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Kinetics of crystallization of $Ge_{30\text{-}x}Se_{70}Sb_x$ (x = 15, 20, 25) chalcogenide glasses

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Abstract

The kinetics of crystallization of $Ge_{30\text{-}x}Se_{70}Sb_x$ (x = 15, 20, 25) chalcogenide glasses has been investigated using differential scanning calorimetery at different heating rates under non-isothermal conditions. The kinetic analysis of crystallization has been discussed using different theoretical approaches such as Ozawa model, Augis and Bennet model, Matusita model and Gao-Wang model. It is evident from this study that the activation energy of crystallization E_c is composition dependent. The activation energy decreases with increasing Sb content due to the increasing of rate of crystallization. The minimum value of the frequency factor K_o, which is defined as the number of attempts made by the nuclei per second to overcome the energy barrier, confirms the fact that glass is more stable. It has been found that $Ge_{15}Se_{70}Sb_{15}$ glass is more stable compared to the other compositions.

Keywords: *crystallization, activation energy, frequency factor*

I. Introduction

The materials that are based on the principle of reversible switching between an amorphous and a crystalline phase are widely used for rewritable optical recording applications and use for data storage devices such as CD compact erasable disk [1–5]. Chalcogenide glasses are promising for the applications in integrated non-linear optical component due to their high refractive index, large non-linearties as well as optical losses [6]. These materials have attracted much attention of scientist and technologist because of their amazing properties such as chemical durability, optical transparency and electrical properties [7]. Germanium chalcogenide glassy materials have wide applications in electronics and opto-electronics devices [8].

The amorphous state is essentially a metastable one; therefore it inherently possesses the possibility of transforming into a more stable crystalline state. The most promising properties of chalcogenide glasses have been found to deteriorate drastically during crystallization. Understanding the micro mechanism of crystallization to impede or control crystallization is, therefore a prerequisite for most of the applications, as stability against the crystallizations determines the effective working limit of the glasses. In this regard, the activation energy of crystallization is an important parameter and therefore this paper reports the activation energy of crystallization (E_c) using different theoretical models such as Ozawa model, Augis and Bennet model, Matusita model and Gao-Wang model. Besides, crystallization rate factor and frequency factor have also been determined to investigate the stability of glassy alloys with different composition.

II. Experimental details

$Ge_{30\text{-}x}Se_{70}Sb_x$ (x = 15, 20, 25) glassy materials were prepared by melt quenching method. In melt quenching method, high purity (99.999 %) germanium, selenium and antimony were weighed and the weighed materials were then introduced into clean quartz ampoule with appropriate atomic weight percent. The contents of the ampoule (length 5 cm and internal diameter 8 mm) were

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sealed in vacuum of 10^{-6} torr and then heated in furnace where temperatures were raised at a rate of 3–4 K/min up to 925 °C. The contents were kept around that temperature for 12–14 hours with continuous rotation to ensure the homogeneity of the sample. The molten sample was rapidly quenched in ice-cooled water to get glassy state. The ingots of so produced glassy samples were taken out of the ampoule by breaking the ampoule and then grinded gently in mortar and pestle to obtain them in powder form.

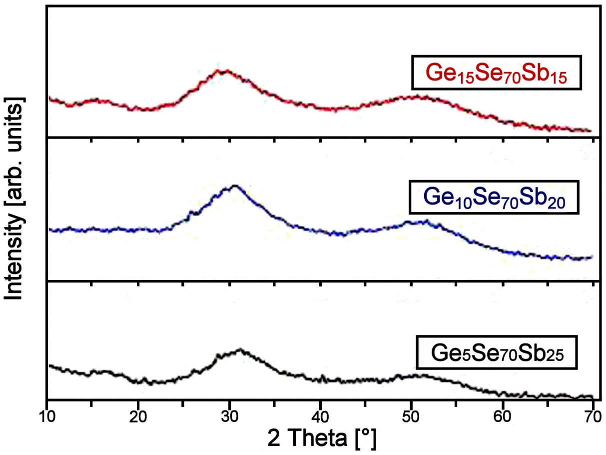

Figure 1. XRD diffractograms of the $Ge_{30\text{-}x}Se_{70}Sb_x$ (x = 15, 20, 25) glassy materials

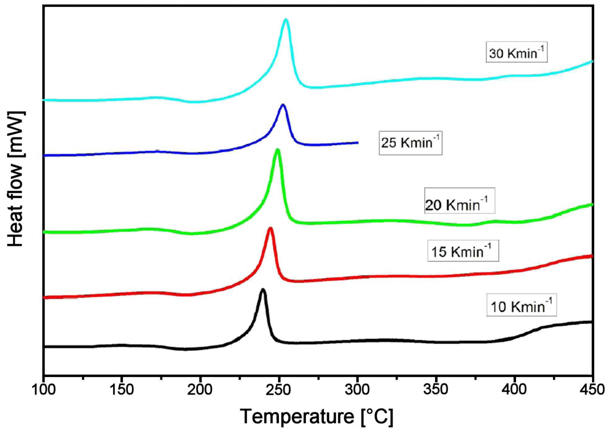

Figure 2. DSC thermograms of $Ge_5Se_{70}Sb_{25}$ with different heating rates (10, 15, 20, 25 and 30 K/min)

The glasses are amorphous material therefore amorphous nature of these samples were characterized by X-ray diffraction pattern using Bragg-Brentano geometry on a Panalytical X'pert diffractometer with a CuKα radiation source (1.5406 Å). Figure 1 shows the XRD diffractograms of the $Ge_{30\text{-}x}Se_{70}Sb_x$ (x = 15, 20, 25) glassy materials. The calorimetric measurements were carried out using differential scanning calorimetery (Rigaku DSC-8230) with an accuracy of ±0.1 K. 10 mg-powdered samples were crimped into aluminium pans and scanned at different heating rates (10, 15, 20, 25 and 30 K/min). Figure 2 shows the DSC thermograms of $Ge_5Se_{70}Sb_{25}$ chalcogenide glasse at a heating rate of 10 K/min. To evaluate the transformed portion of the amorphous material, partial area analysis of the DSC peaks had been used.

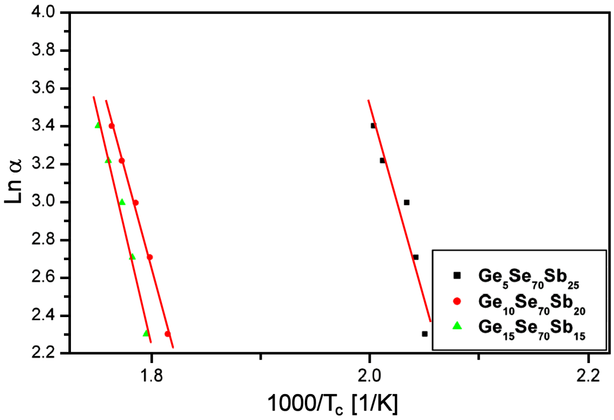

Figure 3. Plot of ln against $1000/T_c$

III. Results and discussion

3.1. Crystallization

The kinetics of crystallization region of $Ge_{30\text{-}x}Se_{70}Sb_x$ (x = 15, 20, 25) glassy system under non-isothermal conditions can be investigated using various parameters such as activation energy E_c (kJ/mole), Avrami index n, frequency factor K_o (1/s) and crystallization rate factor K (1/s).

3.2. Activation energy of crystallization

It has been pointed out that in an amorphous-crystalline transformation process, three types of activation energies to be considered are activation energy for nucleation (E_n), activation energy for crystal growth (E_g) and activation energy of crystallization for whole process (E_c) [9]. Further, it has been shown through various studies that the activation energy for growth may be taken equal to the activation energy of whole crystallization E_c (kJ/mole) provided it is evaluated using thermal analysis of samples.

It has been pointed out that in non-isothermal measurements, generally due to a rapid temperature rise and the big difference in the latent heat of nucleation and growth, the crystallization exotherm characterizes the growth of the crystalline phase from the amorphous matrix; nucleation is more or less calorimetrically unobservable at temperatures below the crystallization exotherm, or it takes place very rapidly and immediately after overheating the material in the initial stages of the crystallization exotherm which results in the deformed beginning of measured exotherm. Consequently, the obtained value of E_c can be taken to represent the activation energy of growth.

The activation energy of crystallization E_c has been calculated from the variation of the onset crystallization temperature T_c with the heating rate using Ozawa's formulation [10].

$$\ln\alpha = -\frac{E_c}{RT_c} + \text{const.} \tag{1}$$

Figure 3 shows the plot of $\ln\alpha$ against $1000/T_c$ for $Ge_{30\text{-}x}Se_{70}Sb_x$ (x = 15, 20, 25) glassy alloys. The curves are found to be linear for different concentration of Sb content. The activation energy of crystallization E_c is obtained from the slope of these plots.

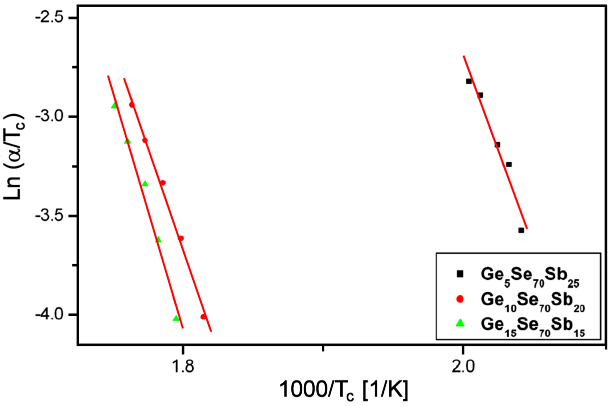

Figure 4. Plot of $\ln(\alpha/T_c)$ versus $1000/T_c$

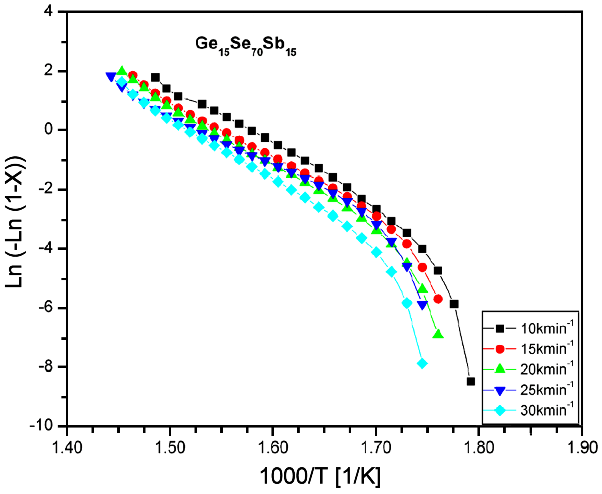

Figure 5. Plot of $\ln[-\ln(1-X)]$ versus $1000/T$

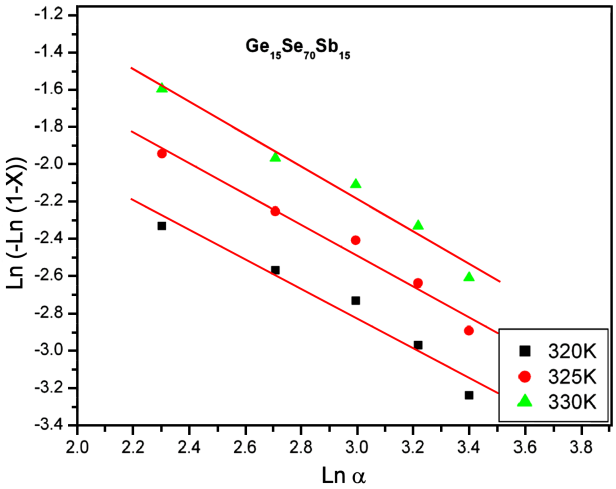

Figure 6. Plots of $\ln[-\ln(1-X)]$ versus α

The activation energy for crystallization E_c, frequency factor (K_o) and crystallization rate factor (K) have been evaluated through the model suggested by Augis and Bennett [11]:

$$\ln\frac{\alpha}{T_c} = -\frac{E_c}{RT_c} + \ln K_o \tag{2}$$

where T_c is onset crystallization temperature and K_o is the frequency factor (in 1/s).

The relation between $\ln(\alpha/T_c)$ and $1/T_c$ for $Ge_{30\text{-}x}Se_{70}Sb_x$ (x = 15, 20, 25) glasses is plotted in Fig. 4. The activation energy E_c can be calculated through the slope of the straight lines of Fig. 4. The value of K_o, which is defined as the number of attempts made by the nuclei per second to overcome the energy barrier, can be evaluated from equation 2. The value of K_o provides information for the calculation of nucleation site, present in the material for crystal growth. The values of K_o for different compositions are given in Table 1. The minimum value of K_o confirms the fact that glass is most stable, as the number of attempts made by nuclei's are lowest for a glass. Number of attempts made by nuclei's reduces with decreasing percentage of Sb, suggesting increase in the stability of glasses. Besides these, crystallization rate factor (K) has also been evaluated with the help of Arrhenius equation:

$$K = K_o \exp -\frac{E_c}{RT_c} \tag{3}$$

The importance of crystallization rate factor (K) is that its minimum value gives an indication of the retardation of the crystallization while its higher value diminishes the glass-forming ability [12]. The value of crystallization rate factor (K) is also observed to decrease with decreasing Sb content, which suggests the increase in stability of glass samples.

The activation energy of crystallization region E_c and the order of crystallization reaction (Avrami index n) of the amorphous alloys are obtained using the Matusita model [13]. Matusita equation expressing volume fraction (X) of crystal precipitated when glass is heated at a constant heating rate α was derived as a function of temperature and heating rate

$$\ln[\ln(1-X)] = -n\ln\alpha - 1.052\frac{mE_c}{RT} + \text{const.} \tag{4}$$

where quantity X represents the crystallized fraction of the amorphous matrix at a constant heating rate at a particular temperature and is given as $X = A_t/A$, where A is the total area of the exotherm between the temperature T_i where the crystallization just beginning and T_f where the crystallization is completed and A_t is the area between the initial temperature and a generic temperature T. To evaluate the portion of the amorphous material, partial area analysis of the DSC peaks had been used. In the equation 4, m and n are constants that depend on the mechanism of the growth and the dimensionality of the

Table 1. Values of frequency factor (1/s) and rate of crystallization K (1/s) for $Ge_{30-x}Se_{70}Sb_x$ (x = 15, 20, 25) glassy samples using Augis-Bennett

Sb [wt.%]	Frequency factor, K_o [1/s]	Rate of crystallization, K [1/s]
15	5.47×10^{12}	5.209×10^{12}
20	4.11×10^{14}	3.958×10^{14}
25	7.70×10^{15}	1.035×10^{15}

Table 2. Values of mE_c/R, Avrami exponent (n) and dimensionality of growth (m) for $Ge_{30-x}Se_{70}Sb_x$ (x = 15, 20, 25) glassy samples using the Matusita model

Sb [wt.%]	mE_c/R	Avrami exponent, n	Dimensionality of growth, m
15	22.26	0.829	1
20	41.20	3.202	2
25	59.49	4.328	3

Table 3. Values of the activation energy of crystallization E_c (kJ/mole) for $Ge_{30-x}Se_{70}Sb_x$ (x = 15, 20, 25) glassy samples using different models

Sb	Activation energy of crystallization, E_c [kJ/mol]			
[wt.%]	Ozwa model	Augis & Bennet model	Matusita model	Gao & Wang model
15	204.81	200.15	184.75	145.39
20	176.71	172.05	170.98	135.48
25	171.51	163.02	168.59	119.20

crystal respectively. If the formations of nuclei are dominant during a constant heating rate, n is equal to $(m+1)$. If the nuclei are predominantly formed during any previous heat treatment prior to the thermal analysis, n is equal to m [14].

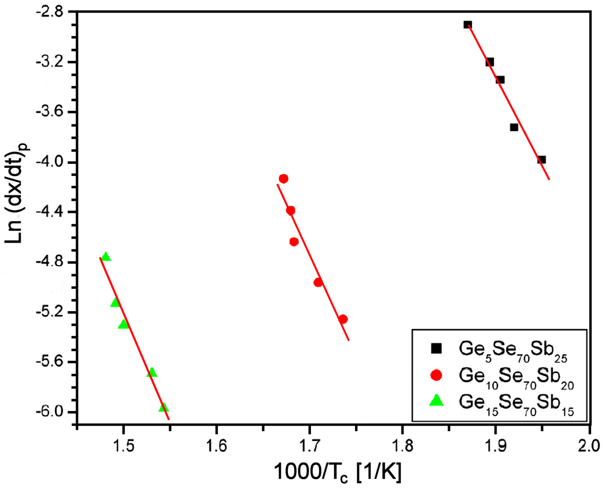

Figure 7. Plots of $\ln(dX/dt)_p$ versus $1000/T_p$

The plot of $\ln[-\ln(1-X)]$ versus $1000/T$ for $Ge_{15}Se_{70}Sb_{15}$ glassy sample is shown in Fig. 5. The curves are straight line for most of the temperature range but show deviation from the linear behaviour at high temperatures. This deviation may be attributed to the saturation of nucleation sites in the final stage of crystallization or to a restriction of the crystal growth by the small size of the particles [15]. From Fig. 5 the value of mEc/R has been calculated from the slope of the $\ln[-\ln(1-X)]$ versus $1000/T$ for different heating rates. It has been seen that the value of mEc/R weakly dependent on the heating rate. Therefore the average values of mEc/R have been calculated by considering all the results of mEc/R at different heating rates.

Figure 6 shows linear plots of $\ln[-\ln(1-X)]$ versus $\ln\alpha$ at three fixed temperatures for $Ge_{15}Se_{70}Sb_{15}$ glass sample. The average value of n has been calculated from the slopes of the straight lines of Fig. 6.

The calculated values of Avrami exponent (n) and dimensionality of growth (m) of all the samples under investigation have been listed in Table 2. A non-integer value of n indicates that two crystallization mechanisms were working during the amorphous-crystalline transformation. It is observed that all the glassy materials predominantly crystallize in one, two and three dimensions suggesting surface and bulk nucleation. The activation energy of crystallization for the glassy alloys has been calculated using the value of n and the average of mEc/R.

Gao and Wang [16] has proposed a slightly different method to analyse DSC thermograms in terms of the activation energy E_c, during the crystallization process. This theory is based on the same fundamental assumptions as imposed on the JMA transformation equation. It assumes that the nucleation is randomly distributed and the growth rate of the new phase depends on the temperature. The theory of Gao and Wang provides the relationship between the maximum crystallization rate and the peak crystallization temperature, which is given by:

$$\ln\left(\frac{dX}{dt}\right)_p = -\frac{E_c}{RT_p} + \text{const.} \tag{5}$$

where $(dX/dt)_p$ is the rate of volume fraction crystallized at the peak of crystallization temperature T_p, which is proportional to exothermic peak height. Plot of $\ln(dX/dt)_p$ versus $1000/T_p$ for $Ge_{30-x}Se_{70}Sb_x$ (x = 15, 20, 25) is shown in Fig. 7. The slope of curves (straight lines) gives the activation energy of crystallization (E_c).

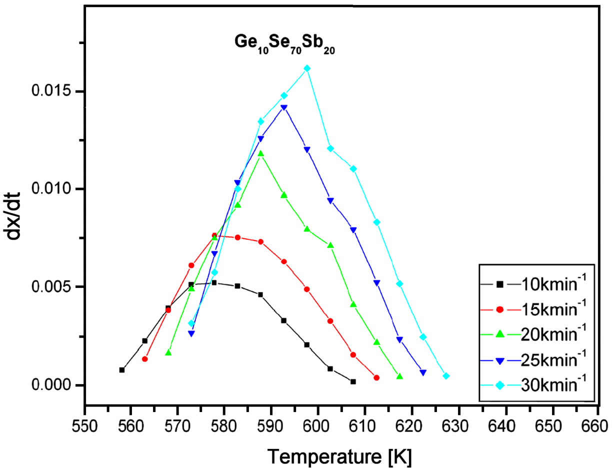

Figure 8. Plots dX/dt versus temperature for $Ge_{10}Se_{70}Sb_{20}$ glass

It is clear from Fig. 8 that the peak height increases and shifts towards higher temperature values with the increase in heating rate. This is due to the fact that the rate of crystallization increases and crystallization shifts towards higher temperatures as well as heating rate increase from 10 K/min to 30 K/min, i.e. more volume fraction is crystallized in a smaller time as compared to the low heating rate.

The values of activation energy of crystallization (E_c) of $Ge_{30-x}Se_{70}Sb_x$ (x = 15, 20, 25) glassy systems using different theoretical models have been mentioned in Table 3. It has been observed from Table 3 that the values of activation energy are different for different models for each glassy system. This is because of the iso-kinetic nature of the models to study the detailed mechanism and mode of crystallization whereas a single value of activation energy exists throughout the conversion in iso-conversional method [17]. It is clear that activation energy of crystallization decreases with the increase of the percentage of Sb. This suggests that energy barrier for crystallization decreases with increasing percentage of Sb. Therefore one can conclude that stability of sample decreases with increasing concentration of Sb.

IV. Conclusions

The kinetics of crystallization of $Ge_{30-x}Se_{70}Sb_x$ (x = 15, 20, 25) chalcogenide glasses has been carried out using several theoretical models and following conclusions could be made:

1. Crystallization rate factor (K) and frequency factor (K_o) suggest that glass forming ability and stability is maximum for $Ge_{15}Se_{70}Sb_{15}$ alloy compared to other compositions of Ge-Se-Sb system.
2. It is observed that values of activation energy in crystallization region increase with decreasing concentration of Sb content and hence making the glassy sample $Ge_{15}Se_{70}Sb_{15}$ is more stable compared to others.

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References

1. D. Lezal, J. Zavadil, M. Prochazka, "Sulfide, selenide and telluride glassy systems for optoelectronic applications", *J. Optoelectron. Adv. Mater.*, **7** (2005) 2281–2291.
2. T. Ohta, "Phase-change optical memory promotes the DVD optical disk", *J. Optoelectron. Adv. Mater.*, **3** (2001) 609–626.
3. B. Bureau, X.H. Zhang, F. Smektala, J. Adam, J. Troles, H. Ma, C. Boussard-Pledel, P. Lucas, D.L. Coq, M.R. Riely, J.H. Simmsons, "Recent advances in chalcogenide glasses", *J. Non-Cryst. Solids*, **345-346** (2004) 276–283.
4. M.H.R. Lankhorst, "Modelling glass transition temperature of chalcogenide glasses applied to phase change optical recording materials", *J. Non-Cryst. Solids*, **297** (2002) 210–219.
5. G. Saffarini, J.M. Saiter, "Compactness in relation to the mean coordination number in glasses $Ge_xBi_6S_{94-x}$", *Chalcogenide Lett.*, **3** (2006) 49–53.
6. R.P. Wang, A.V. Rode, S.J. Madden, C.J. Jha, R.A. Jarvis, B.J. Luther-Davies, "Structrul relaxation and optical properties in amourphous $Ge_{33}As_{12}Se_{55}$ films", *J. Non-Cryst. Solids.*, **353** (2007) 950–952.
7. R.M. Mehra, S. Kaur, P.C., Mathur, "Crystalline kinetics of bulk amorphous $Se_{80-x}Sb_xTe_{20}$", *J. Mater. Sci.*, **26** (1991) 3433–3437.
8. W. Wen-Hou, F. Linag, S. Xiang, P.W. Rong, "Crystalline kinetics and thermal stability in Ge-Sb-Se glasses", *Phys. Status Solid B*, **250** (2013) 59–64.
9. I.S. Yahia, A.M. Shakra, M. Fadel, N.A. Hegab, A.M. Salem, A.S. Farid, "Kinetics of non-isothermal crystallization of ternary $Se_{85}Te_{15-x}Sb_x$ glassy alloys", *Chalcogenide Lett.*, **8** (2011) 453–467.
10. T. Ozawa, "Kinetics of non-isothermal crystallization", *Polymer*, **12** (1971) 150–158.

11. J.A. Augis, J.E. Bennett, "Calculation of avrami parameters for heterogenous solid state reaction using a modification of the Kissinger method", *J. Therm. Anal. Calor.*, **13** (1978) 283–292.

12. K. Matusita, T. Konatsu, R. Yokota, "Kinetics of non-isothermal crystallization and activation energy for crystal growth in amorphous materials", *J. Mater. Sci.*, **19** (1984) 291–296.

13. K. Matusita, S. Sakka, "Kinetic study of crystallization of the glasses by differential scanning calorimetery", *Phys. Chem. Glasses*, **20** (1979) 81–84.

14. A.M. Elnalim Abd, K.A. Aly, N. Afify, A.M. Abousehlly, "Glass transition and crystallinzation kinetics of $In_x(Se_{75}Te_{25})_{100-x}$ chalcogenide glasses", *J. Alloys Compd.*, **491** (2010) 85–91.

15. M.M. Wakkad, "Crystallization kinetics of $Pb_{20}Ge_{17}Se_{63}$ and $Pb_{20}Ge_{22}Se_{58}$ chalcogenide glass", *J. Therm. Anal. Calor.*, **63** (2001) 533–547.

16. Y.Q. Gao, W. Wang, "On the activation energy of crystallization in metallic glasses", *J Non-Cryst. Solids*, **81** (1986) 129–134.

17. A. Kaswan, V. Kumari, D. Patidar, N.S. Saxena, K. Sharma, "Kinetics of phase transformations and thermal stability of $Ge_xSe_{70}Sb_{30-x}$ (x = 5, 10, 15, 20) chalcogenide glasses", *New J. Glasses Ceram.*, **3** (2013) 99–103.