measurements are possible. In contrast, using non - isothermal technique the measurements can be made in a relatively rapid and precise manner. In the present work, three different methods of analysis namely, Kissinger's relation [23], Matusita - Sakka theory [24-25] and Augis - Bennett approximation [26] have been used to analyze the crystallization kinetics of Te-In-Se glassy alloys under non - isothermal conditions.

The experimental details of sample preparation and measurements are described in section 2. Various results of DSC measurements are presented and discussed in section 3. The conclusions drawn from the present work are contained in the last section.

2. Experimental

Various samples of $\text{Te}_5(\text{In}_x\text{Se}_{100-x})_{95}$ glassy system ($x = 10, 15, 20$ and 25) were prepared in bulk form by melt quenching technique. For each sample, materials of 99.999% purity weighed according to their atomic percentage are sealed in evacuated quartz ampoules ($\sim 10^{-5}$ Torr). The sealed ampoules were then heated to $\sim 1000^\circ\text{C}$ in an electric furnace at a heating rate of $2\text{-}3^\circ\text{C}/\text{min}$. and were frequently rocked for about 10 hours at the highest temperature to make the melt homogenous. The quenching was done in ice-cooled water. X-ray diffraction pattern of the samples confirmed the glassy nature of the material. The samples so obtained were ground to powder form for carrying out DSC measurements. Four heating rates $5, 10, 15$ and $20^\circ\text{C}/\text{min}$ were selected for DSC measurements. About 10-15 mg. powder was heated at constant heating rate and the changes in heat flow with reference to empty reference pan were measured. The presence of a well-defined endothermic peak at the glass transition temperature and an exothermic peak at the crystallization temperature is observed in each DSC scan. The studies were made under almost identical conditions so that the activation energy of glass transition (ΔE_i) could be compared to get an insight into the effect of increasing In concentration.

3. Results and discussion

Fig. 1 depicts various thermograms at different heating rates of $x = 10$ alloy. As seen from the figure, well-defined endothermic and exothermic peaks representing T_g and T_c respectively are present at different heating rates. One can clearly see from the plots that both T_g and T_c increase with heating rate in $x = 10$ glass and a similar behavior is observed in other compositions as well. For the sake of comparison, variation of T_c in different glasses is presented in Fig. 2, at a heating rate of $10^\circ\text{C}/\text{min}$. As seen from Fig. 2, the crystallization temperature increases as indium concentration is increased in present set of glasses. A similar behavior with increasing indium content is observed in case of glass transition temperature as well [27].

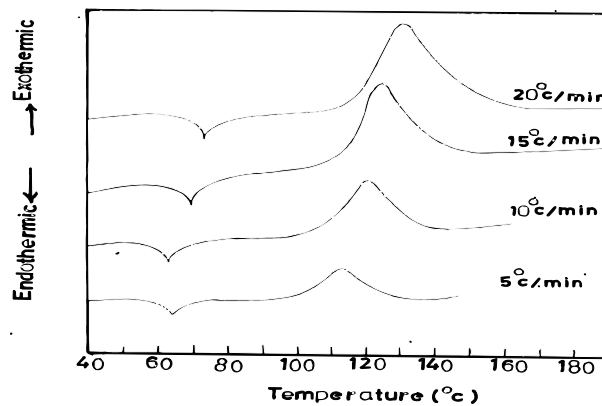


Fig. 1. DSC thermograms for $x = 10$ alloy at different heating rates.

In present set of glasses, T_c values of each alloy are much higher than the room temperature. This is an important advantage of these alloys, which is essential to prevent self transition of recording materials between the two phases: amorphous and crystalline. Hence, one can expect each of these alloys to remain stable in its amorphous and crystalline phases at room temperature. Moreover, each alloy has been found to stay in single phase during a-c transformation, which is an essential requirement of PC optical recording materials.

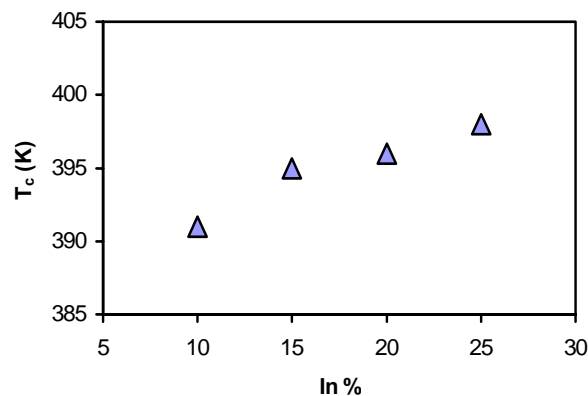


Fig. 2. Variation of T_c with In % at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$.

The crystallization kinetics of amorphous alloys has been extensively studied in past using the classical Johnson - Mehl - Avrami (JMA) theoretical model [28 - 30] in which the crystallization fraction (α) can be described as a function of time (t) according to the relation:

$$\alpha(t) = 1 - \exp[-(K.t)^n] \quad (1)$$

where n is the Avrami index dependent upon mechanism of growth and the dimensionality of the crystal growth. K is defined as the reaction rate constant, which is assumed to have the temperature dependence as:

$$K = K_0 \exp(-E_c / RT) \quad (2)$$

with E_c is the activation energy of crystallization, R the universal gas constant and K_0 is also a constant (frequency factor). It has been reported that the three parameters E_c , n and K_0 can be determined using one of many methods based on the JMA model. The underlying hypothesis for this purpose is constant temperature during the crystallization reaction i.e. the isothermal

techniques. These methods can however be applied to analyze the data obtained in the non-isothermal techniques albeit with certain restrictions and yield satisfactory results. In non-isothermal crystallization, the rate of crystallization is obtained from the relation between the sample temperature and the heating rate (β) with the assumption that the reaction rate constant ($\dot{\alpha}$) is a function of time and is given as

$$\dot{\alpha} = n(Kt)^{n-1} [K + K' \cdot t](1 - \alpha) \quad (3)$$

The sample temperature T is related to heating rate (β) as

$$T = T_o + \beta t \quad (4)$$

The peak temperature of crystallization T_c in terms of the heating rate, according to Kissinger [23], is given as:

$$\ln(\beta / T_c^2) = -E_c / R T_c + \text{constant} \quad (5)$$

Equation (5) is used to calculate the activation energy of crystallization by plotting $\ln[\beta / T_c^2]$ vs $1/T_c$ curves. Various plots for different compositions are depicted in Fig. 3.

At a particular temperature T , the extent of crystallization (α) is given as [24,25]:

$$\ln(1 - \alpha)^{-1} = (C / \beta^n) \cdot [(-nE_c) / RT] \quad (6)$$

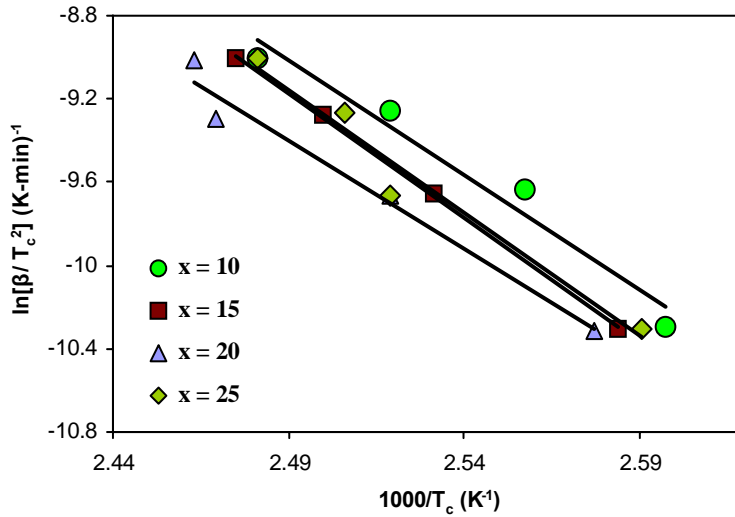


Fig. 3. Variation of $\ln(\beta / T_c^2)$ vs. $1000/T_c$ for $Te_5(In_xSe_{100-x})_{95}$ glasses.

As the values of α are independent of β at $T = T_c$ [31], so at $T = T_c$, the equation (6) modifies as:

$$\ln\beta = -E_c / RT_c + \text{constant} \quad (7)$$

Equation 7 is used to calculate the activation energy of crystallization by plotting $\ln\beta$ vs. $1000/T_c$ curve. Different plots for glassy $Te_5(In_xSe_{100-x})_{95}$ ($x=10,15,20$ and 25) alloys are shown in Fig. 4.

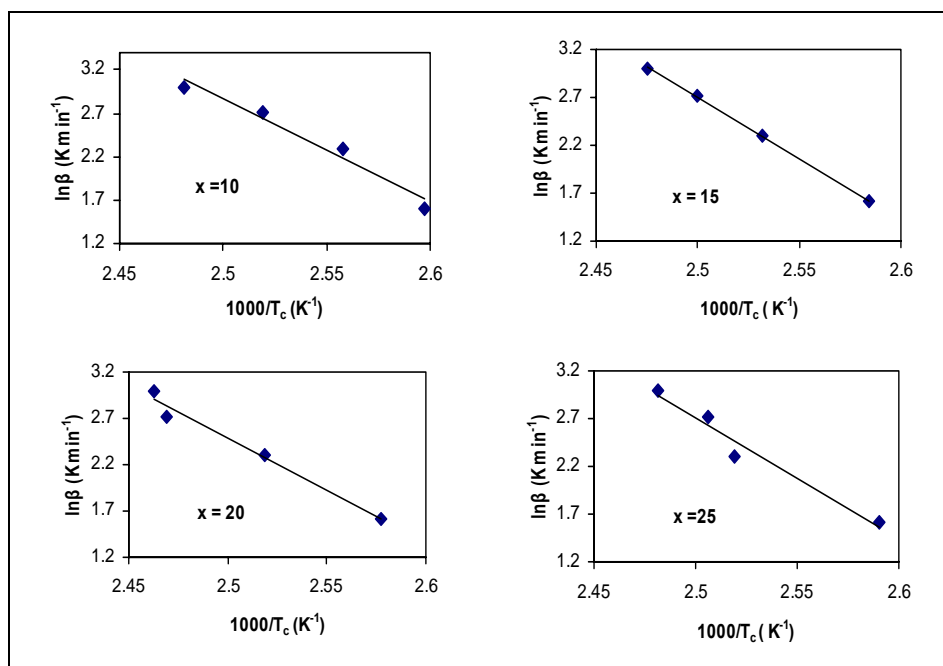


Fig. 4. Plots of $\ln\beta$ vs. $1000/T_c$ for $\text{Te}_5(\text{In}_x\text{Se}_{100-x})_{95}$ glasses.

The approximation approach by Augis and Bennett [26] has also been employed to determine the activation energy of crystallization E_c . According to this treatment, E_c is related to the heating rate and crystallization temperature as:

$$\ln(\beta/T_c) = -E_c/RT_c + \ln K_0 \quad (8)$$

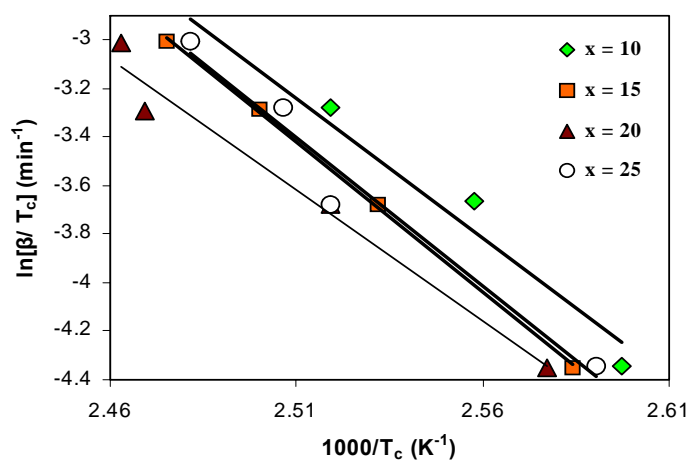


Fig. 5. Plots of $\ln\beta$ vs. $1000/T_c$ for $\text{Te}_5(\text{In}_x\text{Se}_{100-x})_{95}$ glasses.

Using temperature dependence of peak temperature upon heating rate, activation energy of crystallization can be computed from the plots of $\ln\beta/T_c$ against $1000/T_c$. Related plots for glassy for $\text{Te}_5(\text{In}_x\text{Se}_{100-x})_{95}$ glasses are presented in Fig. 5 which seem to be in fair agreement with the approach in equation 8. E_c values obtained for various glasses based upon the treatment of above described three methods are presented in Table 1. Comparison of E_c values of different alloys obtained from equations (5), (7) and (8) shows that the values are in good agreement. It is further

added that the values of E_c obtained according to the treatment by Augis and Bennet [26] are quite closer to the average values obtained during the analysis.

Table 1. Values of activation energy of crystallization E_c calculated from different non-isothermal methods.

Non-isothermal method	Activation energy of crystallization E_c (eV)			
	$Te_5(In_{10}Se_{90})_{95}$	$Te_5(In_{15}Se_{85})_{95}$	$Te_5(In_{20}Se_{80})_{95}$	$Te_5(In_{25}Se_{75})_{95}$
Kissinger's relation	0.952	1.036	0.897	1.017
Matusita and Sakka theory	1.024	1.108	0.968	1.087
Augis and Bennet's relation	0.986	1.070	0.931	1.051
Average value	0.987	1.072	0.932	1.052

As seen from Table 1, E_c increases with increasing indium% in ternary Te-In-Se glassy alloys. Such an increase in E_c of with increasing indium concentration in present set of alloys may be analyzed by considering the atomic weights of In and Se as Te content in each alloy is kept constant. The activation energy of crystallization is known to be associated with the nucleation and growth process that dominates the devitrification of most glassy solids [32-34]. The atomic weight of In (114.8 gm/mol) is greater than of Se (79.0 gm/mol). In the present set of alloys, In is systematically increased at the cost of Se thereby resulting in an increase in the mean atomic weight of ternary alloys with increasing indium concentration. The increasing atomic weight in turn is expected to result in a decrease in the nucleation and growth rate and as such the activation energy (E_c) should increase with increasing x values. In present glassy alloys as seen from Fig. 6, E_c increases with increasing In% and shows a trend reversal at $x = 20$ alloy where it is minimum and increases thereafter. A similar discontinuity in respect of other physical parameters of $x = 20$ alloy has been observed as well [35].

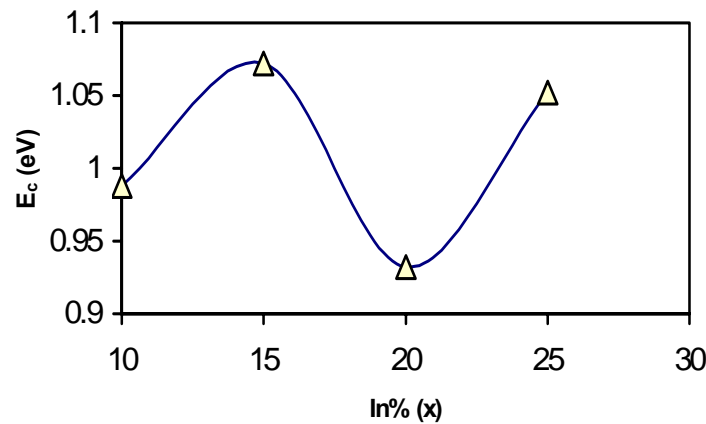


Fig. 6. E_c vs Indium concentration in $Te_5(In_xSe_{100-x})_{95}$ glasses.

Chalcogenide glasses are reported to exhibit a discontinuity in various physical properties when the average co-ordination number $\langle z \rangle$ reaches 2.4 for a particular composition [36-38]. Such behavior may be explained in terms of a mechanically optimized structure at a critical glass composition [39]. In present alloys, the co-ordination number of Se and Te is 2 and that of In is 3, whereas, in the composition $Te_5(In_{20}Se_{80})_{95}$, where a minimum in E_c occurs, $\langle z \rangle$ comes out to be nearly 2.19. However, according to Phillips and Thorpe model, a threshold is expected at $\langle z \rangle = 2.4$. The $\langle z \rangle$ value in the present case is slightly less. This may be due to an important limitation

of Phillips and Thorpe model [39]. In this model, Phillips considered the interaction between atoms to be purely covalent while arriving at the balance condition. In present glasses, addition of indium is expected to change the character of some of the Se-Se homo-polar bonds. The In-Se bonds created as a result of the breaking up of Se_8 rings are polar in nature and in turn disturb the covalent Se-Se bonds to some extent. Thus the shift in character of bonding from homo-polar to polar to a certain extent may be the reason for trend reversal of E_c at slightly lesser value of $\langle z \rangle$ in Te-In-Se alloys.

4. Conclusions

DSC technique has been used to investigate the crystallization kinetics in glassy $\text{Te}_5(\text{In}_x\text{Se}_{100-x})_{95}$ alloys ($x = 10, 15, 20$ and 25) at different heating rates. The analysis of experimental results is done by using three different methods under non - isothermal condition and the activation energy of crystallization (E_c) is obtained for each treatment. The effect of a systematic increase in indium concentration (x) has been investigated and it is found that E_c values increase with increasing In% with an exception at $x = 20$. This behavior of ternary alloys is analyzed in terms of their mean atomic masses. A reversal in the trend of activation energy of crystallization in ternary alloys has been observed at a particular value of $\langle z \rangle$ which is slightly less than value of $\langle z \rangle = 2.4$ as predicted by Philips and Thorpe model. Such behavior is probably due to change in character of bonds from existing Se-Se homo-polar to polar In-Se bonds created as a result of breaking up of Se_8 rings due to addition of Indium.

References

- [1] M. Nakamura, Y. Wang, O. Matsuda, K. Inoue, K. Murase, *J. Non-Cryst. Sol.* **198-200**, 740 (1996).
- [2] L. Men, F. Jiang, F. Gan, *Mater. Sci. Eng. B* **47**, 18 (1997).
- [3] R. V. Woudenberg, *Jpn. J. Appl. Phys.* **37**, 2159 (1998).
- [4] Tz. Babeva, D. Dimitrov, S. Kitova, I. Konstantinov, *Vacuum* **58**, 496 (2000).
- [5] V. I. Mikla, I. P. Mikhalko, V.V. Mikla, *Mater. Sci. Eng. B* **83**, 74 (2001).
- [6] A. K. Kolobov, J. Tominaga, *J. Optoelectron. Adv. Mater.* **4** (3), 679 (2002).
- [7] S. A. Khan, M. Zulfequar, M. Husain, *Vacuum* **72**, 291 (2003).
- [8] T. Wagner, *J. Optoelectron. Adv. Mater.* **4**(3), 717 (2002).
- [9] K. Ramesh, S. Asokan, K. S. Sangunni, E.S.R. Gopal, *J. Phys. Chem. Solids* **61**, 95 (2000).
- [10] M. Frumar, Z. Cernosek, J. Jedelsky, B. Frumarova, T. Wagner, *J. Optoelectron. Adv. Mater.* **3** (2), 177 (2001).
- [11] Y. Y. Chang, L. H. Chou, *Jpn. J. Appl. Phys. Part 2*, **39** (4A), L294-L296 (2000).
- [12] G. F. Zhou, *Mater. Sci. Eng. A*, **A304 - A306**, 73 (2001).
- [13] L. H. Chou, Y. Y. Chang, Y. C. Chai, S. Y. Wang, *J. Appl. Phys. Part 1*, **40**(8), 4924-4925 (2001).
- [14] J. Li, L. Hou, H. Raun, Q. Xie, F. Gan, *Proceedings SPIE - Int. Soc. Opt. Eng.* **125**, 4085, (2001).
- [15] T. Wagner, M. Frumar, S. O. Kasap, *Mir. Vlecek, Mil. Vlecek, J. Optoelectron. Adv. Mater.* **3** (2), 227 (2001).
- [16] J. Gutwirth, T. Wagner, T. Kohoutek, *Mir. Vlecek, S. Schroeter, V. Kovanda, Mil. Vlecek, M. Frumar, J. Optoelectron. Adv. Mater.* **5** (5) 1139 (2003).
- [17] M. A. Abkowitz in "The Physics of Se and Te" edited by E. Gerlach, P. Grosse (Springer, Berlin, 1979) 178.
- [18] M. F. Kotakata, M. K. El-Mously, *Acta Physica Hungarica* **54**(3), 303 (1983).
- [19] G. Lucovsky, *J. Non Cryst. Solids*, **97/98**, 3950 (1987).
- [20] K. Weiser, R. J. Gambino, J. A. Reinhold, *Appl. Phys. Lett.* **22**, 48 (1973).
- [21] A. W. Smith, *Appl. Optics* **13**, 795 (1974).
- [22] Z. H. Khan, M. Zulfequar, M. Illyas, M. Hussain, Kh. Selima Begum, *Current Appl. Phys.* **2**, 164 (2002).

- [23] H. E. Kissinger, *Anal. Chem.* **29**, 1702 (1957).
- [24] K. Matusita, S. Sakka, *Phys. Chem. Glasses* **20**, 81 (1979).
- [25] K. Matusita, S. Sakka, *Bull. Inst. Chem. Res. Kyoto Univ.* **59**, 159 (1981).
- [26] J. A. Augis, J. E. Bennett, *J. Therm. Anal.* **13**, 283 (1978).
- [27] A. S. Maan, D. R. Goyal, *J. Ovonic Research* 3(2), 45 (2007).
- [28] W. A. Johnson, R. F. Mehl, *Trans. Am. Inst. Min. (Metal) Engs.* **135**, 416 (1939).
- [29] M. Avrami, *J. Phys. Chem.* **7**, 1103 (1939).
- [30] M. Avrami, *J. Phys. Chem.* **8**, 212 (1940).
- [31] T. Ozawa, *J. Therm. Anal.* **2**, 301 (1970).
- [32] L. H. Chou, M. C. Kuo, *J. Appl. Phys.* **77**(5), 1964 (1995).
- [33] R. Chiba, N. Funakoshi, *J. Non-Cryst. Solids* **105**, 105 (1998).
- [34] N. Mehta, M. Zulfequar, A. Kumar, *J. Optoelectron. Adv. Mater.* **6** (2) 441 (2004).
- [35] A. S. Maan, D. R. Goyal, A. Kumar, *Chalcogenide letters* **4**, (4) 48 [2007].
- [36] A. Feltz, H. Aust, A. Blayer, *J. Non-Cryst. Solids* **55**, 179 (1983).
- [37] A. K. Agnihotri, A. Kumar, A. N. Nigam, *Philos. Mag. Lett.* **58**, 63 (1988).
- [39] S. Asokan, G. Parthasarthy, E. S. R. Gopal, *Philos. Mag. B* **57**, 49 (1988).
- [39] J. C. Phillips, M. F. Thorpe, *Solid State Commun.* **53**, 699 (1985).