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Study of the crystallization behaviour in arsenic-sulphide glasses doped with Pb

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A kinetic analysis of the crystallization processes in arsenic-sulphide glasses doped with Pb was performed using the DSC method. According to the results of X-ray diffraction measurements of the annealed $Pb_3(As_2S_3)_{97}$ samples, it was found that the crystallization processes take part through the formation of As_2S_3, As-S and PbS centers. The dependence of crystallization activation energy on crystallized fraction determined using both Kissinger, Akahira and Sunose (KAS) and Vyazovkin methods, revealed that the first and second crystallization are a single-step processes, while the third one is a complex one. Using the methods of Šatava, Ozawa, and Ozawa-Chen, the occurrence of voluminous 3D crystal growth in investigated samples was found. Glass stability parameters indicated on increase in crystallization affinity with Pb content.

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Keywords: Chalcogenide glasses, DSC measurements, Crystallization kinetics, Thermal stability

1. Introduction

The introduction of small amounts of impurity into the content of chalcogenide glasses (ChG) or variations in the technological procedure of their preparation significantly affects the majority of their physical properties, which is why they are being investigated for advanced applications over the past few decades [1-3]. The knowledge of glass crystallization behaviour is essencial for finding the suitable operating temperature range for a specific industrial application. However, ChG are often characterized with poor thermal/mechanical properties, which limits their practical use. In order to improve these properties without modifying in infrared transmission [4] the process of controlled crystallization showed to be optimal. Significant kinetic parameters such as activation energy, pre-exponential factor and reaction model can be determined using the kinetic analysis of the crystallization phenomena. The procedures developed to calculate these parameters can be selected into two groups: isokinetic and isoconversional methods. Isokinetic methods assume that the mechanism of transformation and kinetic parameters are constant. The isoconversional methods are based on a hypothesis that the transformation rate for the constant degree of the transformation χ depends only on the temperature [5], and therefore, at selected temperatures, the kinetic parameters show dependence only on the volume fraction [6]. The knowledge of kinetic parameter values can provide extrapolation of the kinetic behaviour of the glassy system in different conditions, which is very important for the use of these materials in practice.

Thermal stability indicates on glass resistance to the devitrification of glasses during the nucleation and growth processes [7,8]. Apart from the utility, implementation of these investigations is also significant for the estimation of durability of the devices fabricated from these materials [9].

This work reports the results of the kinetic analysis of crystallization processes in the glasses with x=1, 2 and 3 at. % of Pb in the As_2S_3 matrix using the DSC in non-isothermal regime. The DSC data is analyzed with the help of isoconversional and isokinetic methods to investigate

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the growth processes involved in the transformation and to clarify its mechanism and dimensionality, as well as to determine the crystallization affinity of the investigated compounds. The paper also deals with the analysis of thermal stability of studied glasses.

2. Experimental

Bulk glassy samples of the system $(Pb)_x(As_2S_3)_{100-x}$, x=1, 2 and 3 at. % were synthetized by using a cost-effective and conventional melt-quench technique, for details see Ref. [12]. Amorphous character of as-prepared samples was previously confirmed by XRD analysis [13]. In order to perform the DSC measurements using a Mettler Toledo DSC 822e instrument, investigated samples were sealed in standard pan and scanned over a temperature range from 300 to 770 K at selected heating rates (10, 15, 20, 25 and 30 K/min). For the needs of crystalline centers identification of thermally treated samples, Philips X-ray diffractometer of 1710-type with CuKα radiation of the wavelength of 1.5418 Å was used. The samples were previously annealed to the peak temperature of detected crystallization processes. The scanning angle was varied within a range of 5°–80°.

3. Results and discussion

In order to obtain an insight at the crystallization kinetics in $Pb_x(As_2S_3)_{100-x}$ glassy system calorimetric measurements of the samples with x=1, 2 and 3 at.% of Pb were performed in the 300-770 K temperature range at 5 heating rates. Implementation of DSC technique in investigation is significant since it provides detection of all thermal phenomena in the course of heating and enables determination of some important parameters. Fig. 1 show DSC curves for the investigated samples, obtained at heating rate 15 K/min. Fig. 2 presents the DSC curves of the $Pb_2(As_2S_3)_{98}$ glass at different heating rates. The DSC thermograms are characterized by three different thermal events. The first endothermic change refers to the kinetic effect of softening, which is studied in details by analysis presented in Ref. [10]. The exothermic peaks correspond to the crystallization phenomena, which appears to be a complex process, consisted of two (for the glass $Pb_1(As_2S_3)_{99}$), or even three consecutive effects (for the glasses $Pb_2(As_2S_3)_{98}$ and $Pb_3(As_2S_3)_{97}$). The corresponding onset and peak temperature values are given in Table 1. The second endothermic process on DSC curves represents the change in enthalpy of melting of crystalline centers. The characteristic temperatures of all thermal events are given in Table 1. It should be noted that the first crystallization process, detected for the samples with x=2 and 3 at. % of Pb is missing on DSC curves of the sample with the lowest amount of Pb. Also, the second crystallization process in the glass with the highest Pb content is registered but not well defined to be analized by isoconversion methods.

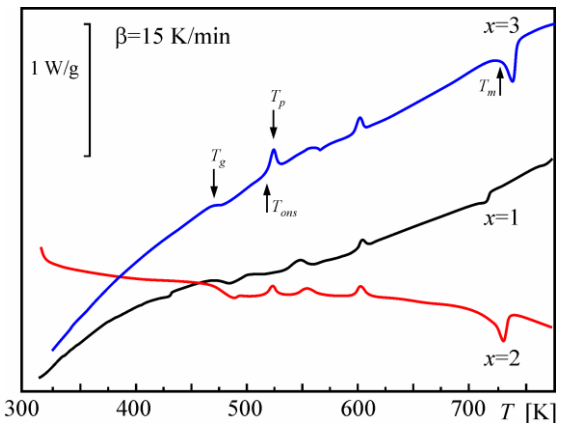

Fig. 1. DSC curves of the $Pb_x(As_2S_3)_{100-x}$ glasses at heating rate of β=15 K/min.

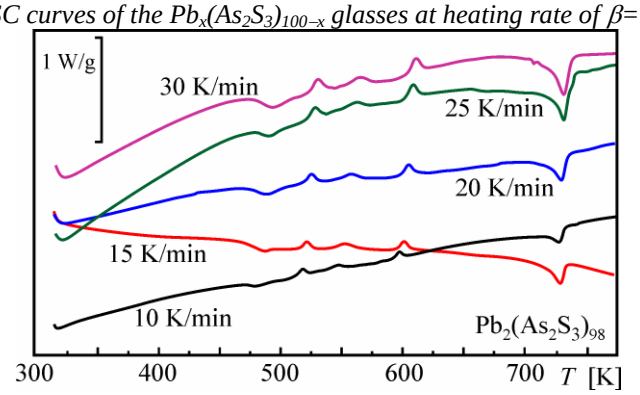

Fig. 2. DSC curves of the $Pb_2(As_2S_3)_{98}$ glass at different heating rates.

As it is known, the crystallization process is governed by nucleation and there exists an induction time for the nucleation. The temperature at which the induction time becomes zero increases with increase in heating rate, leading to the observed shift of crystallization temperature to higher values (see Fig. 2). The change in crystallization temperature with the heating rate can be used to study and analyze the heating rate dependence of the glass stability criteria.

Table 1. The onset (T_{ons}) and maximum temperature of crystallization (T_p) of $Pb_x(As_2S_3)_{100-x}$ glassy samples.

x [at. % Pb]	β [K/min]	T_{ons} [K]	T_p [K]	T_{ons} [K]	T_p [K]	T_{ons} [K]	T_p [K]
		process 1		process 2		process 3	
1	10	—	—	526.7	540.0	593.7	599.3
	15	—	—	533.1	547.4	598.3	604.0
	20	—	—	538.4	552.3	601.5	607.7
	25	—	—	545.5	558.1	603.7	610.6
	30	—	—	545.6	559.9	605.4	612.4
2	10	512.8	517.9	535.2	547.0	591.1	597.2
	15	515.0	521.4	540.0	552.3	594.0	601.0
	20	518.5	525.0	544.0	557.8	598.0	604.4
	25	521.0	528.1	549.9	561.8	601.3	608.2
	30	523.7	530.3	553.3	564.9	603.2	610.6
3	10	510.3	516.2	—	—	588.7	594.5
	15	516.6	522.4	—	—	594.2	600.0
	20	516.7	523.9	—	—	596.4	602.6
	25	519.5	526.7	—	—	597.6	604.3
	30	521.7	528.3	—	—	599.9	606.2

In order to estimate the crystallization activation energy, the Kissinger method was used [11]. It established a connection between the thermal treatment rate β and temperature of maximum enthalpy change T_p at which the crystallization rate $\dot{\chi}$ reaches its maximum:

$$\ln\left(\frac{T_p^2}{\beta}\right) = \ln\left(\frac{E}{RK_0}\right) + \frac{E}{RT_p} \tag{1}$$

where K_0 is a frequency factor of the reaction rate constant K.

The model of Kissinger applied on experimental data of the investigated glasses gives the linear dependence between $\ln(T_p^2/\beta)$ and $1/T_p$, as shown in Fig. 3. The activation energy E and frequency factor K_0 are calculated from the slope of functional dependance and presented in Table 2. Higher values of parameters E and K_0 of the glass with the highest Pb content can be interpreted by the fact that Pb as impurity modifies the amorphous matrix structure and affects the increase in the tendency to crystallize [12,13].

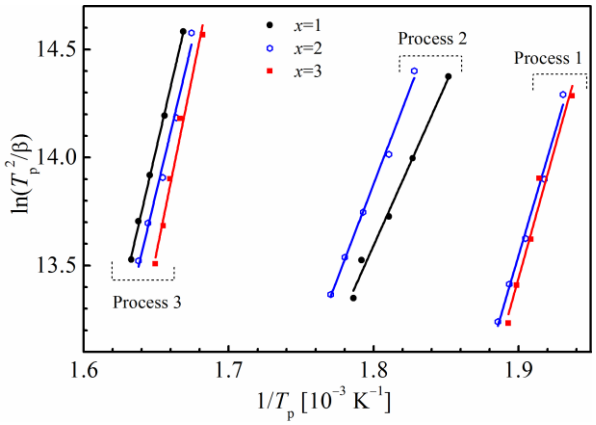

Fig. 3. Dependence of $\ln(T_p^2/\beta)$ *on* $1/T_p$ *and the corresponding linear fits for* $Pb_x(As_2S_3)_{100-x}$ *glassy samples.*

Table 2. The parameters of crystallization kinetics calculated using different methods of the $Pb_x(As_2S_3)_{100-x}$ *glasses; E – activation energy of crystallization; n – Avrami exponent; m – dimensionality of the crystal growth.*

process	x [at.% Pb)	Kissinger		Matusita-Sakka			
		E_a [kJ/mol]	K_0 [s^{-1}]	mE [kJ/mol]	mE/n [kJ/mol]	n	n'
1	1	—	—	—	—	—	—
	2	189(11)	$1.8\cdot10^{17}$	764(46)	182(3)	3.71(7)	4.20
	3	200(19)	$2.3\cdot10^{18}$	758(52)	186(2)	4.0(1)	4.08
2	1	125(6)	$1.0\cdot10^{10}$	446(23)	115(1)	3.18(5)	3.88
	2	146(6)	$8.2\cdot10^{11}$	530(27)	138(2)	3.26(7)	3.84
	3	—	—	—	—	—	—
3	1	240(5)	$1.1\cdot10^{19}$	1129(79)	220(7)	4.1(3)	5.13
	2	233(16)	$3.6\cdot10^{18}$	1021(88)	220(4)	4.4(3)	4.64
	3	274(20)	$1.9\cdot10^{22}$	1199(50)	257(3)	4.1(2)	4.67

The variation of the activation energy with the degree of crystallization can provide useful information about the different mechanisms involved in the transformation process. In order to reveal this variation and to investigate different nucleation and growth mechanisms associated with this transformation the linear isoconversional methods of Kissinger, Akahira and Sunose (KAS model) [14] and Vyazovkin [15] were applied.

The KAS model is based on relation that establishes a connection between the heating rate β and temperature T_χ for corresponding crystalline fraction:

$$\ln\left(\frac{T_\chi^2}{\beta}\right) = \text{const.} + \frac{E_\chi}{RT_\chi} \tag{2}$$

From the slope of $\ln(T_\chi^2/\beta)$ versus $1/T_\chi$ it was possible to determine the activation energy value.

Using the Vyazovkin method, for a series of n experiments carried out at different heating rates, the activation energy range for selected degree of crystallization (χ) can be determined by finding the value of E_χ for which the function:

$$\Omega = \sum_{i=1}^{n}\sum_{j\neq i}^{n}\frac{I(E_\chi, T_{\chi,i})\beta_j}{I(E_\chi, T_{\chi,j})\beta_i} \tag{3}$$

is a minimum. The integral $I(E,T)$ was evaluated ussing the approximation proposed by Gorbachev [16]:

$$I(E,T) = \int_0^T \exp\left(-\frac{E}{RT}\right) dT = \frac{RT^2}{E+2RT}\exp\left(-\frac{E}{RT}\right) \tag{4}$$

The obtained values of the activation energy for individual volume shares of crystallized fractions for detected crystallization processes in the samples with x=1, 2 and 3 at. % Pb according to KAS model are shown in Fig. 4.

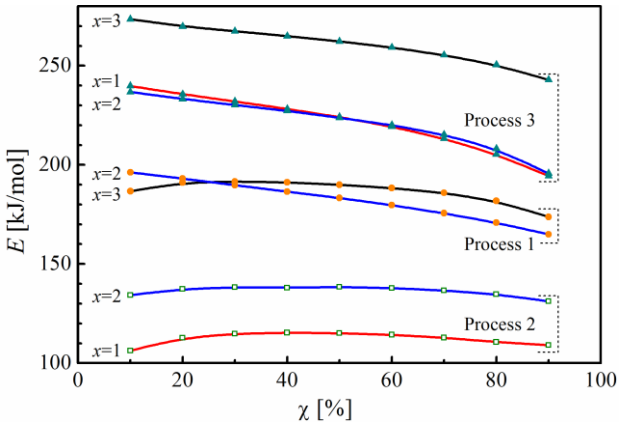

Fig. 4. Activation energy of crystallization versus volume fraction for $Pb_x(As_2S_3)_{100-x}$ glassy samples determined by Kissinger-Akahira-Sunose method.

The change in parameter E of the second crystallization is negliglible in the entire transformation range while in the case of the first crystallization it is weakly explored and corresponds to reaction mechanism that determines the crystallization of the first two processes as a unique process (diffusion-controlled growth of crystal centers) [17]. For the third crystallization process of all the samples we encounter a continuous decrease of the activation energy, indicating a decrease in the nucleation rate over time. This points to a conclusion that high-temperature crystallization is complex process, resulting in a variety of crystallized structural units. In order to identify these crystalline centers, X-ray analysis of the annealed samples was applied. Fig. 5

present diffractograms of the $Pb_3(As_2S_3)_{97}$ samples, annealed at peak temperatures of the first and third crystallization. Intercomparison with the PDF database [18] reveals that As_2S_3 crystalline centers are formed during the first thermal treatment. The second treatment is attributed to thermal activation of As-S and PbS centers. These results are consistent with the Raman investigations of studied glasses, reported in [10].

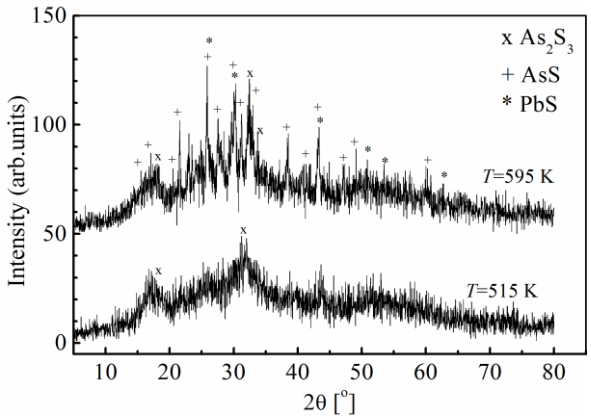

Fig. 5. Diffractograms of the $Pb_3(As_2S_3)_{97}$ glass annealed at peak temperatures of the 1st and 3rd crystallization process.

The results of Vyazovkin method implementation on investigated samples agree well with the results of KAS model. As an illustration, Fig. 6 shows the dependence of minimization factor Ω on activation energy of crystallization E_χ at different degrees of amorphous-crystalline transformation in the sample $Pb_1(As_2S_3)_{50}$.

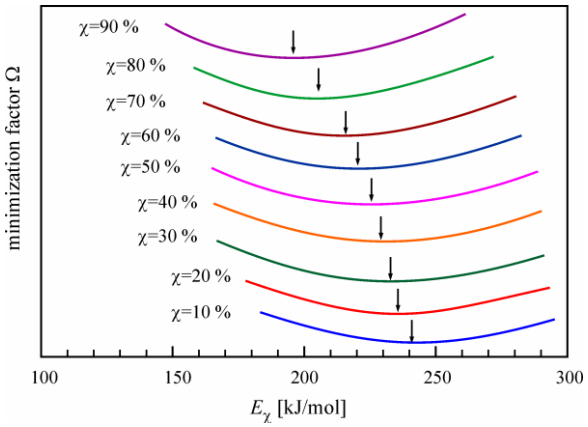

Fig. 6. Minimization factor Ω veruss activation energy of crystallization for different crystallization volume fractions of the $Pb_1(As_2S_3)_{99}$ glass.

To investigate the growth processes involved in the transformation, parameters *n* and *m* that define the mechanism and dimensionality of crystalline growth are determined using the Matusita and Sakka method. This method is based on the following equation [19]:

$$\ln\left[-\ln(1-\chi)\right] = -n\ln\beta - 1.052\frac{mE}{RT} + \text{const.} \qquad (5)$$

From the slope of $\ln[-\ln(1-\chi)]$ versus $1/T$ it was possible to calculate the parameter *mE* (Šatava method [20]). The order of reaction *n* was determined from the linear fit of dependence $\ln[-\ln(1-\chi)] = f(\ln\beta)$ for the selected temperature using the Ozawa method [21]. Figs. 7 and 8 show implementation of these two methods on experimental data for the third crystallization process of $Pb_3(As_2S_3)_{97}$ composition. Numerical values of parameters *mE* and *n* are given in Table 2. The Avrami exponent *n* was also estimated from the ratio of the quantities *mE* and *mE/n* (*n*′ - see Table 2). A satisfactory agreement of the calculated and experimental values was obtained for all the samples. In addition, parameter *mE/n* was defined by fitting the functional dependence $\ln\beta = f(1/T)$ for the corresponding crystalline fractions χ according to the modified Ozawa-Chen method [22]. The obtained values are listed in Table 2.

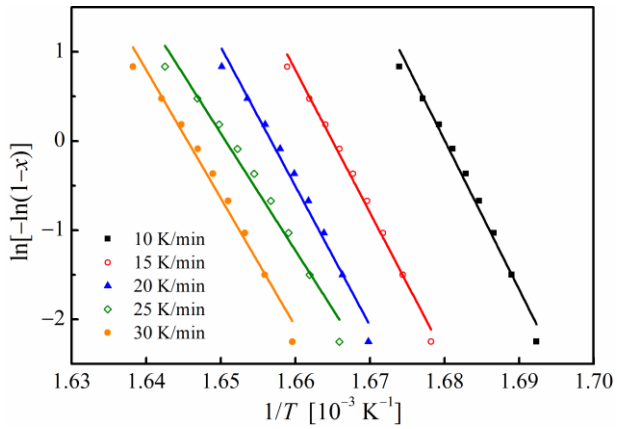

Fig. 7. Dependence of ln[−ln(1−χ)] *on* 1/*T (process 3) at different heating rates and the corresponding linear fits for the* $Pb_3(As_2S_3)_{97}$ *glass.*

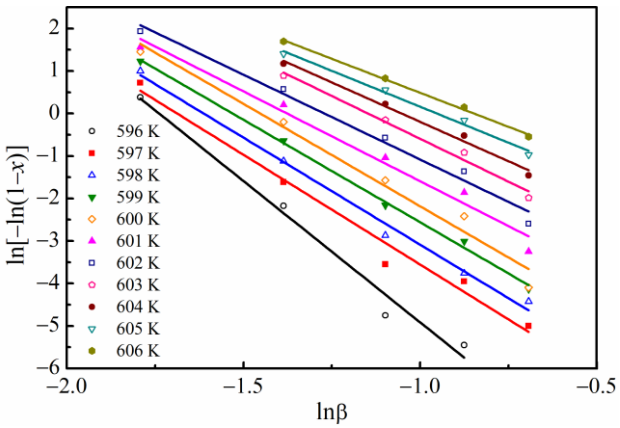

Fig. 8. Dependence of ln[−ln(1−χ)] *on* lnβ *(process 3) at different temperatures and the corresponding linear fits forthe glass* $Pb_3(As_2S_3)_{97}$.

Comparison of the values of parameters *mE* and *E* according to Kissinger model (Table 2) indicates that all crystallization effects in the investigated samples are three-dimensional processes. Based on values of the reaction order parameter *n* we conclude that during the

crystallization in the studied glasses a voluminous 3D crystal growth mechanism of nucleation is taking place.

The thermal stability of chalcogenide glasses and its tendency of glass formation are the most important limiting parameters to estimate the utility of these materials for use in practice, such as specific technological applications. Thermal stability is the direct measurement of stability against crystallization and so the aging effects are found less dominant in the glasses having high thermal stability [8, 9].

There are several glass stability criteria that can be estimated based on the characteristic temperature values of thermal events detected on DSC curve (glass transition temperature T_g, onset crystallization temperature T_{ons}, melting temperature T_m, see Figs. 1 and 2). One of the frequently used criteria is the Hruby parameter [23] defined with relation:

$$Hr = \frac{T_{ons} - T_g}{T_m - T_{ons}} \tag{6}$$

The obtained values for investigated samples are listed in Table 3. Higher values of parameter *Hr* indicate greater stagnation in the process of crystalline centers formation and crystallization itself, and hence a greater tendency to vitrification. Therefore, it can be conluded that introduction od Pb improves the crystallization affinity of studied glasses. The deficiency of this approach is impossibility to determine the material stability in a certain temperature range instead of selected temperatures.

Table 3. Glass stability parameters; Hr – Hruby parameter; Kr – reaction rate of crystallization.

process	x [at.% Pb)	Hr	$K(T_g)$ [s^{-1}]	$K(T_p)$ [s^{-1}]	$Kr\ (T_g)$ [s^{-1}]	$Kr\ (T_p)$ [s^{-1}]
1	1	—	—	—	—	—
	2	0.20	$1.6\cdot10^{-4}$	$1.6\cdot10^{-2}$	$1.0\cdot10^{13}$	$2.5\cdot10^{13}$
	3	0.20	$7.8\cdot10^{-5}$	$1.3\cdot10^{-2}$	$6.0\cdot10^{13}$	$1.7\cdot10^{14}$
2	1	0.32	$1.0\cdot10^{-4}$	$8.1\cdot10^{-3}$	$3.1\cdot10^{5}$	$1.3\cdot10^{6}$
	2	0.34	$4.6\cdot10^{-5}$	$9.4\cdot10^{-3}$	$2.4\cdot10^{6}$	$1.4\cdot10^{7}$
	3	—	—	—	—	—
3	1	1.07	$1.6\cdot10^{-8}$	$1.3\cdot10^{-2}$	$2.3\cdot10^{-10}$	$5.0\cdot10^{-4}$
	2	0.87	$4.2\cdot10^{-8}$	$1.5\cdot10^{-2}$	$3.8\cdot10^{-5}$	3.2
	3	0.86	$3.2\cdot10^{-9}$	$1.6\cdot10^{-2}$	$5.6\cdot10^{-5}$	33.7

In that sense, Surinach [24] and Hu [25] developed the thermal stability criteria based on crystallization rate constant K at two characteristic temperatures: glass transition temperature $K(T_g)$ and maximum temperature of crystallization $K(T_p)$. Since these quantities show dependence on the heating rate, the equation for the reaction rate constant was modified by introducing the Hruby parameter as a stability factor [26]:

$$K_r(T_p) = K_0 \exp\left(-\frac{Hr\,E}{RT_p}\right) \tag{7}$$

Lower values of quantity K_r mean higher thermal stability of glasses. The results of Surinach-Hu approach applied on investigated glasses are given in Table 3. They also indicate decrease in glass stability as a function of dopant content.

4. Conclusion

The kinetics of transformation from amorphous to crystalline phase in glassy samples $Pb_x(As_2S_3)_{100-x}$ was studied using DSC technique. The activation energy of crystallization processes was estimated using Kissinger method. Higher values of parameter *E* of the glass with *x*=3 at. % of Pb indicated modifying influence of dopant on the network structure. Based on results of isoconversional methods, it was found that the first two crystallization are a single-step processes, while the third one is a complex process, resulting in a variety of crystallized structural units, identified as As-S and PbS by X-ray analysis. A close agreement between KAS and Vyazovkin isoconversional methods was observed. Determination of kinetic parameters characterizing the phase transformations of crystallization indicated the occurrence of voluminous 3D crystal growth in investigated samples. Analysis of thermal stability based on Hruby parameter and Surinach-Hu criteria revealed the lower glass stability of the compositions with higher amount of Pb.

Acknowledgements

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