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Dielectric Properties of SbSI in the Temperature Range of 292–475 K

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Methodology of impedance measurements and ferroelectric hysteresis loops observed in temperature range 292–475 K for antimony sulfoiodide (SbSI) grown from vapour phase are discussed. Temperature dependences of spontaneous polarization and coercive field of SbSI crystals are presented.

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1. Introduction

The crystalline antimony sulfoiodide (SbSI) has a chain structure and is one of the best piezoelectric crystals with high volume piezoelectric modulus $d_v = 1\times10^{-9}$ C/N [1] and extremely high electromechanical coupling coefficient $k_{33} = 0.90$ [2]. It is well known that the ferroelectric phase Pna2$_1$ (C_{2v}^9) disappears in SbSI crystals near room temperature. The transition temperatures reported are distributed from 283 K [3] to 298 K [4]. It was found that they presumably depend upon the growth method and chemical composition of the crystal [5]. Unfortunately, the recognition of the phase of SbSI above the room temperature is a subject of some controversy. Most of the investigators described the structure of SbSI above the room temperature phase transition as the paraelectric phase *Pnam* (D_{2h}^{16}). For example, this structure was reported for the SbSI crystals at temperatures 308 K [6] and 333 K [7]. However, the same authors verified this information by a detailed study of diffuse scattering in the crystal structure of SbSI at 320 K [8]. In [8] the average crystal structure of SbSI is described by the space group Pnam in which the $[\mathrm{Sb(S,I)}]_\infty$ chains are not uniform but consist of sections of different length and opposite polarity. These sections form nanodomains elongated in the [001] direction [8]. Recently [9] the antiferroelectric phase transition was found by a measured capacitance change at a frequency of 1 kHz for SbSI crystals grown by the Bridgman–Stockbarger technique. It was argued that SbSI has three phases: ferroelectric ($T < 295$ K), antiferroelectric ($295 < T < 410$ K) and paraelectric ($T > 410$ K).

The aim of this paper is to present another scope of the ferroelectric properties of SbSI. It is based on interpretation of the capacitance measurements as well as on the measurements of hysteresis of the investigated material. These conclusions are very important for the understanding the properties of SbSI and for the possible applications of this material as nanosensors [10–12], actuators [13] and photonic crystals [14].

2. Experiment

The measurements have been performed on SbSI single crystals grown from vapor phase. The presynthesized polycrystalline SbSI was used as the starting material. It was kept in evacuated ($p = 0.1$ Pa) Pyrex ampoules of length 0.2 m and diameter 1.5×10^{-2} m. The growing was performed in two-zone vertical furnace, the temperatures of both zones could be controlled independently. The lower part of the ampoule was wrapped with a sheet of aluminum foil in order to obtain a homogeneous temperature distribution in the source zone. The aluminium foil restricts the position of nucleation only at the top of the ampoule and allows the growth of larger crystals. The source temperature was $T_1 = (623\pm5)$ K and the seed temperature $\mathrm{T}_2 = (603\pm5)$ K. The typical size of the crystal grown by this method (after 24 h) was about $1\times0.5\times30$ mm^3. It had good-looking surfaces and no hollow. The obtained sample ($1\times0.5\times2$ mm^3) was equipped with electrodes, made of silver paste (SPI Supplies), and electrical connection from these electrodes allowed investigations of electric properties along *c*-axis of SbSI.

All electric measurements were performed in darkness in air at atmospheric pressure. The temperature was measured with Pt-100 sensor and DMM Keithley 196. The capacity measurements were made in weak fields at 1 kHz by means of a HIOKI 3532-50 LCR meter. The ferroelectric hysteresis loops were measured with Metrix OX8627 oscilloscope in a modified Sawyer-Tower circuit [15] ($f = 350$ Hz, amplitude of the sinusoidal signal $E = 800$ V/cm). The capacity as well as ferroelectric hysteresis measurements have been controlled by PC computer using programs in LabView environment. Spontaneous polarization ($\mathrm{P_s}$) and coercive field ($\mathrm{E_c}$) were evaluated from the hysteresis loops.

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3. Results and discussion

Figure 1 presents temperature dependences of impedance and phase signals registered for SbSI single crystal under heating. These dependences have been used to calculate capacitance of sample. Because the investigated ferroelectric material is semiconducting, the equivalent electric circuit must contain not only a capacitor but also a resistor. Therefore one can elaborate the measured impedance and phase of signals applying different equivalent circuits, i.e. the serial and parallel connections of capacitor and resistor (see insets in Fig. 2). One can see that in both cases (Fig. 2a and b), in the low temperature range ($293 < T < 350$ K), the equivalent capacitance increases with the increase of temperature, attains maximum, and then decreases (an adequate behavior is observed under cooling the sample in the same temperature range — the temperature hysteresis is about 1 K). However, Fig. 2a and b presents quite different temperature dependences of the evaluated capacitances in the high temperature range ($T > 350$ K). The calculated capacitances for serial (Fig. 2a) and parallel (Fig. 2b) equivalent circuits increase and decrease, respectively, with increase of temperature above 375 K. The first behavior is similar to the reported for SbSI in [9]. Unfortunately, the authors of [9] did not present any details of their measurement equipment and the used equivalent circuits. In general, parallel equivalent circuit mode should be used for elements, which have relatively low capacitance (C_p) and high impedance, since parallel resistance can cause great loss in this case. In our opinion it is the case of semiconducting SbSI.

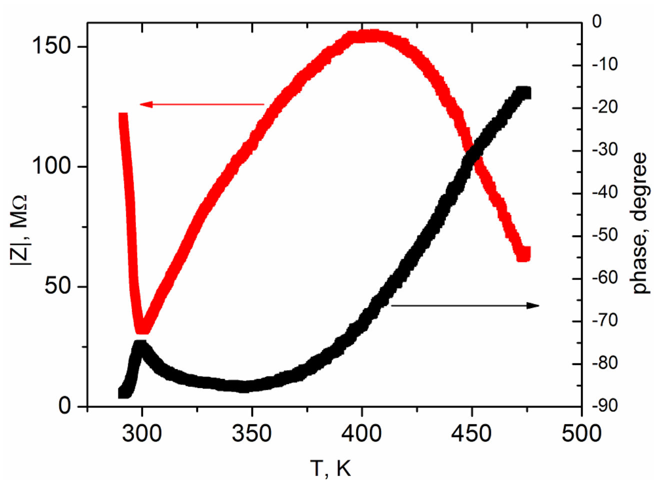

Fig. 1. Temperature dependences of impedance and phase signals registered for SbSI single crystal (f = 1 kHz, $V = 0.5$ V).

Figure 3 presents the registered hysteresis loops at different temperatures of SbSI single crystal. The obtained results are at least qualitatively identical with the hysteresis loops reported in [16]. Figure 4 shows the temperature dependences of spontaneous polarizability (P_s)

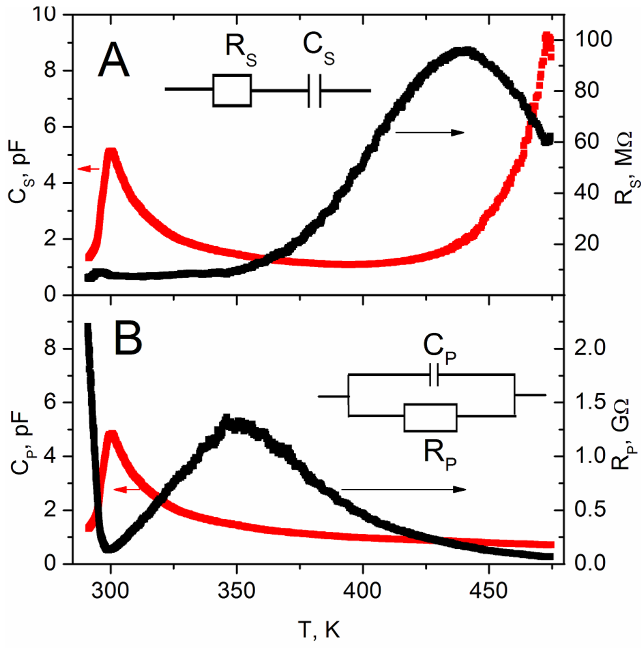

Fig. 2. Comparison of temperature dependences of SbSI single crystal capacitances and resistance evaluated from the data presented in Fig. 1 using different models: serial (A) and parallel (B) connections of capacitor and resistor (insets present the applied equivalent sets).

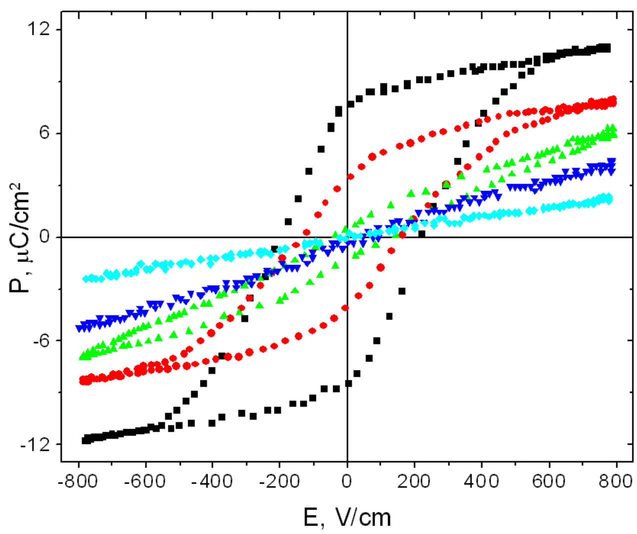

Fig. 3. Hysteresis loops at different temperatures of SbSI single crystal (■ — 292 K, ● — 296 K, Δ — 300 K, ▼ — 305 K, ◊ — 323 K).

and the coercive field (E_c) of the investigated SbSI. The presented values of P_s are smaller than reported in [17] but comparable with published in [5, 18]. The measured values of E_c are comparable to results reported in [19, 17] but smaller than reported in [20].

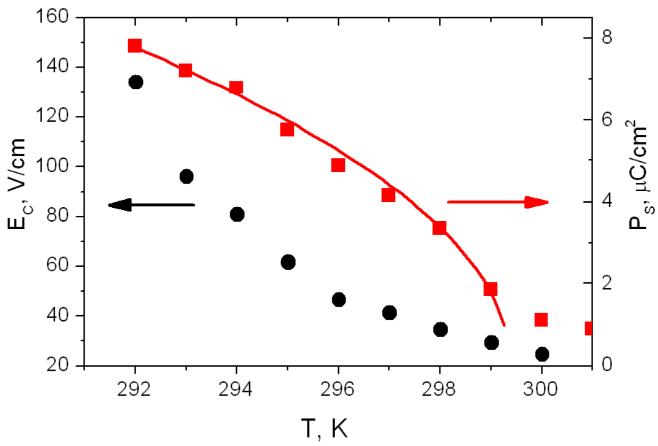

Fig. 4. Temperature dependences of spontaneous polarization (■) and coercive field (●) of SbSI single crystal.

4. Conclusions

SbSI single crystals grown from vapour phase are characterized by the Curie constant $C_C = 221.3(2) \times 10^3$ K and the Curie temperature $T_C = 289.9(5)$ K. Maximum value of the measured dielectric constant is $\varepsilon = 16.2(5) \times 10^3$. Due to relatively low capacitance and high impedance of the investigated semiconducting SbSI single crystal, the model of parallel equivalent circuit is adequate to the case of ac investigations of this material. Taking into account the presented data, one can exclude antiferroelectric phase in the investigated single crystals of SbSI in the temperature range $295 < T < 475$ K.

Acknowledgments

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