

Kinetic Analysis of Thermal Processes in Ag–As–S–Se System Based on DSC Measurements

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Thermal properties of glasses from the system $\text{Ag}_x(\text{As}_{40}\text{S}_{30}\text{Se}_{30})_{100-x}$ for $x = 0, 0.5, 1, 3,$ and 5 at.% were investigated by differential scanning calorimetry. The DSC curves were obtained under non-isothermal conditions which allowed determination of the glass transition temperature T_g (onset temperature), crystallization temperature T_p (corresponding to the crystallization peak maximum), melting temperature T_m , crystallization enthalpy H_c , and melting enthalpy H_m . The DSC curves obtained at the same heating rate were analyzed in order to study the variation of glass transition temperature with Ag concentration. Observed T_g shift toward higher values, with increase in the heating rate, is in agreement with the Lasocka equation. Samples with 3 at.% and 5 at.% Ag were further thermally treated at different heating rates with the aim of analyzing kinetic processes of crystallization. The Moynihan and Kissinger models were used to calculate the activation energy of glass transition and activation energy of crystallization. For the samples that showed the crystallization processes an assessment of the thermal stability was done based on different criteria.

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1. Introduction

Ag-doped chalcogenide glasses and thin films are attractive materials with many applications such as solid electrolytes (batteries, thin film batteries), electrochemical sensors, photoresists, optical waveguides, diffraction elements, the Fresnel lenses, holography and other optical and non-linear optical elements [1]. Nowadays in particular, there is a great interest for the research of photo-induced changes in their physical and chemical properties, i.e. surface silver photodeposition, used for the production of optical memories. Several studies of chalcogenide glasses with silver in the three and four-component system confirmed the appearance of this phenomenon [2].

Investigation of thermal properties of amorphous semiconductors is important for both, their characterization and their technological application. Properties that glasses exhibit during their heating or cooling indicate the existence of phase transitions such as softening, crystallization and melting of crystalline centers, which are important information in the optimization of the synthesis parameters. The differential scanning calorimetry (DSC) is suitable experimental technique for this kind of analysis and it can be performed on chalcogenide glasses under isothermal and non-isothermal conditions [3]. Likewise, in the glassy materials it is of great importance to examine the thermal stability. This parameter indicates and classifies utilization of the investigated material by examining the ability of a material to resist the formation of the crystalline phases. In the literature there are

several criteria that are used to examine this property of a material.

In this work DSC measurements of quaternary Ag–As–S–Se system under non-isothermal regime have been performed, allowing several parameters in glass kinetics to be obtained, also providing data on the impact of the addition of silver and thermal characteristics and glass stability.

2. Experimental

Chalcogenide glasses of $\text{Ag}_x(\text{As}_{40}\text{S}_{30}\text{Se}_{30})_{100-x}$ system for $x = 0, 0.5, 1, 3$ and 5 at.% were prepared by melt quenching technique. Synthesis has taken place in a rocky furnace, where molten material in ampoule was shaken at regular intervals to ensure obtaining the best possible homogenization. The maximum temperature of the synthesis was 950°C . At that temperature, the ampoules with the melt were taken out from the furnace and were air-quenched [4]. The amorphous nature of the chalcogenide glasses was verified by X-ray diffraction.

The calorimetric measurements were carried out on a DSC822 Mettler Toledo differential scanning calorimeter, with the temperature measurement precision of 0.2 K. Investigated materials in the form of bulk (with at least one flat side) were put in the standard aluminium pans ($40 \mu\text{l}$) and were placed in the atmosphere of pure nitrogen of 50 ml/min flow. For the purposes of determining the activation energy, samples were heated at different heating rates over a wide temperature range. For these measurements 6 mg to 8 mg of each sample was used. The errors in the indirect determination of characteristic temperature ranged up to ± 0.5 K.

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3. Results and discussion

Figure 1 shows the DSC thermograms of the investigated amorphous system obtained at a heating rate of 20 K/min. In this figure a single endothermic peak can be observed for all Ag-doped samples which is an indication of a glass transition. Only samples with 3 at.% and 5 at.% of silver show exothermic peaks as well which is a confirmation of a double crystallization. The first exothermic peak is a consequence of a complex crystallization, while the second one originates from the crystallization process followed by the process of melting. The values of glass transition temperatures at four heating rates for all investigated glasses are given in Table I. Glass transition temperature T_g , as it can be seen from Table I, shifts toward higher values when heating rate (β) increases from 10 K/min to 30 K/min. Also by increasing the silver content in the matrix of chalcogenide glasses the value of T_g decreases for each of the heating

rates. Dependence of T_g with silver content at two fixed heating rates is given in Fig. 2a.

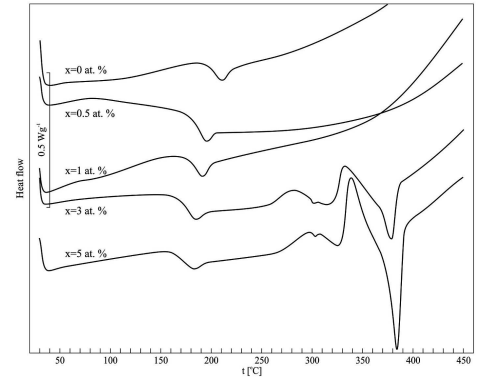


Fig. 1. DSC scans for the system $\text{Ag}_x(\text{As}_{40}\text{S}_{30}\text{Se}_{30})_{100-x}$ at a heating rate of 20 K/min.

TABLE I

The values of pre-crystallization parameters T_g , A , B and E_a for $\text{Ag}_x(\text{As}_{40}\text{S}_{30}\text{Se}_{30})_{100-x}$ system.

Glasses	T_g [K]				A [K]	B	E_a [kJ/mol] Moy.	E_a [kJ/mol] Kiss.
	10	15	20	30				
	[K/min]							
$\text{As}_{40}\text{S}_{30}\text{Se}_{30}$	464.6	465.5	468.3	470.8	474.67 ± 1.33	5.93 ± 1.02	290 ± 49	282 ± 49
$\text{Ag}_{0.5}(\text{As}_{40}\text{S}_{30}\text{Se}_{30})_{99.5}$	450.0	450.5	452.0	455.8	458.56 ± 1.90	5.24 ± 1.45	282 ± 78	275 ± 78
$\text{Ag}_1(\text{As}_{40}\text{S}_{30}\text{Se}_{30})_{99}$	448.1	448.6	449.8	453.7	456.33 ± 1.95	5.05 ± 1.49	285 ± 84	278 ± 84
$\text{Ag}_3(\text{As}_{40}\text{S}_{30}\text{Se}_{30})_{97}$	437.1	438.1	439.3	442.9	445.83 ± 1.48	5.22 ± 1.14	282 ± 61	275 ± 61
$\text{Ag}_5(\text{As}_{40}\text{S}_{30}\text{Se}_{30})_{95}$	434.4	436.2	436.9	439.5	442.30 ± 0.69	4.48 ± 0.53	345 ± 40	338 ± 40

3.1. Glass transition activation energy

Dependence of glass transition temperature T_g with the heating rate β can be analyzed using empirical relation suggested by Lasocka [5]:

$$T_g = A + B \ln \beta, \quad (1)$$

where A and B are constants (Table I). The value of constant A indicates the glass transition temperature for the heating rate of 1 K/min. The constant B is related to the cooling rate of the melt and its physical significance seems to be related to the response of the configurational changes within the glass transformational region. The value of B is calculated from the slope of T_g versus $\ln \beta$ plots (Fig. 2b). Different values of the parameter B with the silver content indicate the existence of structural changes in the Ag-As-S-Se system. In the literature, the influence of silver incorporation on T_g is usually explained through the structural model of amorphous Se that includes two molecular species, which contain helical chains of trigonal Se and Se_8 ring molecules of monoclinic Se. Therefore, as Ag contents are incorporated they are dissolved in the Se chains increasing relatively the number of Se_8 ring while the numbers of long chain Se-Se are

decreased [6]. It is known that the glass transition temperature should increase with increasing chain length and decrease with increasing ring concentration [7]. In this case, it is evident that the glass transition temperature decreases with increasing Ag content, probably due to the somehow different structural changes that occur by adding Ag content, compared to the mentioned above.

The activation energy of glass transition E_a was first investigated using the theory of structural relaxation developed by Moynihan et al. [8]. The plots presented in Fig. 3a were obtained using Moynihan relation [8]:

$$\ln \beta = -\frac{E_a}{RT_g} + \text{const}, \quad (2)$$

where R is the universal gas constant. The activation energy of glass transition E_a was calculated from the slope of these plots. The calculated values of E_a using Eq. (2) are shown in Table I. The second most common way to determine the activation energy of glass transition E_a is by using Kissinger relation [9, 10]:

$$\ln \left(\frac{T_g^2}{\beta} \right) = \frac{E_a}{RT_g} + \text{const}. \quad (3)$$

Applying this model on chalcogenide glasses from the present system, values of E_a for each glass are calculated and presented in Table I. The plots of $\ln(T_g^2/\beta)$ versus

$1000/T_g$ given in Fig. 3b, are found to be straight lines for all samples (according to Eq. (3)).

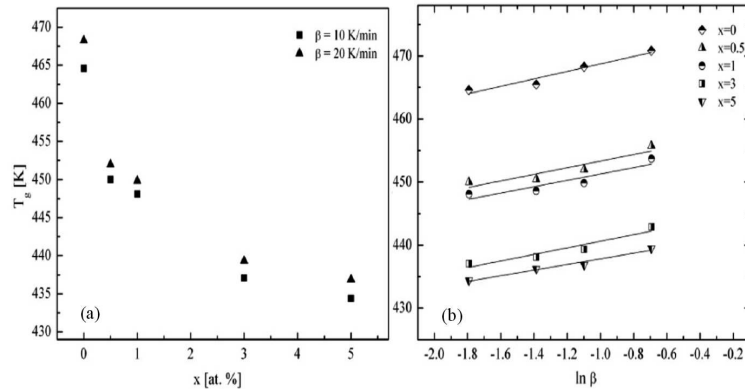


Fig. 2. Dependence of the glass transition temperature T_g with silver content at heating rates of 10 K/min and 20 K/min (a); dependence of T_g for the investigated samples with $\ln \beta$ in the matrix of $\text{Ag}_x(\text{As}_{40}\text{S}_{30}\text{Se}_{30})_{100-x}$ system (b).

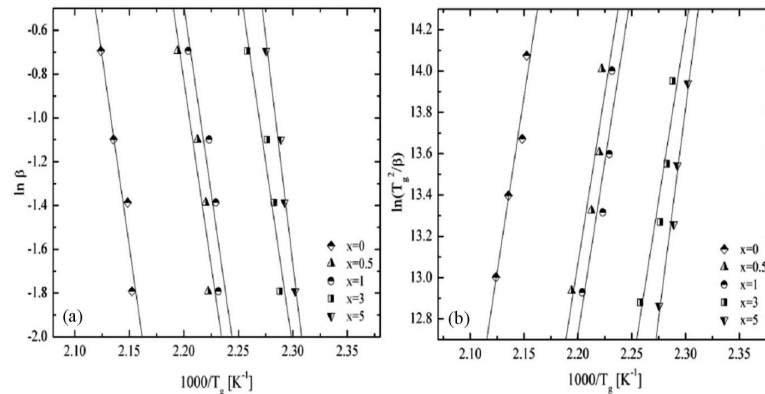


Fig. 3. (a) Plots of $\ln \beta$ vs. $1000/T_g$ and (b) $\ln(T_g^2/\beta)$ vs. $1000/T_g$ for amorphous $\text{Ag}_x(\text{As}_{40}\text{S}_{30}\text{Se}_{30})_{100-x}$ glasses.

As it can be seen from Table I calculated values of E_a from Moynihan and Kissinger relations are almost the same and are in a good agreement with each other (Fig. 4). This implies that both methods can be used for successful calculation of the glass transition activation energy. As known, the glass activation energy E_a is the amount of energy that is absorbed by a group of atoms in the glassy region so that a jump from one metastable state to another is possible [11]. Among all investigated glasses no significant change in the E_a value was found for the glasses with up to 3 at.% of Ag. Only $\text{As}_{40}\text{S}_{30}\text{Se}_{30}$ matrix with 5 at.% of Ag has a jump in E_a parameter, which indicates its most difficult change from metastable state to the state with minimum energy. Similar E_a orders of magnitude have been found in other silver containing Ag-As-Se systems [12].

3.2. Crystallization activation energy and thermal stability

Evidently (seen from Fig. 1) the analyses of crystallization kinetics can be applied only for samples with 3 at.% and 5 at.% of Ag. One of the most used methods for determining the activation energy of glass crystallization E_c

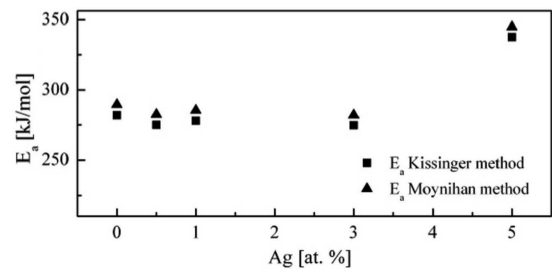


Fig. 4. Activation energies of glass transition from two different methods dependent on the percentage of silver content.

is the Kissinger method [9, 10]:

$$\ln \left(\frac{T_p^2}{\beta} \right) = \ln \left(\frac{E_c}{RK_0} \right) + \frac{E_c}{RT_p}, \quad (4)$$

where T_p is the peak crystallization temperature and K_0 is the frequency factor. Dependence of $\ln(T_p^2/\beta)$ versus $1000/T_p$ for the first and the second crystallization peak for $\text{Ag}_3(\text{As}_{40}\text{S}_{30}\text{Se}_{30})_{97}$ and $\text{Ag}_5(\text{As}_{40}\text{S}_{30}\text{Se}_{30})_{95}$

glasses is given in Fig. 5a. The activation energy of crystallization E_c for both exothermic peaks is determined

from the slope of the straight line and obtained values are shown in Table II

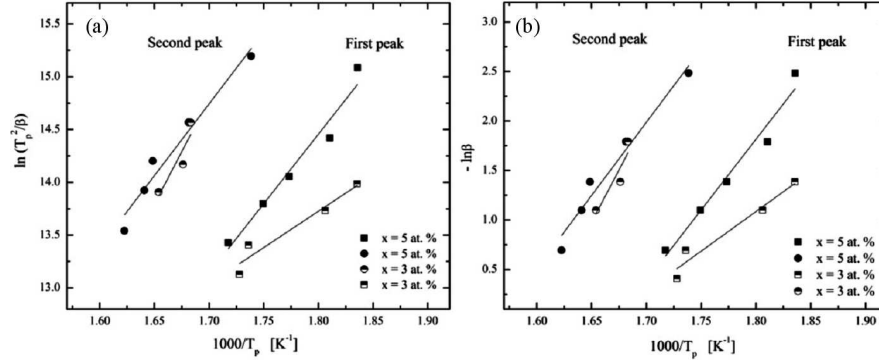


Fig. 5. Plots of $\ln(T_p^2/\beta)$ versus $1000/T_p$ (a) and $\ln \beta$ versus $1000/T_p$ (b) for the first and second crystallization peak of $\text{Ag}_x(\text{As}_{40}\text{S}_{30}\text{Se}_{30})_{100-x}$ glasses.

TABLE II

Values of crystallization activation energy of the glasses with 3 and 5 at.% of silver, K_0 , enthalpies of crystallization H_c and melting H_m .

Composition	E_c [kJ/mol]				K_0 [s ⁻¹]		H_c [J/g] at 20 K/min		H_m [J/g] at 20 K/min
	Kissinger		Mahadevan		I peak	II peak	I peak	II peak	
	I peak	II peak	I peak	II peak					
$\text{Ag}_3(\text{As}_{40}\text{S}_{30}\text{Se}_{30})_{97}$	57.22	165.37	66.56	175.34	1.80	3.64×10^9	6.24	6.87	8.97
$\text{Ag}_5(\text{As}_{40}\text{S}_{30}\text{Se}_{30})_{95}$	109.47	113.06	118.83	122.95	1.36×10^5	5.89×10^4	6.12	8.22	23.70

Another method which can be used to determine activation energy of crystallization is proposed by Mahadevan et al. [13]:

$$\ln \beta = -\frac{E_c}{RT_p} + \text{const.} \quad (5)$$

Equation (5) represents approximation of Eq. (4) when the value of $\ln T_p^2$ changes negligibly in comparison with $\ln \beta$. Figure 5b shows plots of $\ln \beta$ versus $1000/T_p$ for both crystallization peaks, where from the slope of the straight line E_c was calculated. Obtained kinetic parameters are given in Table II. Due to the difficulties in precise reading of T_p value of the second crystallization peak at 30 K/min for $\text{Ag}_3(\text{As}_{40}\text{S}_{30}\text{Se}_{30})_{97}$ glass sample, the analysis included only three speeds. The results show that sample with 5 at.% of silver has a higher value of E_c in the first crystallization stage. The increase of E_c with silver content in the chalcogenide glasses for the first crystallization is also found in other silver containing systems Ag-As-Se [12]. In the three-component system like Se-S-Ag adding Ag also increases E_c values [14]. Values of E_c are higher for the second crystallization peak.

The frequency factor K_0 is related to the possibility of the transformation rate and shows the number of attempts made by the nuclei per second to overcome the

energy barrier. The obtained values for K_0 are shown in Table II. The minimum value of K_0 has the glass with higher content of Ag indicating that the transformation rate for this glass is slower. The enthalpy release refers to the metastability of the glasses [3]. Analyzing only the first crystallization peak, the minimum value of H_c has the glass sample with 5 at.% Ag which confirms its higher stability. The enthalpies of crystallization H_c and melting H_m at a heating rate of 20 K/min are also presented in Table II.

An important indicator of thermal stability is the difference between the onset temperature of crystallization T_c and the glass transition temperature T_g , known as the Dietzel criteria [15] $\Delta T = T_c - T_g$. The greater the difference between these two temperatures the greater is the thermal stability of the investigated glass sample. The $T_c - T_g$ difference increases with silver concentration and β parameter increases. Another criterion that can be used to analyze thermal stability of a glass is introduced by Hruby [16] and it is based on the ration of the temperature differences $H_r = (T_c - T_g)/(T_m - T_p)$. In this paper the values of the onset temperatures (T_c) that refers only to the first crystallization peak (T_{c1}) are used for the analysis of the thermal stability of the inves-

tigated glasses. The higher values of H_r parameter mean a delay in the nucleation process. One more parameter useful for analyzing thermal stability is weighted thermal stability $H_w = (T_c - T_g)/T_g$ introduced by Saad and Poulin [17]. Obtained values of thermal stability analyzed through three mentioned criteria at four heating rates are given in Table III. According to all of the analyzed criteria glass sample with higher content of silver is more thermally stable.

TABLE III

Calculated values of stability parameters based on different criteria.

Glass	β [K/min]	$\Delta T = T_{c1} - T_g$ [K]	H_r	H_w
$Ag_3(As_{40}S_{30}Se_{30})_{97}$	10	90.2	0.929	0.206
	15	88.91	0.856	0.203
	20	92.67	0.941	0.211
	30	99.38	1.234	0.224
$Ag_5(As_{40}S_{30}Se_{30})_{95}$	10	97.74	0.946	0.225
	15	102.65	1.101	0.235
	20	103.52	1.202	0.237
	30	105.06	1.334	0.239

4. Conclusion

Kinetic analysis of thermal processes of $Ag_x(As_{40}S_{30}Se_{30})_{100-x}$ chalcogenide glasses for $x = 0, 0.5, 1, 3$ and 5 at.% has been performed at different heating rates. The glass transition temperature, representing the rigidity of the glass network, decreases with an increase in Ag content and increases with the increase of the heating rate. Changes in the glass transition temperatures are determined by structural changes caused by the addition of silver. It was found that calculated values of the activation energy of glass transition E_a , from two different methods, are in a good agreement with each other, and abrupt increase in this value occurs with the highest silver content. Crystallization kinetics analysis could be performed only for the glasses with 3 at.% and 5 at.% of silver. The obtained values of E_c parameter, using the Kissinger and Mahadevan methods, are almost the same for the first and second crystallization peak. This shows that each of these methods can be used to successfully

calculate E_c . The values of K_0 and H_c indicate that the $Ag_5(As_{40}S_{30}Se_{30})_{95}$ glass is more stable than the glass with 3 at.% of Ag. High values of thermal stability parameters: ΔT , H_r and H_w , further confirm that the glass sample with highest content of silver has the highest thermal stability.

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