The kinetics of phase transitions in bismuth-modified selenide glasses $As_xSe_{100-x-y}Bi_y$ as studied by differential thermal analysis and exoelectron emission

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The kinetics of the glass transition (retrification) in bismuth-modified selenide glasses $As_xSe_{100-x-y}Bi_y$ ($x = 10.2$, 8, 6 and $y = 0$, 2, 4) have been investigated by parallel differential thermal analysis (DTA) and exoelectron emission (EEE) measurements. EEE is a surface effect connected with structural transformations in the surface layer, whereas the DTA measurements give information about transformations occurring in the bulk of the sample. It was found that the phase transitions occurring in the investigated selenide glasses are evidenced by anomalies in the temperature dependence of both the EEE intensity and DTA curves. Consequently, the validity of the DTA and EEE techniques for studies of phase transitions in vitreous chalcogenide semiconductors has been demonstrated. Admixture of bismuth causes a significant lowering of the temperature of the retrification process, both in the surface layer and in the bulk. It causes a decrease of the activation energy for the retrification process on the surface as well as in the bulk, reducing the thermal stability of the investigated materials. A more detailed comparison of the DTA traces indicates that the areas under the endotherms of the samples containing Bi are systematically (by about 36 %) lower than those of the corresponding samples without Bi.

Chalcogenide glasses / Exoelectron emission / Activation energy / Retrification

Introduction

Vitreous chalcogenide glasses remain a subject of intensive investigation due to the broad range of their potential applications [1], as well as because of interesting fundamental phenomena occurring in them. Potential applications of chalcogenide glasses are, however, limited by two processes: retrification (glass transition) and crystallization. After crystallization the properties change drastically and, as a rule, the materials become useless [2,3], therefore investigations of their retrification and crystallization behaviour are of great importance. Being metastable, amorphous materials tend to crystallize at a proper combination of temperature and time. Their structural instability results from the production process, in which a liquid phase is quenched to ambient temperature [4]. One of the factors affecting the properties of chalcogenide glasses is the process of thermal ageing of the as-quenched material [1,4-7].

The stability of vitreous chalcogenide semiconductors may be characterized by the activation energies and temperatures of the retrification and crystallization processes. One of the factors limiting

potential applications of amorphous materials is the fact that the parameters determining the thermal stability of the surface layer and of the bulk may differ. In a series of papers [2,3,8-10] it has been shown that exoelectron emission (EEE) in combination with conventional bulk techniques (DTA, DSC) is very useful in studies of the kinetics of phase transitions in amorphous materials by making it possible to determine the temperatures and the activation energies for both the surface and bulk crystallization and retrification.

Recently Golovchak *et al.* [11] reported on the effect of modifications of the structure of arsenic selenide glasses by addition of bismuth. Admixture of Bi leads to the formation of coordination defects [11] and to a lowering of the potential barriers for structural transitions in bismuth-modified selenide glasses. Addition of Bi causes a lowering of the activation energy for retrification of arsenic selenide glasses [12].

The aim of the present study was to continue the investigations of the effect of Bi additions on the kinetics of the retrification process in the bulk and in the surface layer of arsenic selenide glasses.

Experimental conditions

The investigated bulk arsenic selenide glasses were prepared in Moscow Institute of General and Inorganic Chemistry of RAS by conventional melting of appropriate mixtures of high-purity (99.999 %) precursors.

Measurements of the temperature dependence of photostimulated exoelectron emission (EEE) intensity were carried out by means of the arrangement described in [13]. An open point counter with saturated ethanol quenching vapour was used to detect the exoelectrons. The temperature of the sample, controlled using a Ni–CrNi thermocouple with an accuracy of about 5 K, was changed at four constant heating rates (2, 5, 10, and 20 K/min). The sample surface was irradiated during the measurements by unfiltered radiation from a quartz lamp with a Q-400 burner.

The calorimetric investigations of the bulk retrification were performed at five heating rates (0.5, 1, 2, 5, and 10 K/min) using a NETZSCH DSC 404/3/F differential calorimeter with an E-type thermocouple with an empty crucible made of high density Al_2O_3 as reference.

All the EEE and DTA measurements were performed in air at ambient pressure.

Results and discussion

The temperature dependencies of the DTA signal and of the photostimulated exoelectron emission (EEE) from $As_xSe_{100-x-y}Bi_y$ are shown in Fig. 1. For all of the investigated samples the registered thermograms and temperature dependencies of the EEE intensity are very similar. All of them display single peaks corresponding to the retrification process in the surface layer (EEE) or in the bulk (DTA) of the investigated materials. Admixture of bismuth causes a significant lowering of the retrification temperature both in the surface layer and in the bulk. A comparison of the DTA traces indicates that the areas under the endotherms of the samples with Bi are systematically (by about 36 %) lower than those of the samples without Bi.

The measurements of the temperature dependence of the DTA signal, performed at five heating rates ranging from 0.5 to 10 K/min, together with the registration of the temperature dependence of EEE intensity, performed at four heating rates ranging from 2 to 20 K/min, enabled the determination of the activation energies for both the bulk and the surface retrification processes governing the appearance of the maxima on the temperature dependencies of the DTA signal and EEE intensity. Typical DTA traces and temperature dependencies of the EEE intensity for the $As_6Se_{90}Bi_4$ chalcogenide glass, registered at different heating rates, are presented in Fig. 2. It is seen that with increasing heating rate the peaks on the DTA and

EEE curves systematically shift towards higher temperatures. This behaviour is typical of thermally activated processes.

From the shifts of the DTA and EEE peaks the activation energies for bulk and surface retrification of the investigated materials were determined by Ozawa's well-known method [14], *i.e.* from plots of the $\ln v = f(1/T)$ dependence, where v denotes the heating rate and T the retrification temperature determined from the positions of the DTA endotherms (bulk retrification) and of the EEE peaks (surface
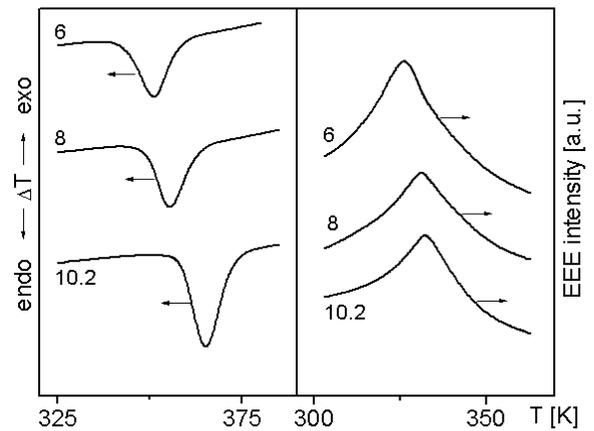
Fig. 1 Temperature dependence of the DTA signal and of the photostimulated exoelectron emission (EEE) from $As_xSe_{100-x-y}Bi_y$ glasses registered at a heating rate of 2 K/min. Number near the curve – As content in at.%.
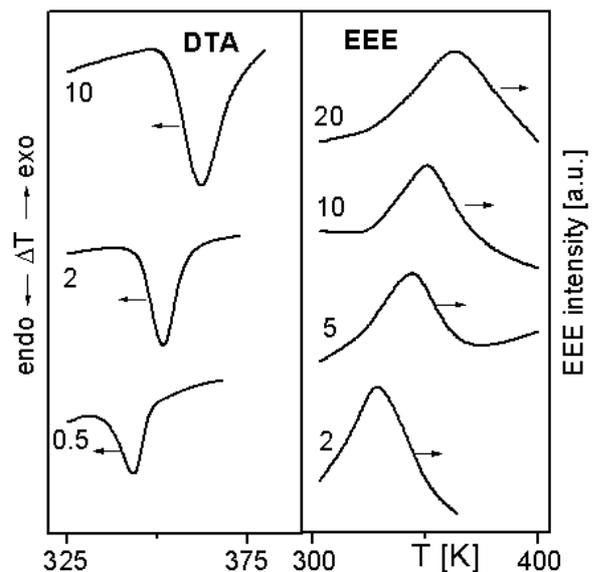
Fig. 2 Temperature dependence of the DTA signal and photostimulated exoelectron emission (EEE) for the $As_6Se_{90}Bi_4$ glass. Number near the curve – heating rate in K/min.

Table 1 Temperatures and activation energies for bulk and surface retrification of the investigated chalcogenide glasses as determined from DTA and EEE measurements.

	Activation energy, eV		Retrification temperature, K (measured at a heating rate of 2 K/min)	
	Surface retrification	Bulk retrification	Surface retrification	Bulk retrification
$As_{10.2}Se_{89.8}$	0.76	2.08	333	364
$As_8Se_{90}Bi_2$	0.72	1.95	331	353
$As_6Se_{90}Bi_4$	0.75	2.01	326	348
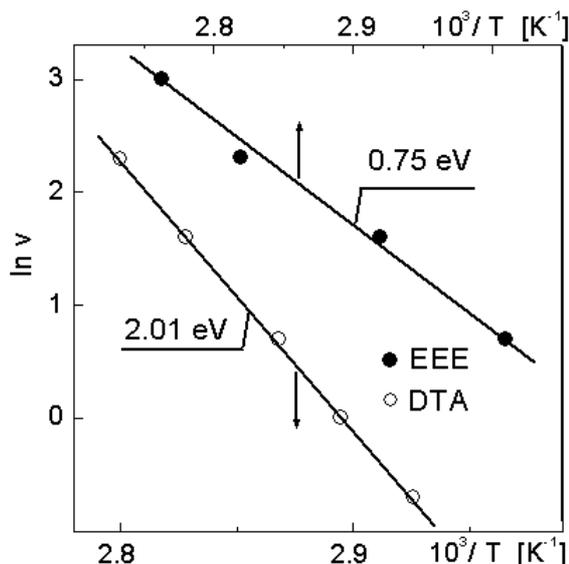
Fig. 3 Ozawa plots for the surface (EEE) and volume (DTA) retrification temperatures of the $As_6Se_{90}Bi_4$ glass.

retrification). The retrification temperature T was determined from the position of the maximum on the EEE curves [13] and the deflection point (from the base line) on the DTA curves [15]. The slope of the Ozawa plot multiplied by the Boltzmann constant gives the value of the activation energy.

The dependencies of the retrification temperatures T, determined from the temperature dependencies of the EEE intensity (surface retrification) and of the DTA signal (bulk retrification), on the heating rate v, represented in Ozawa coordinates $\ln v = f(1/T)$, for the $As_6Se_{90}Bi_4$ chalcogenide glass are shown on Fig. 3. The accuracy of the determination of the activation energies was better than 0.2 eV. The same procedure was applied for determining the activation energies of all of the investigated chalcogenide glasses.

The value of the activation energy of the retrification process is an important parameter characterizing well the thermal stability of amorphous materials. The retrification temperatures (measured at the heating rate 2 K/min) and the values of the

activation energies for surface and bulk retrification of the selenide glasses investigated in the present work, determined by the Ozawa method on the basis of systematic DTA and EEE measurements, are collected in Table 1.

The data presented in Table 1 indicate that:
- admixture of bismuth causes a significant lowering of the temperature of the retrification process both in the surface layer and in the bulk,
- addition of Bi causes a decrease of the activation energy for the retrification process in both the surface and in the bulk, reducing the thermal stability of the investigated materials,
- a comparison of the DTA traces indicates that the areas under the endotherms for the samples with Bi are systematically (by about 36 %) lower than for the corresponding samples without Bi.

Further studies are in progress.

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