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# Optical properties and local structure of $(\text{As}_2\text{S}_3)_{100-x}(\text{SbSI})_x$ glasses

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Received: 18.03.2010

## Abstract

We report experimental results for the spectral dependences of the optical absorption edge in  $(\text{As}_2\text{S}_3)_{100-x}(\text{SbSI})_x$  ( $0 \leq x \leq 90$ ) glasses. Our studies have shown that increasing of antimony sulfoiodide (SbSI) content in the glass composition and the temperature increase lead to shift in the absorption edge towards long-wavelength range. The optical absorption edge  $E_g^\alpha$  positions are determined. The slope change observed for the absorption edge in the temperature range of  $T_g \div T_c$  is conditioned by generation of nanocrystals of antimony sulfoiodide in the glassy matrix.

**Keywords:** chalcogenide glasses, local structure, dielectric properties, ferroelectric glass ceramic

**PACS:** 42.25.Bs  
**UDC:** 535.3

## Introduction

Development of modern technologies and their industrial applications involve an important problem of searching for new technological materials, especially nanostructural ones, with the parameters that could be predicted and well governed. A usual interest in the nanocrystals is caused by spatial limitation of motion of charge carriers, thus leading to quantisation of their energy bands and showing up quantum size effects in the optical spectra. The unique properties of nanostructures stipulate many possibilities for their practical applications, e.g. in functional elements of opto- and nanoelectronics, or in media for recording and storing information.

Though a number of new classes of nanodimensional objects are created in the last decades using the molecular beam epitaxy, ionic implantation, colloid synthesis and some other techniques, formation of new nanostructures still remains urgent, e.g. those manifesting ferroelectric properties. The latter materials have already found wide applications in various domains of modern technologies (ferroelectric memory elements, pyro-, piezo- and photoelectric sensors, hydrostatical pressure sensors, etc.).

As the brightest representative of a wide class of ferroelectric semiconductors  $A^V B^{VI} C^{VI}$ , chalcogenide glasses on the basis of antimony sulfiodide represent a considerable interest [1]. In combination with the electric field influence, it is possible to apply the technique of oriented crystallisation of the above materials for efficiently shaping nanocrystals, involving predefined nanocluster sizes and orientations, and ferroelectric properties [2–5]. It is known that, depending on the origin and the growth technique, anomalies in the temperature dependences of dielectric permittivity ( $\epsilon$ ) and dielectric losses ( $\text{tg } \delta$ ) may occur in those crystals. At the same time, the optical properties of chalcogenide glasses and the nanostructures based on SbSI have in fact not been studied.

In this work we report the results of studies for the chemical composition and temperature changes in the fundamental absorption edge for the glasses of  $\text{As}_2\text{S}_3$ -SbSI system.

### Experimental

Using a vacuum melting technique, the glasses of  $\text{As}_2\text{S}_3$ -SbSI system were prepared on the basis of relevant mixture of SbSI and  $\text{As}_2\text{S}_3$  components, which were synthesised from high-purity elementary substances. The melts were homogenised at the temperatures of 800–870 K (the homogenisation time 24 h). The melts were periodically mixed. Hardening for the melts with  $x = 80, 90$  was carried out in the cold water ( $T = 273$  K), while the melts with  $x < 80$  were hardened in the air.

The absorption edge energy position  $E_g^\alpha$  was determined from the measurements of spectral dependence of the absorption edge at the level of absorption  $\alpha$ , which corresponded to the middle of the interval  $0.3 \leq \alpha d \leq 3$  (with  $d$  being the sample thickness). This was done in order to keep a constant light transmission of the sample at a certain absorption level, while the external factors were changed. The latter was achieved by changing the wavelength of the incident light during the measurements. Finally, the spectral resolution was of the order of  $10^{-3}$  eV.

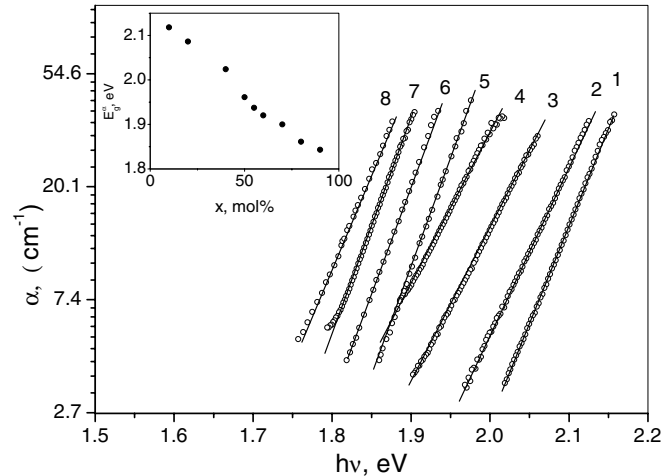
### Results and discussion

The earlier investigations have indicated that the spectral dependences of the absorption edge for the  $(\text{As}_2\text{S}_3)_{100-x}(\text{SbSI})_x$  glasses at the absorption levels  $\alpha > 100 \text{ cm}^{-1}$  are described by the relation [6]

$$\alpha(h\nu) = \alpha_g \exp \left[ \frac{h\nu - E_g^\alpha}{w} \right], \quad (1)$$

where  $w$  is the energetic width of the exponential absorption edge (i.e., disorder of the glass structure network), and  $E_g^\alpha$  at  $10^3 \text{ cm}^{-1}$  is the optical pseudogap ( $E_g^*$ ).

The spectral dependences of the absorption edge for the glasses from our system measured at the room temperature are presented in Fig. 1. It should be noted that the absorption edge for these glasses has an Urbach shape at the absorption levels  $\alpha > 100 \text{ cm}^{-1}$  [7].



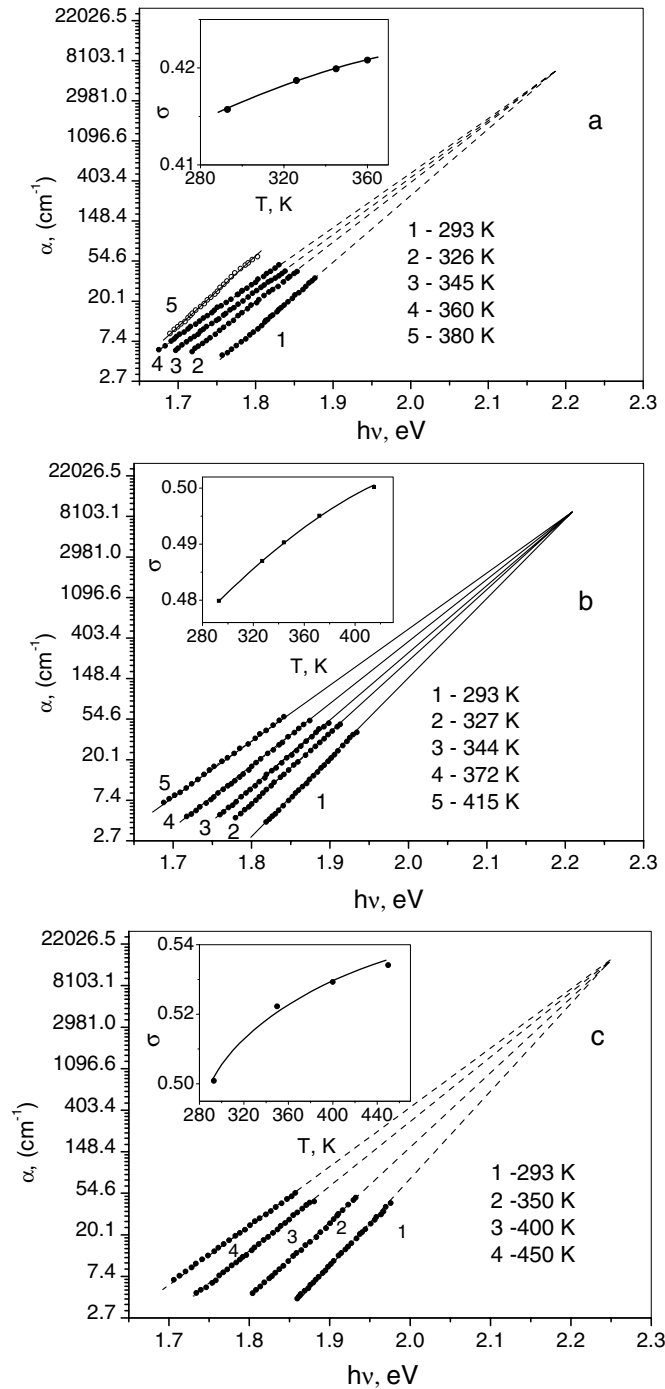
**Fig. 1.** Spectral dependences of optical absorption edge and concentration dependence of  $E_g^\alpha$  (insert) for the  $(As_2S_3)_{100-x}(SbSI)_x$  glasses with 1 – 10, 2 – 20, 3 – 40, 4 – 50, 5 – 55, 6 – 70, 7 – 80, 8 – 90 mol %.

When the content of sulfoiodide in the glass composition increases, the absorption edge is shifted towards the long-wavelength spectral region, revealing a decrease in the pseudo-forbidden gap width. Increase in the antimony sulfoiodide content in the glasses also produces the shift of the absorption edge towards a long-wavelength region and a reduction of the optical pseudogap width.

The concentration dependence of  $E_g^\alpha$  for the  $(As_2S_3)_{100-x}(SbSI)_x$  glasses is shown in Fig. 1 (insert). The energy position of the absorption edge determined at  $p = 0.1$  MPa changes from 2.23 eV for  $As_2S_3$  down to 1.84 eV for  $(As_2S_3)_{10}(SbSI)_{90}$  glass. Here narrowing of the optical gap is caused by structural rearrangements as a result of transition from  $As_2S_3$  to  $SbSI$ .

It has been shown in the work [8] that the structure of glassy  $As_2S_3$  is determined mainly by trigonal pyramids of  $As_3S$  cohered through doubly coordinated sulphur atoms. The glassy  $SbSI$  is characterised by a nanoheterogeneous (“quasi-eutectic”) structure [2]. Its matrix is built mainly of trigonal pyramids  $SbS_{3/2}$  and includes separate  $SbI_3$  molecules or the associates on their basis. The glasses of the mixed  $As_2S_3$ - $SbSI$  system have a nanoheterogeneous structure, too. The binary structural clusters of  $SbS_{3/2}$ ,  $As(Sb)S_{3/2}$ ,  $AsS_{3/2}$ ,  $SbI_3$  and  $AsI_3$  and a certain amount of structural fragments with homopolar bonds take part in the construction of structural network of these glasses [5]. Their correlation in the glass matrix is determined by the chemical composition.

It is evident from Fig. 1 that the concentration dependence of  $E_g^\alpha$  has an S-shaped character. It can testify considerable mutual perturbations of the structural clusters forming the matrix of the glasses [9]. Some deviations from additivity may evidence a statistical character of distribution of the structural clusters in the glass matrices and a presence of certain amount of molecular fragments with the homopolar bonds.



**Fig. 2.** Spectral dependences of optical absorption edge for  $(\text{As}_2\text{S}_3)_{10}(\text{SbSI})_{90}$  (a),  $(\text{As}_2\text{S}_3)_{30}(\text{SbSI})_{70}$  (b) and  $(\text{As}_2\text{S}_3)_{45}(\text{SbSI})_{55}$  (c) glasses at different temperatures. Inserts show temperature dependences of the  $\sigma_0$  parameter.

Our studies demonstrate that the absorption edge is shifted towards lower energies with increasing temperature (Fig. 2). The temperature changes in the absorption edge occurred in the glasses under test in the temperature region given by  $T < T_g$  (with  $T_g$  being

the vitrification temperature) are described by the exponential dependence [10],

$$\alpha = \alpha_0 \exp\left[\frac{\sigma(T)}{kT}\right](h\nu - E_0), \quad (2)$$

where  $\alpha_0$ ,  $E_0$  and  $\sigma(T)$  are parameters of the Urbach rule and  $\sigma(T)/kT = 1/W$ .

The convergence points of the  $\ln\alpha(h\nu)$  dependences for the  $(\text{As}_2\text{S}_3)_{100-x}(\text{SbSI})_x$  glasses with  $x = 90, 70$  and  $55$  at  $p = 0.1$  MPa are respectively  $\alpha_0 = 6.2 \times 10^4, 9.2 \times 10^4$  and  $1.47 \times 10^5 \text{ cm}^{-1}$  (see Fig. 2). These  $\alpha_0$  values correspond to  $E_0 = 2.18, 2.21$  and  $2.25$  eV, respectively. The  $E_0$  value may be related conventionally to the pseudo-forbidden band of the glasses at  $T = 0$  K. The analysis of the  $\alpha(T)$  dependence has revealed that the parameter  $\sigma(T)$  grows with increasing temperature and may be approximated by the formula [10]

$$\sigma(T) = \sigma_0 \frac{2kT}{h\nu_0} \tanh \frac{h\nu_0}{2kT}. \quad (3)$$

Here  $\sigma_0$  denotes a constant that characterises the electron-phonon interaction strength and  $h\nu_0$  is the effective phonon energy shaping the absorption edge. Somewhat different behaviour of the spectral dependences of the absorptions edge for the  $(\text{As}_2\text{S}_3)_{100-x}(\text{SbSI})_x$  ( $50 \leq x \leq 90$ ) glasses is found at  $T > T_g$ . The value of  $T_g = 370$  K correlates with that for these glasses specified from the DTA curves obtained for the heating rate of 3 K/min (370–430 K [11]).

The crystallisation temperature  $T_c$  for our glasses derived as a maximum of exothermic effect on the DTA curves is equal to 409–450 K. The parameters  $T_g$  and  $T_c$  decrease with growing SbSI content in the glass composition. Fig. 2 unambiguously shows that the edge slope for the  $(\text{As}_2\text{S}_3)_{10}(\text{SbSI})_{90}$  glass at  $T = 383$  K ( $T_g = 370$  K) is considerably larger than that for the case of  $T < T_g$ . This testifies a greater ordering of the structure of material at  $T > T_g$ . The dependences of the absorption edges for the other glasses of this system ( $50 \leq x \leq 90$ ) have a similar character.

An explanation for the temperature behaviour of the absorption edge may be given following from the structure of these materials. The structural clusters forming the glass matrix of the  $\text{As}_2\text{S}_3$ -SbSI system are "frozen" at relatively low temperatures ( $T < T_g$ ) and get some freedom of rotation at the temperatures between  $T_g$  and  $T_c$ , thus allowing the atoms included in a given cluster to move on small distances. During this process, the atoms of Sb, S and I appear in these positions in some moments. This facilitates possible breaking and alteration of the chemical bonds Sb-S, Sb-I, As-I and As-S in the binary structural clusters, with formation of triple chain basic units of  $\text{SbS}_{2/2}\text{I}$ . The latter can be attributed to appearance of crystalline antimony sulfoiodide [12]. This conclusion is confirmed by the results for the Raman spectra and the crystallograms of the glass ceramics [5, 11]. The crystallograms for the annealed glasses in the temperature region  $T_g \div T_c$  manifest reflexes which coincide satisfactorily with the lines available for the polycrystalline SbSI and their Raman spectra contain sharp bands at 108–110, 138–140 and 318–320  $\text{cm}^{-1}$ . The maximums of these bands are located at 108, 138 and 318  $\text{cm}^{-1}$  for the polycrystalline antimony sulfoiodide.

The studies for influence of annealing mode on the structure and properties of the  $(As_2S_3)_{100-x}(SbSI)_x$  glasses have revealed [4, 5] that, at the temperatures close to the freezing one and for short annealing times, the ferroelectric nanoceramic is obtained, with the sizes of crystalline inclusions of the order of correlation length. Increase in the temperature and the annealing time result in growing sizes of crystalline inclusions available in the glassy matrix. Then the intensities of the reflexes on the crystallograms and the IR spectral bands grow, whereas their half-widths decrease. Moreover, the increase in the crystalline inclusions is accompanied by growing dielectric permittivity.

## Conclusion

The spectral absorption dependences in the region of optical absorption edge for the  $(As_2S_3)_{100-x}(SbSI)_x$  glasses are well described by the Urbach rule. Electron-phonon interactions play a primary part in the formation of their absorption edge. Larger antimony sulfoiodide (SbSI) content in the glass composition and increasing temperature impose a shift of the absorption edge towards the long-wavelength spectral region, thus confirming reducing in the pseudo-forbidden bandwidth. Finally, formation of the nanocrystalline inclusions of antimony sulfoiodide in the glassy matrix is accompanied by growing slope of the absorption edge.

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Shpak A.P., Rubish V.M., Mykaylo O.A., Kaynts D.I., Guranich O.G. and Rosul R.R., 2010. Optical properties and local structure of  $(\text{As}_2\text{S}_3)_{100-x}(\text{SbSI})_x$  glasses. *Ukr.J.Phys.Opt.* **11**: 107-113.

*Анотація.* В даній роботі представлені результати експериментального дослідження спектрального положення краю поглинання стекол  $(\text{As}_2\text{S}_3)_{100-x}(\text{SbSI})_x$  ( $0 \leq x \leq 90$ ). Показано, що зростання концентрації сульфойодиду сурми (SbSI) у складі скла, як і зростання температури приводить до зміщення краю поглинання у довгохвильову область. Визначене положення краю поглинання  $E_g^\alpha$ . Зміна нахилу кривої поглинання в області температур  $T_g \div T_c$  зумовлюється утворенням нанокристалів сульфойодиду сурми в скляній матриці.