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FEATURES OF PHOTOLUMINESCENCE AND DIELECTRIC PROPERTIES OF GLASS – FERROELECTRIC SbSI

A. A. Babaev*, I. K. Kamilov, C. N. Kallaev, S. B. Sultanov, A. A. Amirova, A. M. Dzhabrailov

Institute of Physics, Daghestan Scientific Center, Russian Academy of Sciences, Makhachkala, Russia

The temperature dependence of dielectric properties and photoluminescence (PL) of glass semiconductor SbSI is studied. According to measurements of the dielectric constant and polarization the first-order structural phase transition into the polar state (dipole glass) takes place at T=198 K. A complex spectrum of the PL in the glass SbSI is responsible for two types of structural units. A wide radiation band, location, and large PL maximum of the Stokes shift prove the existence of a strong electron-phonon interaction.

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1. Introduction

The high interest in chalcogenide glassy materials is due to a specific character of their band energy spectrum which is at variance with the corresponding crystal. The main feature of these materials is the violation of long range order, which influences the network dynamics and the electric properties. The glass SbSI is a specimen of such system. An interest to the SbSI compounds is stimulated by their semiconductor and ferroelectric properties.

Recent papers on SbSI are related to the effect of thermal annealing on the structural properties of glassy alloy [1] and the characterization of nanocrystalline material got by ball milling [2].

A first order structural phase transition into the ferroelectric phase ($D^{16}_{2h} \rightarrow C^{9}_{2v}$) is observed in the semiconductor crystal SbSI [3,4] at $T_c \approx 295$ K. The impurities and defects essentially influence the character and temperature of the phase transition and lead to new phenomena.

Unlike the crystal, the glass system SbSI is insufficiently known. This work is devoted to the study of electric properties (dielectric constant ε and polarization P) and photoluminescence (PL) of glassy SbSI in a wide temperature range.

2. Experiments and results

The glasses of Sb-S-I system were synthesized into the quartz ampoule pumped out up to 10^{-4} mm Hg by following method. Firstly, the ampoules were heated up to 280 °C and kept at this temperature for three hours. Then, the temperature was raised up to 700 °C and the samples were held for six hours. The cooling down to 400 °C was made by switching off the oven, the samples being hardened in air. The shell-like fracture, optical homogeneity observed under the polarized light through a microscope and the absence of lines in the debyegrams indicate the glass-formation. The glass-formation region in Sb-S-I system has an insular character and is in a region of eutectic quasi-binary section Sb_2S_3-SbS_3. Structure researches show that in the glasses of this system are realized

* Corresponding author: analit@dinet.ru

two types of structural units: trigonal $SbS_{3/2}$ and three-component structural units on the basis of the compound SbSI [5].

The samples are rectangular plates with 0.1 cm thickness and size 0.4×0.3 cm^2, with painted electrodes of silver paste. The dielectric constant ε is determined using the capacity bridge LCR –819 from the firm CW "Intek" on a frequency 1 kHz in a field of amplitude E = 10 V/cm. The piroeffect was measured by the electrometric method. The measurements were carried out in nitrogen cryostat. The rate of the temperature change was 0.1 K/min.

PL was studied using a monochromator. A xenon lamp is used as a source of the excitation. The frequency of the exciting light was 775 Hz. The germanium photodiode served as radiation receiver. The PL excitation spectra are recorded by the monochromator in the self-recorder. The radiation was registered from a surface of new splinter whereupon the exciting light was incident.

The temperature dependences of the dielectric constant ε and of the spontaneous polarization P (in the zero electric field) in the glass SbSI are presented in Fig. 1. As one can see, a strongly pronounced anomaly of the dielectric constant ε and polarization P, characteristic to the structural phase transition of the first order is observed for quenching at the temperature $T_c \approx 198$ K. The value of the temperature hysteresis is approximately 12 K.

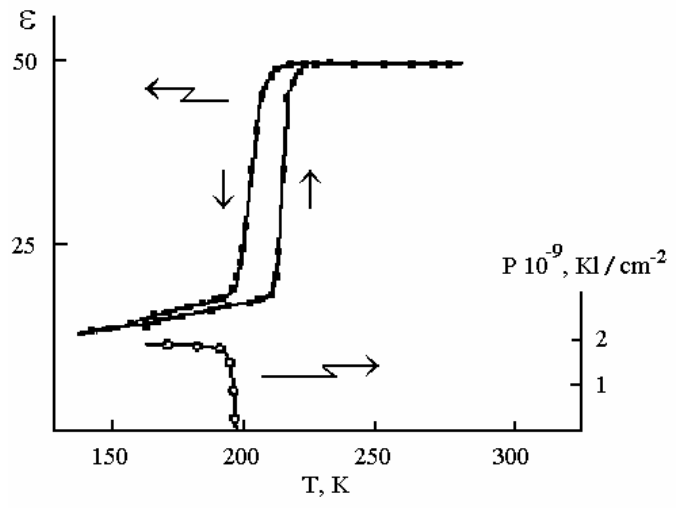

Fig. 1. Temperature dependence of dielectric constant ε and polarization P of glass SbSI. Arrows indicates the directions of the temperature change.

The appearance of polarization at T_c indicates to that the low-temperature phase ($T<T_c$) is polar, i. e. at T_c is produced a transition into the dipole glass state.

After the characteristic behaviour of the dielectric constant ε one may suppose that the non-critical phase transition non-connected with a thermodynamic stability loss (i. e. without a stability loss of symmetric high-temperature phase), described in [6], is realized in the glass SbSI at 198 K. Particularly, the same anomaly ε is observed in some crystals at ferro-elastic and ferro-electric transitions [6]. The observed wide temperature hysteresis ($\Delta T \sim 12$ K) may be caused by a high defectness of glassy materials.

It is well-known that defects, impurities and stoichiometry change of the crystal SbSI essentially modify the temperature of phase transition to the polar state towards low temperature [4]. Therefore, the observed anomaly of the dielectric constant and the polarization at T=198 K is considered as evidencing the transition point into the ferroelectric state.

It should be noted that in comparison with crystal SbSI in glassy SbSI the temperature of phase transition not only shifts into the low temperature range but also the temperature anomaly of the dielectric constant ε changes qualitatively and quantitatively. So λ-anomaly is observed in SbSI crystals at $T_c \approx 295$ K, and the value of ε is 2-3 order of magnitude higher than in glass.

PL is one of the most effective method of investigation of band energy spectrum and of the defective states of chalcogenide glass semiconductors (CGS). The study of PL was carried out in order to define the band energy spectrum and the mechanism of generation and recombination in glassy semiconductor-ferroelectric SbSI. The PL spectra and its excitation at T = 77 K are shown in Fig. 2. The wide band of radiation observed in the spectrum consists of the superposition of two bands with half-width $\delta = 0.4$ eV and maxima situated at $E_2 = 1.0$ eV and $E_2 = 0.85$ eV. The maximum of the luminescence excitation spectrum (LES) corresponds to $E_{LES} = 1.82$ eV, and the Stokes shift is $C = 0.84$ eV.

The wide band of radiation, location of PL spectrum maximum $E_{PL} \approx E_g/2$ (E_g is the width of forbidden band) and large Stokes shift testify about the presence of a strong electron-phonon interaction in this material. According to researches on dielectric properties (Fig. 1) the strong electron-phonon interaction may be connected with realization below 198 K of the polar state (the dipole glass).

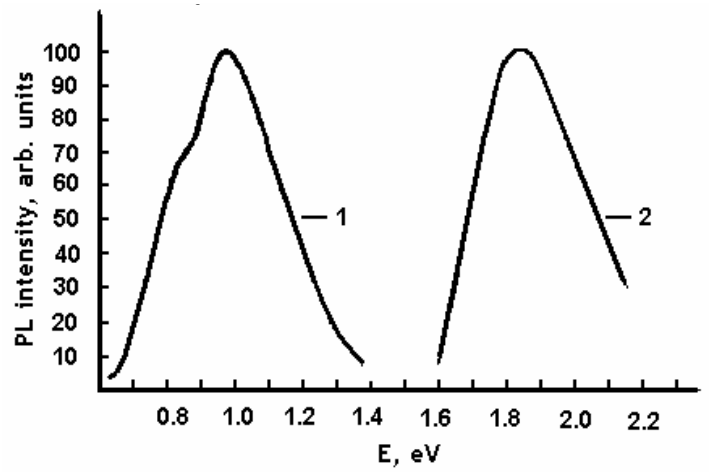

Fig. 2. PL spectrum (1) and LES (2) of glass SbSI at 77 K.

The presence of two radiation bands proves that the centers responsible for radiative recombination are the intrinsic defects with negative correlation energy and consist of two types of structural units. The structural investigations shows the presence of trigonal $SbS_{3/2}$ and a three – component unit based on SbSI. The LES consists of one wide band including strongly overlapping two bands representing the excitation spectrum for E_1 and E_2. The LES maximum is located in a region of low absorption coefficient. The experimental results showing a change of PL spectrum shape at low energetic and high-energetic excitation levels testify about strongly overlapping bands of LES.

3. Conclusions

The experimental results for dielectric properties are indicative for the structural phase transition of the first order into the polar state (dipole glass) triggered in the glass compound SbSI at T=198 K. The PL revealed in the glass semiconductor-ferroelectric SbSI is due to intrinsic defects with a negative correlation energy. The complex PL spectrum shows that two types of structural units are present in the material. The wide radiation band, position of maximum and large Stokes shift testify about the presence of strong electron-phonon interaction in the material.

Detailed information about the nature of structural phase transition, have been obtained, for the first time in SbSI glass, and further researches on the physical properties and structure of this glass are needed.

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