Glass transition and crystallization of Se$_{95}$Te$_5$ chalcogenide glassy semiconductor

S. U. Atayeva[a,b], A. I. Isayev[a], S. I. Mekhtiyeva[a], S. N. Garibova[a,c,*],
R. I. Alekberov[a,d], F. N. Mammadov[e]
[a]*Institute of Physics, Ministry of Science and Education Republic of Azerbaijan,
Baku, 1143, Azerbaijan*
[b]*Department of General and Applied Physics, National Aviation Academy, Baku,
1045, Azerbaijan*
[c]*Department of Physics and Electronics, Khazar University, Baku, 1096,
Azerbaijan*
[d]*Azerbaijan State Economic University (UNEC), Baku, 1001, Azerbaijan*
[e]*Socar Midstream Operations LLC, Baku, Azerbaijan*

The study is dedicated to the investigation of thermo-physical characteristics of Se$_{95}$Te$_5$ chalcogenide glassy semiconductor during its glass formation and crystallization processes, employing various scanning rates of 5, 10, 15 and 20 K/min in non-isothermal modes through DSC measurement. Analysis of the structural relaxation kinetics involves the Kissinger's, Augis and Bennett's, as well as Matusita's approaches. Experimental data yield contains the determination of crucial parameters such as glass transition (T_g), crystallization(T_c), and melting temperatures alongside factors like reduced temperature of glass transition (T_{rg}), Hruby's parameter (K_{gl}), fragility index (F_i), Avrami exponents (n, m), glass transition (140.24 kJ/mol) and crystallization (E$_c$ = 95.11 kJ/mol) energies, respectively. The results confirm that Se$_{95}$Te$_5$ chalcogenide system as an efficient glass former. Matusita's method reveals that the crystallization mechanism (n = 2.51, m = 1.9) corresponds to volumetric nucleation with two-dimensional growth.

1. Introduction

Chalcogenide amorphous semiconductors, due to their unique physical properties, in particular transparency in the visible and infrared spectrum (IR), high optical density, reduced vibrational (phonon) energy and simple technological process mode are considered promising materials for micro- and optoelectronics [1-3]. Glass materials employed in integrated and fiber optics, as well as other optoelectronics devices necessitate stability in physical parameters and resistant to crystallization. Conversely, rapid crystallization is essential for memory cells formation based on phase transition [4]. The kinetics study of glass transition and crystallization will help clarify the stability degree of the structure and materials physical properties, predicting an optimal composition and obtaining approaches to meet various applications requirements.

Although selenium and tellurium are adjacent elements on the periodic table, they possess markedly various tendencies to form glass. Selenium is highly proficient at forming glass, leading to a variety of glass composition. It is valued for its transparency in both visible and infrared bands, as well as crystallization - stable properties. However, selenium's transparency is limited to around 12 μm due to its relatively low atomic mass. As an alternative, tellurium being heavier, when used in conjunction with selenium, extends the infrared threshold 20μm. Se–Te alloys, renowned for their high photosensitivity, exhibit higher glass transition and crystallization temperatures and reduced aging effects compared to pure amorphous selenium [5].Several studies [6-13] have explored the transition processes of amorphous selenium and the Se-Te system from the glassy to crystalline state. In work [6] crystallization process of amorphous selenium were

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studied by the methods of measuring electrical conductivity and estimated numerical value of activation energy characterizing the crystallized state is about 0.78 eV. In [7] the study of glass formation for non-crystalline selenium were investigated in bulk and film samples using DCS measurements, comparing the relation of structural relaxation rate with temperature. In works [8-11], the glass transition and crystallization in amorphous selenium and Se-Te chalcogenide glassy system containing $10 - 30$ at% of tellurium were studied and the results obtained were explained within model proposed by the author of works [12-13]. However, there is no detailed description of the influence tellurium small additions (up to 5 at %) on selenium structural relaxation during the transition to the glass state and crystalline that is a necessary factor for controlling electronic properties.

In presented work the characteristics temperatures of structural relaxation of amorphous $Se_{95}Te_5$, in particular, glass transition temperatures, crystallization temperatures and melting temperatures have been determined by analyzing the DSC curves at 5, 10, 15 and 20 K/min rates. Using Kissinger's [14, 15], Augis and Bennett [16], Matusita's approaches [17], the main parameters characterizing the glass transition and crystallization kinetics such as activation energy, Avrami exponent, Hruby' parameter (an indicator of glass-forming ability), fragility index have been estimated. The numerical values of these parameters and their heating rate dependence will allow suggesting possible mechanisms of the studied relaxation processes.

2. Experimental detail

2.1. Sample preparation

The $Se_{95}Te_5$ chalcogenide glassy semiconductor (ChGS) was synthesized by melting appropriate amounts of the Se and Te elements with a purity of (99.999%) in evacuated to 10^{-4} mmHg quartz ampoules using a rocking furnace. The furnace temperature is maintained above selenium (221^0C) and tellurium (450^0C) melting points. The synthesis heating up 800^0C and annealing for 16 hours followed by cooling of the reagents in the furnace turned off. The prepared ingots were crushed and sieved in powder form.

2.2. Research methods

DSC measurement is used to study the nature of the glassing and crystallization behavior of $Se_{95}Te_5$ ChGS. DSC data obtained from synchronous thermal analyzer STA-6000 was used for study melting and crystallization thermograms. The measurements were conducted within a specific temperature range of $25 \div 500$°C with 30 K/min heat flow rate supplied to selected samples weighing ~15 mg.

DSC curves obtained experimentally represent the temperature or time-dependent heat flow (mJ/s) or heat capacity (J/g·K). Experiments are typically carried out in either isothermal or non-isothermal modes. The isothermal process was followed by rapid heating of sample to a temperature slightly above the glass transition temperature and the heat released during crystallization at a steady temperature is recorded over time. In another mode the sample undergoes heating from room temperature at a stable scanning rate, while the released heat is monitored either with respect to temperature or time. The disadvantage of the isothermal method is that temperature stabilization requires a certain time, during which it is impossible to conduct experiments. The non-isothermal method used in the presented work does not have such disadvantages. Heating takes place in a controlled program at a specified rate within nitrogen atmosphere, and during the measurement, the heat flows of both the standard and the material being studied are compared. An aluminum crucible, left empty, served as a reference.

3. Finding and analysis

3.1. Glassing features of $Se_{95}Te_5$ system

Figure 1 below illustrates the DSC plots for $Se_{95}Te_5$ at the corresponding temperatures indicated on the graph.
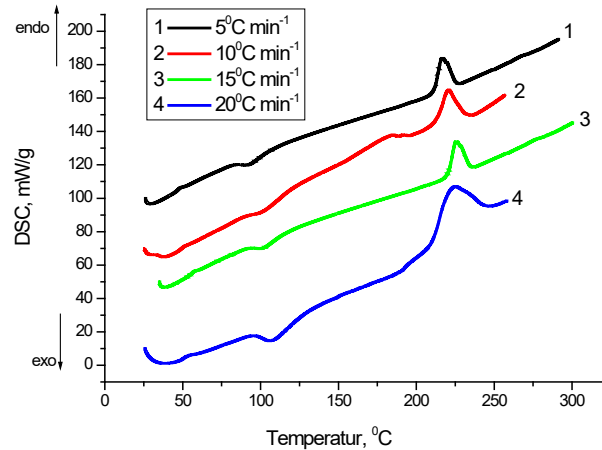

Fig. 1. DSC plots of $Se_{95}Te_5$ chalcogenide glassy semiconductor at specified heating rates.

From the curves above (see fig.1) at endothermic and exothermic peaks the characteristics temperatures are determined and the list is given in table 1, where T_g and T_c are glass transition and crystallization temperatures, respectively. T_m is the high-temperature endothermic peak well-known as the melting temperature.

Table 1. Parameters of structural relaxation processes determined for Se₉₅Te₅ chalcogenide glassy semiconductor.

Heating rate	T_g(K)	T_c(K)	T_m(K)	K_{gl}	F_i	T_g/T_m	T_c-T_m(K)
5	321	365,7	488,9	0,36	22	0,66	44,7
10	326	374,6	457,3	0,59	15	0,71	48,6
15	327,4	377,7	496,2	0,43	13	0,66	50,3
20	328,8	380,8	497,8	0,44	12	0,66	52

Figure 2 reflects the relationship between heating rate (α) and glass transition temperature (T_g) which conforms to empirical expression:

$$T_g = A + B ln\ (\alpha). \tag{1}$$

Derived values of the A and B parameters for $Se_{95}Te_5$ amorphous semiconductor were determined from this plot as follows: A=310.71Kand B =5.71min.
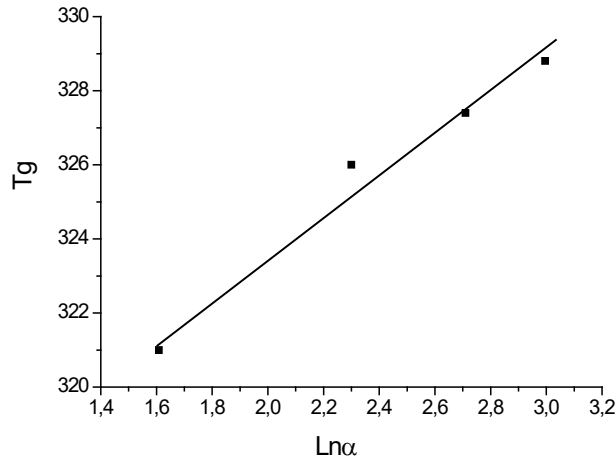
Fig. 2. Relationship between glass transition temperature (T_g) and heating rates (α) for $Se_{95}Te_5$ chalcogenide glass.

Considering that changes in the heating rate increase similarly affect the positions of both the crystallization and glass transition peaks, the equation proposed by the authors of [8, 9, 13-15] describing the correlation between heating rate and crystallization temperature was also employed to establish the glass transition energy:

$$ln\left(\frac{\alpha}{T_g^2}\right) = -\frac{E_g}{RT_g} + const \qquad (2)$$

where α – heating rate, R – universal gas constant. The author of works [13-15], considering relationship between T_g and heating rate as per [13] with thermal relaxation phenomenon, proposed the following formula:

$$ln(\alpha) = -\frac{E_g}{RT_g} + const. \qquad (3)$$

Figure 3 shows the plots of $ln(\alpha/T_g^2)$ and $ln\alpha$ versus $10^3/T_g$. The values of glass activation energy (132.96 kJ/mol and 147.51 kJ/mol) are determined from these plots by using equations (2) and (3), the mean value of which is determined as 140.24 kJ/mol.
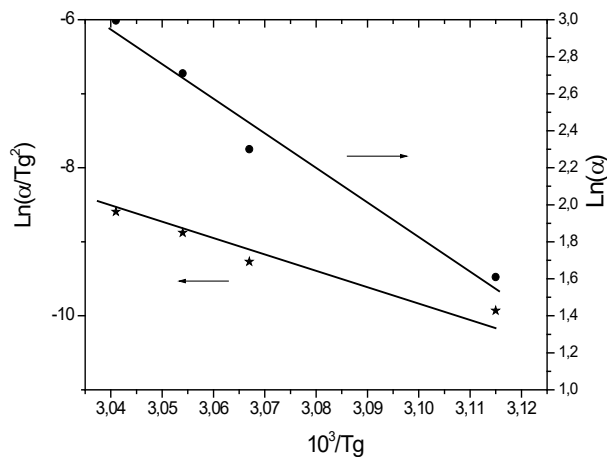

Fig. 3. Plot of $ln\,\alpha/T_g^2$ and $ln\alpha$ versus $10^3/T_g$ for the $Se_{95}Te_5$ chalcogenide glass.

Using the calorimetric observations presented in table 1 and the equation $T_{rg} = T_g/T_m$ proposed by the author [16] the reduced values of T_{rg} describing abilities to form glass, were estimated, results of which are also shown in the same table. As the table shows, all values of T_{rg} obey the rule of two thirds [17] ($T_{rg} \geq 0.65$), i.e. $Se_{95}Te_5$ ChGS system has an essential glass-forming ability. The table 1 also shows difference between T_c and T_g, which characterizes the strength and rigidity of a glass-like structure. As heating rate increases, a numerical value of T_c-T_g also increases. Another important parameter that determines heat resistance and glass-forming ability of an amorphous material is called Hruby' parameter which expressed by the equation $K_{gl} = (T_c$-$T_g)/(T_m$-$T_c)$ [18]. The values of the specified parameter are also shown in table 1. In addition to the specified parameters, an empirical parameter which characterizes the relationship between heating rate and temperature of the relaxation event well-known as fragility [19, 20] is expressed by formula (4):

$$F_i = \frac{E_g}{RT_g ln\,(\alpha)}. \tag{4}$$

The calculated values of the quantity F_i are quite low (table 1), which according to work [21] indicates a good glass-forming ability of the $Se_{95}Te_5$ ChGS system. Thus, applying existing theoretical approaches to the experimental results of calorimetric studies, it has been established that $Se_{95}Te_5$, along with such highly promising properties (high photosensitivity, hardness etc., compared to pure selenium) also have a good glass-forming ability.

3.2. Crystallization of $Se_{95}Te_5$ chalcogenide glass semiconductor

The kinetics and mechanism of ''amorphous-crystalline state'' material transitioning is described by the temperature and crystallization energy, including Avrami exponents (*m*, *n*) as well, characterizing the processes of nucleation and their growth. Using the peak values of the crystallization temperature (Fig. 1, Table 1) the necessary crystallization energy were calculated by formula:

$$ln\,(\frac{\alpha}{T_p^2}) = -\frac{E_c}{RT_p} + const, \tag{5}$$

where T_p -peak value of temperature, E_c - peak value of crystallization energy derived from formula (6) proposed by the authors of [10]

$$ln\left[\frac{\alpha}{(T_p - T_o)}\right] \cong -\frac{E_c}{kT_p} + lnK_0, \tag{6}$$

where T_o – initial temperature for crystallization, K_0 - frequency factor. From the dependency shown in figure 4 the crystallization energy is estimated by different approaches and the results are given below in Table 2.
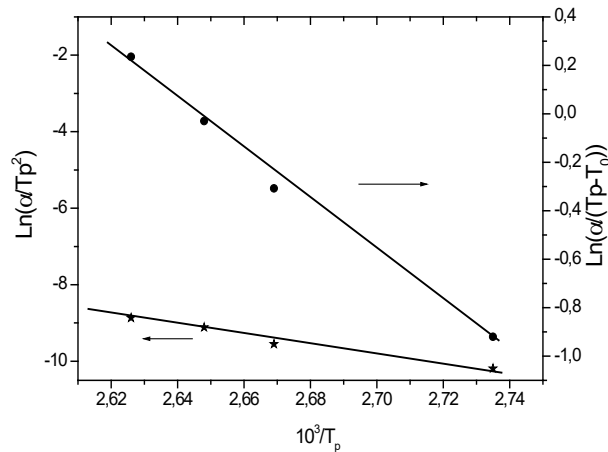
Fig. 4. Plot of $ln\left(\frac{\alpha}{T_p^2}\right)$ and $ln\left[\frac{\alpha}{(T_p-T_o)}\right]$ versus $10^3/T_p$ for $Se_{95}Te_5$.

Table 2. Derived values for crystallization energy (E_c) determined by different approaches.

Approaches	$E_c/$ kJ mol^{-1}
Augis and Bennett	88,48
Kissinger's	99,93
Matusita's	102,05
Average value	96,82

The authors of works [18, 21-23] proposed a formal theory of the kinetics for transformation and equations expressing the volume fraction ($\varkappa$) of crystallization over time *t* to interpret the experimental facts established by DSC research

$$\varkappa = 1 - \exp\left[-(Kt)^n\right] \tag{7}$$

$$K = K_0\exp\left(-\frac{E_c}{RT}\right), \tag{8}$$

where, *K* – effective reaction rate, K_0 – frequency factor.

The kinetics and mechanism of crystallization are often studied using the model proposed by the authors of [18, 21-23] derived for an isothermal process. In the non-isothermal method at steady scanning rate, the relationship between temperature, heating rate and the crystallized fraction of sample volume is expressed by the formula [11]:

$$ln[-\ln(1-\varkappa)] = -nln(\alpha) - 1.052\,{mE_c}/{RT} + const. \tag{9}$$

Here, *m* and *n* - numerical coefficients, relationships depending on a crystallization mechanism. In the case, when nucleation occurs during DSC at the steady scanning rate, the n will equal to m + 1. If the growth of a pre-existing nucleus formed due to some heat before DSC analysis, occurs during the crystallization, then *n* is equal to *m*.
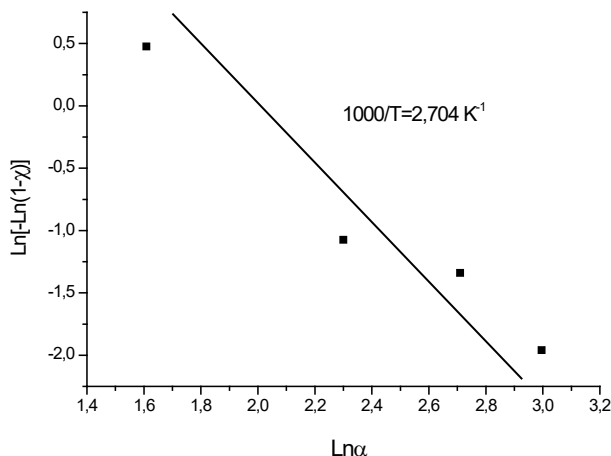
*Fig. 5. Relationship between ln [-ln (1-ϰ)] and ln(**a**) for $Se_{95}Te_5$.*

From the dependencies shown in figure 5 and figure 6 were determined the values of *n* and mE_c, results of which are given in table 2. In our experiments, the values of these coefficients are found equal to n = 2.51 and m = 1.9. According to [24], the indicated values of the coefficients characterizing the crystallization mechanism correspond to volumetric nucleation with two-dimensional growth.
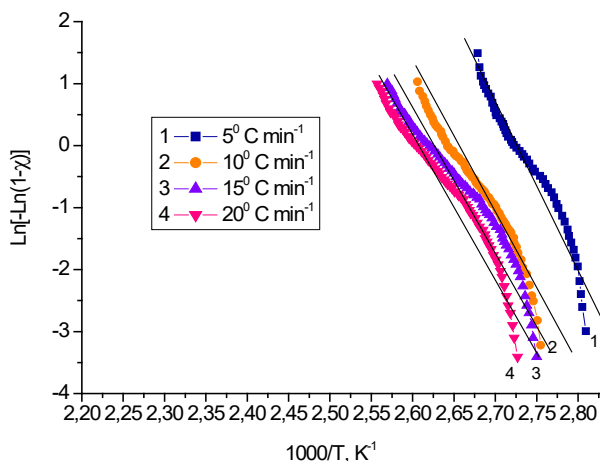

Fig. 6. Relationship between ln [-ln (1-ϰ)] and $10^3/T$ for $Se_{95}Te_5$.

As the plot shows (Fig. 6), the slope in the initial section is high, but with increasing temperature the slope noticeably decreases. It is assumed that both nucleation and growth simultaneously at initial moment of time, each contributing a certain amount to the crystallization process.

4. Summary

The structural relaxation processes of $Se_{95}Te_5$ chalcogenide glassy semiconductor were investigated by DSC method. The glass transition (T_g), crystallization (T_p), and melting (T_m) temperatures were determined at 5, 10, 15 and 20 K/min various scanning rates. It was found that T_g and T_p increase with increasing heating rates. Using the DSC data obtained from the experiment, such parameters of the amorphous matrix as the reduced value of T_g, the difference

$T_c - T_g$, the Hruby' parameter (K_{gl}), and the fragility index (F_i) have been estimated. Certain numerical values indicate that the studied $Se_{95}Te_5$ ChGS is an efficient glass-former. The activation energy (140.24 kJ/mol) for structural relaxations during the transitioning of substance from a glass state to a viscous have been determined by the existing theories about kinetics of structural transformations.

Using various existing theoretical approaches of the mechanism and crystallization kinetics, the crystallization energy and the coefficients (m, n) are also determined; allow making statements about the mechanism for crystallization. The numerical values of the coefficients describing the crystallization mechanism (n=2.51; m=1.9) correspond to volumetric nucleation with two-dimensional growth. The high slope of $ln[-ln(1-\varkappa)]$ versus $10^3/T$ plot in the initial section is related with the contribution of the energy, parallel processes of nucleation and its growth. Over time, the first process weakens, leading to the decrease in the crystallization energy.

Acknowledgements

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