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Peculiarities and properties of SbSI electroceramics

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Abstract

SbSI ferroelectric electroceramics has been developed with the increased Curie temperature ($T_c = 58°C$). Below T_c, the electroceramics possess high volume piezoelectric modulus and other parameters important for applications. Microwave and far IR studies reveled that the main dielectric dispersion lies in the range 1–100 GHz. Ab initio calculations of the soft B_{1u} mode potential have shown that in paraelectric (PE) phase on approaching T_c it becomes of a double well form. The high harmonicity splits the soft mode. The lowest frequency component lies at microwaves and gives the main contribution ($\Delta\varepsilon_m = 25{,}0000$) to static permittivity which follows the Curie–Weiss law. The contribution of IR component ($\Delta\varepsilon_{IR} = 1500$) weakly depends on temperature.

Keywords: Ferroelectric properties; Functional applications; SbSI; Spectroscopy

1. Introduction

SbSI is one of the best piezoelectric crystals having the highest volume piezoelectric modulus. However, the low Curie temperature ($T_c \approx 22°C$) and the needle-shaped form limit the applications of SbSI crystals for electroacoustical transducers and other devices. Modified by selected impurities SbSI electroceramics with the Curie temperature $T_c = 58°C$ has been obtained by the Bridgeman method.

This paper presents the results of microwave and far infrared (IR) investigations of the obtained modified SbSI electroceramics and ab initio calculations of the soft B_{1u} potential. They revealed that the microwave and far IR dielectric dispersion is caused by the soft mode splitting due to its high anharmonism.

2. Piezoelectric and dielectric properties. Soft mode

The electroceramics consists of a number of thin single crystals oriented along the ferroelectric *c*-axis (Fig. 1). The diameter of the single crystals ranges from several to hundreds of microns. The discs can be easily cut from the ceramics perpendicular to the *c*-axis. At the temperature 30°C, the electromechanical coupling constant of the ceramics is $k_{33} = 0.72$, the volume piezoelectric modulus $d_v = 6.5 \times 10^{-10}$ C/N, the other parameters important for electroacoustical transducers are $d_v/\sqrt{\varepsilon} = 18 \times 10^{-12}$ C/N, and $d_v/\varepsilon = 55 \times 10^{-12}$ C/N. The d_v reaches maximum value of 12×10^{-12} C/N at 55°C, d_v/ε is nearly constant up to 40–45°C, while $d_v/\sqrt{\varepsilon}$ increases by 10–15%. These parameters are stable up to $(6 \div 7) \times 10^7$ Pa pressure.

In order to understand dielectric properties and mechanism of the phase transition microwave and far IR studies were performed. Far IR spectrum is similar to the pure SbSI one:[1] for $E \| c$ polarization, in PE phase it consists of two B_{1u} modes at 43 and 173 cm^{-1}, while below T_c six modes have been found. The contribution of the B_{1u} modes give only several percent ($\Delta\varepsilon = 1500$) to the static permittivity and it weakly depends on temperature. For microwave studies the needle shaped single crystals were taken from the sample (Fig. 1) and the needle-shaped crystal methods[1] were applied for microwave measurements and calculations of the permittivities. The imaginary and real parts of permittivity at microwaves strongly depend on temperature (Fig. 2). The temperature dependence of the real part of permittivity shows that the phase transition remains of the first order. The Curie–Weiss constant calculated from the measurements at 1 GHz is $C = 2 \times 10^5$ K, and the Curie temperature is $T_c = 58°C$.

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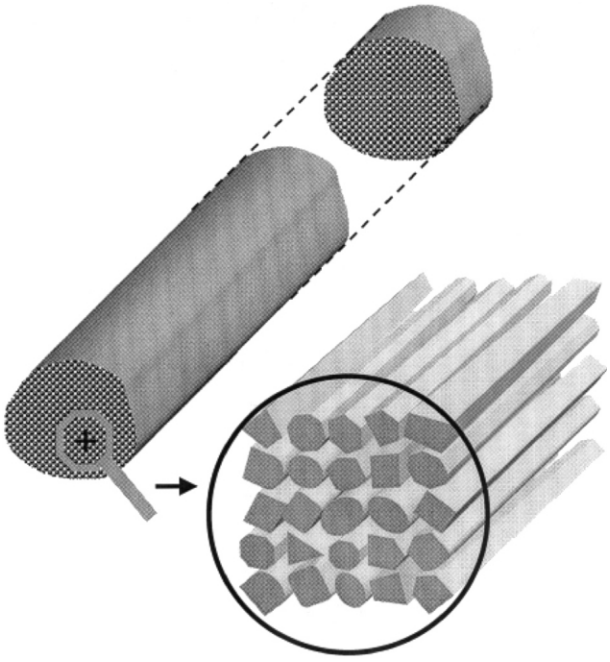

Fig. 1. Shape of SbSI electroceramics.

Frequency dependence of the real and imaginary permittivities caused by the lower frequency B_{1u} mode are shown in Figs. 3 and 4. The main dielectric dispersion lies in the frequency range 1–100 GHz. It can be described by the dispersion relation for a damped oscillator:

$$\varepsilon^*(\nu, T) = \Delta\varepsilon_{IR} + \frac{\Delta\varepsilon_m(T)\nu_s^2(T)}{\nu_s^2(T) - \nu^2 + i\nu\gamma(T)}, \quad (1)$$

where ν_s is the soft mode frequency, γ is the damping constant, $\Delta\varepsilon$ and ε_{IR} are the contribution of the microwave and IR components, respectively. Temperature dependence of the soft mode parameters calculated from the microwave dispersion is shown in Fig. 5. Ab initio calculations of the soft mode potential explain the appearance of this additional overdamped oscillator at microwaves.

3. Electronic potential of the soft mode

We used the all-electron, full-potential, plane-wave method for the exchange and correlation interactions between electrons. The adiabatic electronic potential (EP) at a point **r** in the symmetry plane wave basis can be written as for SbSI crystal:[2]

$$V(\mathbf{r}) = \frac{4\pi}{V_c}\sum_{k,s}|\mathbf{s}|^{-2} f_k(\mathbf{s})\exp[-i(\mathbf{r}+\mathbf{R}_k+\mathbf{Q})\mathbf{s}]\exp[-\mathbf{M}_k(\mathbf{s})], \quad (2)$$

where V_c is the unit cell volume, **s** is the reciprocal lattice vector, k runs over atoms of all types within the unit cell, $f_k(\mathbf{s})$ is the atomic form factor given by:

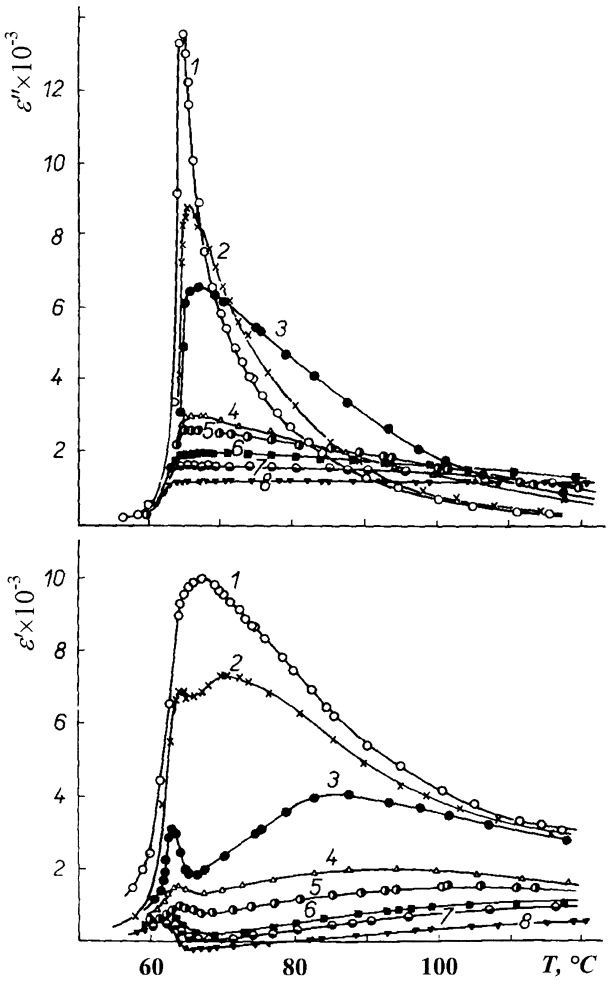

Fig. 2. Temperature dependence of the imaginary and real part of permittivity at microwave frequencies (GHz): (1) 8.6; (2) 12.6; (3) 22.5; (4) 38.7; (5) 52; (6) 65; (7) 72.8; (8) 78.5.

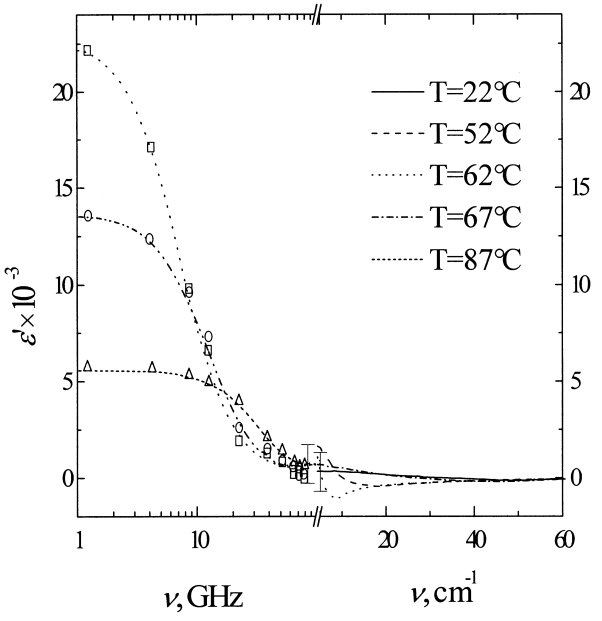

Fig. 3. Frequency dependence of real part of the permittivity for $E \| c$ polarization.

$$f_k(\mathbf{s}) = \sum_{nlm} \langle nlm | \exp[-i(\mathbf{rs})] | nlm \rangle, \quad (3)$$

where nlm is the atom quantum number set, $\mathbf{R}_k$ is the atom vector within the unit cell, $\mathbf{Q}$ is the normal coordinate, and $\exp\{-\mathbf{M}_k(\mathbf{s})\}$ is the Debye–Waller factor. The main contribution to the $f_k(s)$ comes from the internal electronic states. The experimental structural factors

$$F(h,k,l) = \sum_k f_k(s) \exp[-i(R_k, s)] \quad (4)$$

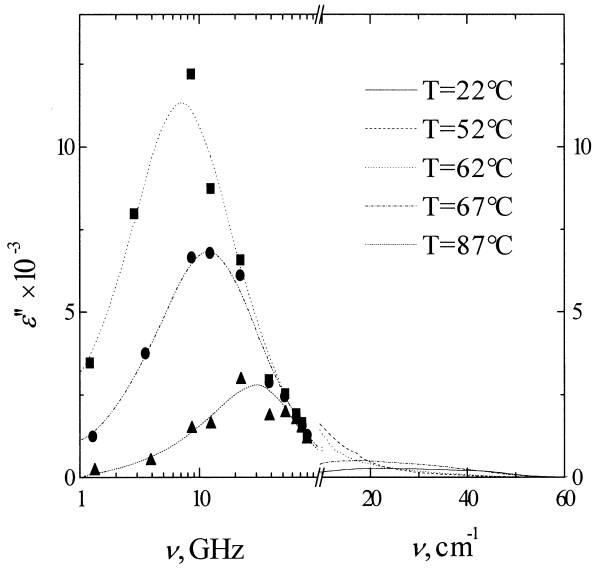

Fig. 4. Frequency dependence of imaginary part of the permittivity.

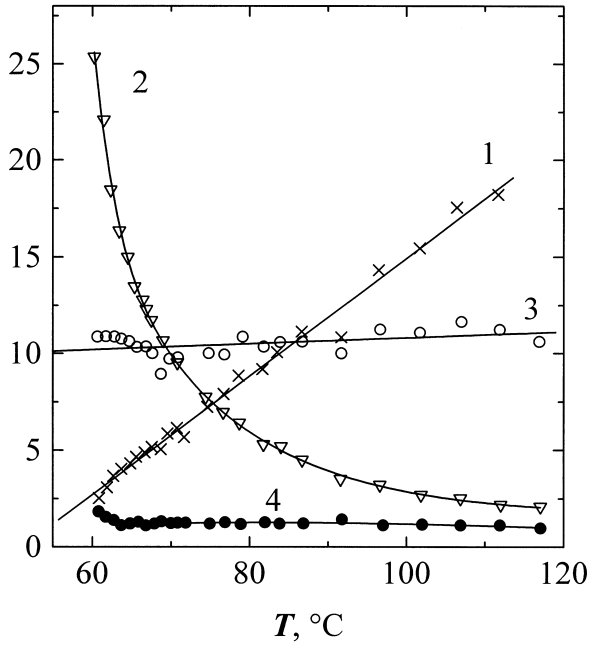

Fig. 5. Temperature dependence of the soft mode parameters in the PE phase: (1) $\nu_s^2 \times 4 \cdot 10^{-2}$ (GHz^2); (2)$\Delta\varepsilon^{-3} \times 10^{-3}$; (3) γ (GHz); (4) $\varepsilon_\infty \times 10^{-3}$.

and coordinates of atoms were obtained from the X-ray analysis. The calculation of EP was carried out by Eq. (2) using 5000 **s** vectors.

The mean value of the EP depends on the mean values of the atomic form factors of Sb, S, I and 20% of oxygen. Fig. 6 shows the EP as a function of the normal coordinates of the soft B_{1u} mode with the displacement along the c-axis at Sb, S and I sites in the far PE phase and near the T_c temperature. At high temperatures, the mean EP is nearly harmonic. When temperature approaches to the T_c, the anharmonicity increases and EP becomes of a double-well form.

4. Splitting of the soft mode

The phonon Hamiltonian of the SbSI- type crystal can be written as[1]

$$\hat{H} = \sum_{mf} H_{mf}^{Sb} - \frac{1}{2} \sum_{mm'} \sum_{ff'}^{\alpha\beta} (mm') \mathbf{u}_{mf}^{\alpha} \mathbf{u}_{m'f'}^{\beta} - \frac{1}{N^{1/2}} \sum_{\substack{qj \\ mf\beta}} e^{iqR_{mf}} \tau_{jf}^{\beta}(\mathbf{q}) \cdot \left(b_{qj}^{-} + b_{-qj}^{+} \right) \mathbf{u}_{mf}^{\beta} + \sum_{qj} \hbar\omega_j(\mathbf{q}) b_{qj}^{-} b_{qj}^{-}, \quad (5)$$

where H_{mf}^{Sb} is the Hamiltonian describing the motion of the Sb atom in the potential well produced by the nearest S and I, $\mathbf{u}_{mf}$ are the displacements of Sb, and b_{qj}^{-} and b_{qj}^{+} are Bose-operators of the "bare" harmonic phonons

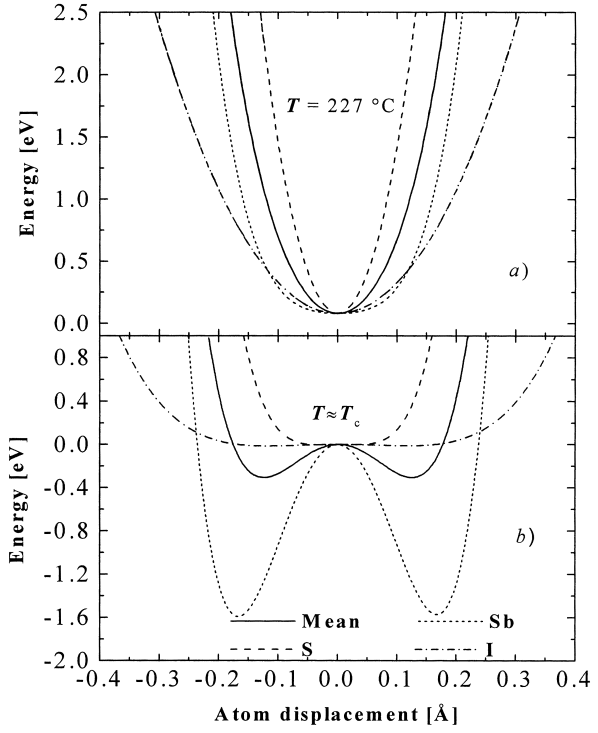

Fig. 6. Dependence of the soft mode potential upon the normal coordinates of B_{1u} symmetry along the c axis in the vicinity of Sb, S, I atoms and its mean value at 227°C (a) and58°C (b).

introduced on the reduced set of normal coordinates, from which the local normal coordinates of the relative motion of Sb, S and I are excluded (m is the cell number, and f is the atom index). The second term in Eq. (5) describes the interaction between Sb, while the third one describes the interaction with the remaining atoms of the lattice arising at their relative displacements.

The spectrum of the frequency of the lattice vibrations can be determined[1,3] by means of the two-time Green functions at the random phase approximation. The anharmonic potential describing the motion of the Sb atom along the c-axis with respect to the surrounding S and I atoms is:

$$W(\omega) = \frac{1}{2}m\omega_0^2 u^2 + V\mathrm{e}^{-\hat{\beta}u^2}. \tag{6}$$

The single-ionic Hamiltonian with the use the dimensional variable $\xi = u(m\omega_0/\hbar)^{1/2}$ can be written as

$$H^{\mathrm{Sb}} = \frac{\hbar\omega_0}{2}\left[\xi^2 - \frac{\mathrm{d}^2}{\mathrm{d}\xi^2}\right] + v\mathrm{e}^{-2\tau\xi^2}, \qquad \tau = \frac{\tilde{\beta}\hbar}{2m\omega_0}. \tag{7}$$

The calculation of the Green function of displacements have shown that under the influence of the anharmonicity, the threefold splitting of the frequency of the local normal vibration of the Sb atom takes place, and the following expressions are obtained for the frequencies and oscillator strength:

$$\tilde{\omega}_1 = 3\tilde{\omega}_0\left[1+\frac{8}{9}A - \frac{\tilde{\alpha}_1}{9\tilde{\omega}_0^2}A\right]^{1/2},\ \tilde{\omega}_2 = \tilde{\omega}_0\left[1+16A^2B^2\frac{\tilde{\omega}_0^2}{\tilde{\alpha}_1}\right]^{1/2} \approx \tilde{\omega}_0,$$

$$\tilde{\omega}_3 = \tilde{\omega}_0\left[1 - 8A - \frac{\tilde{\alpha}_1}{\tilde{\omega}_0^2}(1-A)\right]^{1/2},\ \alpha_1 = \frac{1}{m}\left(V_{11} - \frac{L}{\hbar^2\omega_{f(1)}^2}\right),$$

$$F_1 = \frac{q_{ef}^2}{mv_{\mathrm{c}}}, \qquad F_2 = \frac{q_{ef}^2}{mv_{\mathrm{c}}}(1-A)16A^2B^2\frac{\tilde{\omega}_0^4}{\tilde{\alpha}_1^2},$$

$$F_3 = \frac{q_{ef}^2}{mv_{\mathrm{c}}}(1-A)\left[1 - 16A^2B^2\frac{\tilde{\omega}_0^4}{\tilde{\alpha}_1^2}\right]. \tag{8}$$

The vibration with the frequency $\tilde{\omega}_3$ is the true soft mode. The decrease of $\tilde{\omega}_3$ at $T \to T_{\mathrm{c}}$ corresponds to the temperature instability of the ferroelectric phase at T_{c}, and is caused both by the decrease of $\tilde{\omega}_0$ and by the increase of parameter A.

The frequency $\tilde{\omega}_2$ slightly differs from $\tilde{\omega}_0$ and also decreases at $T \to T_{\mathrm{c}}$. Its oscillator strength and contribution to $\varepsilon(0)$ are considerably smaller than these of the $\tilde{\omega}_3$ mode. The oscillator strength of the mode $\tilde{\omega}_1$ is insignificant.

The dielectric dispersion in SbSI at millimetre waves apparently corresponds to the $\tilde{\omega}_3$ mode. The pseudosoft $\tilde{\omega}_2$ mode appears in the IR spectrum. Such a mode splitting should be a rather common feature in displacive anharmonic ferroelectrics and could explain low-frequency excitations.

5. Conclusions

SbSI electroceramics at $T_{\mathrm{c}} = 58°\mathrm{C}$ undergoes first order ferroelectric phase transition and possess parameters important for applications. On approaching the T_{c}, the soft $B_{1\mathrm{u}}$ mode potential is of a double-well form. The high anharmonicity splits the soft mode. The main component of which lies at microwaves (1–100 GHz) and cause high contribution ($\Delta\varepsilon_m = 25{,}0000$) to static permittivity. The contribution of IR component is $\Delta\varepsilon_{\mathrm{IR}} = 1{,}500$ and it weakly depends on temperature.

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