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The nature of anharmonicity and anomalous piezoelectric properties of ferroelectric SbSBr crystal

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ABSTRACT

The contribution of soft mode at Sb atom's sites, to the temperature dependences of Sb atom's equilibrium position's difference $\Delta z(T)$ has been studied theoretically, when SbSBr crystal is deformed along $\mathbf{a}(x)$, $\mathbf{b}(y)$ and $\mathbf{c}(z)$-axis in paraelectric phase and is deformed along $\mathbf{c}(z)$-axis in ferroelectric phase. The largest change of $\Delta z_{33}(T)$ occurs in the ferroelectric phase near the phase transition temperature in the range from 16 K to 21 K. The temperature dependence of Sb atom's equilibrium position's displacements Δz_{33} is very similar to the temperature dependence of experimental piezoelectric modulus, when SbSBr crystal is deformed in the direction of $\mathbf{c}(z)$-axis in ferroelectric phase.

1. Introduction

SbSI and SbSBr have been extensively studied because they have phase transitions and technological applications as microwave and piezoelectric devices [1–7]. The crystal structure of SbSBr was investigated by Cristofferson et al. [8] and Inushima [9] at temperatures 294 K, 150 K, 60 K, 30 K and 11 K. SbSBr and SbSI has an orthorhombic structure and has four SbSBr molecules (12 atoms) in a unit cell. Each molecule of SbSBr and SbSI extends like a chain along the $\mathbf{c}(z)$-axis. SbSBr and SbSI belongs to the space group Pnam and to the space group Pna21 in paraelectric phase ($T > T_C$) and in the ferroelectric phase ($T < T_C$), respectively.

We found that phase transition temperature in SbSBr and SbSI crystals depends on form-factors of Br and I atoms. Therefore, the phase transition temperature of SbSBr crystal (T_C=22.8 K) and SbSI (T_C=294 K) because form-factor of I atoms f_I is larger than form-factor f_{Br} of Br atoms ($f_{Br} < f_I$) [10]. At temperatures $T \approx T_C$ Sb atoms average potential energy $\overline{V}_P(z)$ depends on amplitude of normal coordinates of $B_{1u}(A_u)$ symmetry soft mode in paraelectric phase which have double-well form. At T_C $\overline{V}_P(z)$ of SbSI and SbSBr have very strong dependence on temperature and deformation [4,6,7].

Therefore theoretical investigation of anomalous piezoelectric properties of ferroelectric semiconductors SbSI and SbSBr in the region of phase transition is very important for technological application in piezoelectric devices.

The piezoelectricity of SbSBr was determined by measuring the resonant and anti-resonant frequencies [1]. In this work, the piezoelectric modulus d_{33} and elastic compliance coefficients s_{33}^D and s_{33}^E of SbSBr were determined by admittance measurement on single crystals. The d_{33} has the highest value of 6×10^{-5} cgsesu near the T_C. Above the T_C=21.8 K SbSBr lost the piezoelectricity. The authors of work [1] came to conclusion that they could not offer clear enough mechanism to explain anomalous temperature dependence of the piezoelectric properties in temperature range from 16 K to 21 K in ferroelectric phase.

The aims of this article are as follows: (1) To determine the mean potential energy $\overline{V}_P(z)$ of Sb atom's sites dependence on amplitude of soft mode normal coordinates in paraelectric phase when SbSBr crystal is deformed along $\mathbf{a}(x)$, $\mathbf{b}(y)$ and $\mathbf{c}(z)$-axis. (2) To determine the temperature dependence of the difference of equilibrium positions $\Delta z_{33}=z_{33}-z_0$ of Sb atoms: z_0 – atomic equilibrium positions when crystal is not deformed (r=0); z_{33} – atomic equilibrium positions when crystal is deformed ($r \neq 0$). (3) To explain anomalous behavior of temperature dependence of Δz_{33} and piezoelectric properties in temperature range from 5 K to 21 K.

2. Investigation of potential energy of Sb atoms in anharmonic soft normal mode

In [5,6] we proposed the method for calculating the potential energy at point $\boldsymbol{r}$ of the unit cell. This method allows determination of the potential energy at any point $\boldsymbol{r}$ in the unit cell based on standard structural data and requires no additional adjustable parameters for fitting the results to the experimental data.

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All 12 atoms of the unit cell induce the following electronic potential at the point $\mathbf{r}$ [7,10]:

$$V_p(\mathbf{r})=\sum_{\alpha}V_\alpha(\mathbf{r})=\sum_{\alpha,\mathbf{s}}e\frac{4\pi}{\Omega}|\mathbf{s}|^{-2}f_\alpha(\mathbf{s})\exp[-i(\mathbf{r}+\mathbf{R}_\alpha)\mathbf{s}], \tag{1}$$

where $f_\alpha(\mathbf{s})$ – atomic form factors; $|\mathbf{s}|$ – reciprocal lattice vectors.

For evaluating the dependence of $V_p(\mathbf{r})$ upon the normal mode coordinates $\mathbf{Q}_\alpha$ one should substitute $(\mathbf{R}_{0\alpha}+\mathbf{Q}_\alpha)$ for $\mathbf{R}_\alpha$.

Then the total electronic potential energy induced by the normal mode atoms is described at point $\mathbf{r}$ by the following formula:

$$V_p(\mathbf{r})=\sum_{\alpha,\mathbf{s}}e\frac{4\pi}{\Omega}|\mathbf{s}|^{-2}f_\alpha(\mathbf{s})\exp\left[-i(\mathbf{r}+\mathbf{R}_{0\alpha}+\mathbf{Q}_\alpha)\mathbf{s}\right]. \tag{2}$$

The electron density depends upon the amplitude of the thermal motion of atoms. Therefore, the temperature dependence of $V_p(\mathbf{r})$ is obtained by introducing the Debye–Waller factor determined by the mean-square amplitude of the thermal vibration of atoms [10]:

$$\exp[-M(\mathbf{s})]=\exp[-(b_{11}h^2+b_{22}k^2+b_{33}l^2+2b_{12}hk+2b_{13}hl+2b_{23}kl)], \tag{3}$$

where h, k, l are Miller indices, and b_{11}, b_{22}, b_{33} are temperature factors in the direction of x, y, z-axes, respectively.

For convenience, we make the following substitutions:

$$b_{11}h^2=\frac{1}{16\pi^2}(s_x^2B_x),\quad \text{where } s_x=\frac{2\pi\cdot h}{a}\quad B_x=4a^2b_{11};$$
$$b_{22}k^2=\frac{1}{16\pi^2}(s_y^2B_y),\quad \text{where } s_y=\frac{2\pi\cdot h}{b}\quad B_y=4b^2b_{22};$$
$$b_{33}l^2=\frac{1}{16\pi^2}(s_z^2B_z),\quad \text{where } s_z=\frac{2\pi\cdot h}{c}\quad B_z=4c^2b_{33},$$

where a, b, c are the unit cell parameters.

For SbSBr crystal, the values of constants b_{11}, b_{22}, b_{33} and atomic coordinates R_α and crystal lattice parameters a, b and c are provided in Refs. [8,9]. s_x, s_y, s_z, $\mathbf{s}$ were calculated using a special computer routine.

With account of Eq. (3), Eq. (2) written as follows:

$$V_p(\mathbf{r})=\sum_{\alpha,\mathbf{s}}e\frac{4\pi}{\Omega}|\mathbf{s}|^{-2}f_\alpha(\mathbf{s})\exp\left[-i(\mathbf{r}+\mathbf{R}_{0\alpha}+\mathbf{Q}_\alpha)\mathbf{s}\right]\exp[-M(\mathbf{s})]. \tag{4}$$

The potential energy of atoms in the normal mode is evaluated by substituting $\mathbf{r}$ with radius vectors $\mathbf{R}_{\mathrm{Sb}}$, $\mathbf{R}_{\mathrm{S}}$, and $\mathbf{R}_{\mathbf{Br}}$ corresponding to the positions of the atoms Sb, S, and Br in the unit cell.

The average value of the potential energy $\overline{V}_P$ of Sb atom of unit cell in the normal mode of SbSI crystal may be written as follows:

$$\overline{V}_p=\frac{V_p(\mathbf{R}_{\mathrm{Sb}_1})+V_p(\mathbf{R}_{\mathrm{Sb}_2})++V_p(\mathbf{R}_{\mathrm{Sb}_3})+V_p(\mathbf{R}_{\mathrm{Sb}_4})}{4}, \tag{5}$$

where $\mathbf{R}_{\mathrm{Sb}_1}=\mathbf{R}_{0,\mathrm{Sb}_1}+\mathbf{Q}_{\mathrm{Sb}_1}$; $\mathbf{R}_{\mathrm{Sb}_2}=\mathbf{R}_{0,\mathrm{Sb}_2}+\mathbf{Q}_{\mathrm{Sb}_2}$; $\mathbf{R}_{\mathrm{Sb}_3}=\mathbf{R}_{0,\mathrm{Sb}_3}+\mathbf{Q}_{\mathrm{Sb}_3}$; $\mathbf{R}_{\mathrm{Sb}_4}=\mathbf{R}_{0,\mathrm{Sb}_4}+\mathbf{Q}_{\mathrm{Sb}_4}$.

Also the coordinates of all S and Br atoms changes according to the equations:

$\mathbf{R}_\alpha=R_{0,\alpha}+\mathbf{Q}_\alpha$, $\alpha=\mathrm{S}_1$; S_2; S_3; S_4; Br_1; Br_2; Br_3; Br_4;

$V_p(\mathbf{R}_{\mathrm{Sb}_3})$, $V_p(\mathbf{R}_{\mathrm{Sb}_4})$, $V_p(\mathbf{R}_{\mathrm{S}_3})$, $V_p(\mathbf{R}_{\mathrm{S}_4})$, $V_p(\mathbf{R}_{\mathrm{Br}_1})$ and $V_p(\mathbf{R}_{\mathrm{Br}_2})$, are potential energies of Sb, S and Br atoms is the some chain.

The atomic form factor is

$$f_\alpha(\mathbf{s})=\sum_{nlm}\langle nlm|\exp[-i(\mathbf{r}\cdot\mathbf{s})]|nlm\rangle, \tag{6}$$

where nlm is a set of quantum numbers for the atom α.

It should be noted that for calculating the form factors $f_\alpha(\mathbf{s})$ by Eq. (6) we used the functions $\langle nlm|$ of all electronic states of an atom. For the sum in Eq. (4) we used about 5000 vectors $\mathbf{s}$. The dependence of the atomic form factors $f_\alpha(\mathbf{s})$ for Bi, Sb, S, Se, I, Br atoms on the modulus of the reciprocal lattice vector $|\mathbf{s}|$ has been published in [6]. We shall study the potential energy $\overline{V}_P(z)$ of Sb atom of the $\mathrm{B}_{1u}(\mathrm{A}_u)$ symmetry soft mode vibrations upon the amplitudes of normal coordinates or symmetry coordinates (relative displacement of atoms) along the $\mathbf{c}(z)$-axis.

Since in the B_{1u} normal mode atoms oscillate along the $\mathbf{c}(z)$-axis, then in Eq. (4) we put $Q_\alpha=z_\alpha$, where Q_α and z_α denote atomic displacements from their equilibrium position $z_{0,\alpha}$. For numerical evaluation of $\overline{V}_P(z)$ by Eq. (5), we need to vary all $Q_\alpha=z_\alpha$ by small steps from $-Q_\alpha(\max)$ to $+Q_\alpha(\max)$.

In SbSBr crystal the average potential energy $\overline{V}_P(z)$ of S and Br atoms in ferroelectric phase in the region of phase transition is single-well and only slightly depends on temperature and deformation. However $\overline{V}_P(z)$ of Sb atoms in ferroelectric phase in the region of phase transition strongly depends on a temperature and deformation. So we will investigate $\overline{V}_P(z)$ only of Sb atoms and Δz_{33} dependence on temperature and deformation.

3. Investigation of Sb atoms anharmonic mean potential energy $\overline{V}_P(z)$ on deformation in paraelectric phase

The most precise way to determine Δz_{33} is to use Sb atoms potential energy's $\overline{V}_P(z)$ dependence on amplitude of soft mode normal coordinates (relative displacements of all atoms from their equilibrium positions) [11]. For investigation of anharmonicity it is handy to expand $\overline{V}_P(z)$ using polynomial:

$$\overline{V}_p(z)=V_0+a^*z+b^*z^2+d^*z^3+c^*z^4, \tag{7}$$

where a^*, b^*, d^*, c^* are polynomial expansion coefficients.

In paraelectric phase the average potential energy $\overline{V}_P(z)$ of Sb atoms on amplitudes of soft mode normal coordinates (relative displacements of all atoms from their equilibrium positions) along $\mathbf{c}(z)$-axis are presented in Figs. 1 and 2 when deformation have been created by pressure and stretching along $\mathbf{a}(x)$, $\mathbf{b}(y)$ and $\mathbf{c}(z)$-axis at $T=30$ K, respectively. In Tables 1 and 2 the values of expansion coefficients a^*, b^*, d^*, c^*, and height of potential barrier $\Delta\overline{V}_P(z)$ between two minima of double-well $\overline{V}_P(z)$ are presented when deformation have been created by pressure and stretching along $\mathbf{a}(x)$, $\mathbf{b}(y)$ and $\mathbf{c}(z)$-axis at $T=30$ K, respectively.

As seen from Figs. 1, 2 and Tables 1 and 2 height of potential barrier $\Delta\overline{V}_P(z)$ increases when deformation $r=\Delta c/c$ increases for all kinds of deformations along $\mathbf{c}(z)$-axis and vice versa.

But $\Delta\overline{V}_P(z)$ have differently dependence on pressure and stretching, when deformation have been created along $\mathbf{a}(x)$-axis ($r=\Delta a/a$) or along $\mathbf{b}(y)$-axis ($r=\Delta b/b$). Very large changes of $\Delta\overline{V}_P(z)$ have been found when deformations have been created along $\mathbf{b}(y)$-axis ($r=\Delta b/b$).

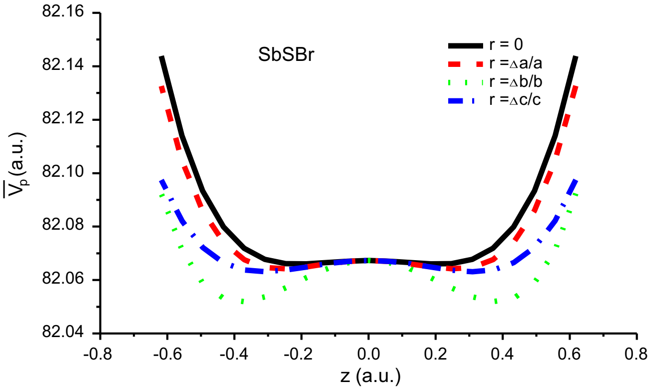

Fig. 1. The SbSBr mean potential energy dependence on soft mode normal coordinates (relative displacements of all atoms from their equilibrium positions) at the Sb atoms sites along $\mathbf{c}(z)$-axis in paraelectric phase ($T=30$ K), when deformation (pressure) $r=0.02$ along $\mathbf{a}(x)$, $\mathbf{b}(y)$ and $\mathbf{c}(z)$-axis and $r=0$. $\Delta z=1$ a.u.$=0.53$ Å.