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Elastic constants of $Na_{0.5}Bi_{0.5}TiO_3$ single crystal

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The elastic constant matrix at room temperature and the temperature dependence of C_{11} constant (30–400°C) of $Na_{0.5}Bi_{0.5}TiO_3$ single crystal have been measured for the first time. The anomaly at the temperature, which corresponds to disappearing of ferroelectric state (∼200°C), and broad minimum about temperature, which correlates to maximum of electric permittivity (∼320°C), has been revealed. It has been concluded, that this minimum can be dynamic effect and does not indicate of the structural phase transition. Also the use of NBT for device applications has been indicated. © *2002 Kluwer Academic Publishers*

1. Introduction

Lead oxide-based perovskites are widely used in electromechanical devices due to their high field-induced strains and most efficient electrical-mechanical energy conversion. However, the toxicity of lead oxide (PbO) and its high vapour pressure during processing causes search for alternative lead-free materials with comparable properties. $Na_{0.5}Bi_{0.5}TiO_3$ (NBT)-based materials are very useful candidates with promising electromechanical properties [1].

Ferroelectricity in perovskite structure NBT compound was discovered in 1960 [2]. This compound has been widely investigated due to its possible applicability to electromechanical actuators, sensors, and transducers. But these studies have also resulted in conflicting views regarding the number of different phases existing, their electric order and the temperature range over which they exist. The highest-temperature phase of NBT is cubic, and it makes a phase transition to tetragonal at 540–520°C, and to rhombohedral at ∼200°C. The tetragonal and rhombohedral phases are known to exibit ferroelasticity and ferroelectricity, respecively. However, according to [3] both phases are expected to be ferroelastic, in contradiction. Considerable controversy is connected with a temperature range between tetragonal and rhombohedral phases. Broad maximum of electric permittivity occurs about 320°C, which manifests the phase transition. Nevertheless, X-ray [4], neutron scattering [5], Raman scattering [6] etc. measurements do not show any structural phase transition around this temperature. Regarding this contradiction, the antiferroelectric order has been suggested [7]. However, the majority of the published results deny this hypothesis [4–6, 8–11], and rather indicate coexistence of both phases (i.e. tetragonal and rhombohedral). This may be caused by preexistence of the unstable polar regions, whose correlation radii increase with decreasing temperature [5]. Below 280°C, these regions are stable and are expected to become the nuclei of low-temperature ferroelectric state. From this point of view, the broad maximum of electric permittivity at about 320°C may originate from relaxation processes connected with electromechanical interaction between polar regions and nonpolar matrix [8]. Indeed, dielectric dispersion measurements [8] demonstrate the occurence of relaxational phenomena which can be connected with the existence of polar regions. Recently it has been suggested that two intermediate structures (cubic or monoclinic) may be considered from the symmetry point of view [12], in contradiction.

Electromechanical actuators directly transform electrical energy into mechanical energy. Among the material properties determining actuator performance, elastic constants are important parameters for actuators. In addition the elastic constants of materials can indicate the phase transition, because they change abruptly near a phase transition temperature. Up to now, there has been no literature data concerning elastic constants of NBT. For the first time, this paper presents the elastic constant matrix at room temperature and temperature dependence (30–400°C) of C_{11} constant for NBT single crystal.

2. Experimental conditions

The measurements were performed on the single crystals produced by the Czochralski method. The crystals obtained were homogeneous and slightly yellowish transparent. Transit times of 1-MHz ultrasonic waves were measured using usual pulse echo technique [13] (to an relative accuracy of $\pm 10^{-5}$). The sample temperature was measured to an absolute accuracy of ±0.5°C by thermocouple. The experimental technique allows to measure both in heating/cooling (with rate of 1.5°C/min) or in temperature stabilization during 30 minutes. The obtained data were corrected for dimensional changes of NBT single crystal by using the thermal expansivity given in Ref. [14].

3. Results and discussion

At room temperature NBT has rhombohedral symmetry with point group 3 m. In this situation elastic constant matrix contains six independent single crystal elastic constants ($C_{11}, C_{12}, C_{13}, C_{14}, C_{33}, C_{44}$) [15]. Measurements are made in four crystallographic directions as follows:

Propagation down the *a*-axis (pure longitudinal wave and two pure shear waves):

$$\rho v_{\mathrm{L1}}^2 = C_{11} \tag{1}$$

$$\rho\left(v_{\mathrm{S2}}^2 + v_{\mathrm{S3}}^2\right) = C_{44} + C_{66} \tag{2}$$

$$\rho^2 v_{\mathrm{S2}}^2 v_{\mathrm{S3}}^2 = C_{44}C_{66} - C_{14}^2 \tag{3}$$

Propagation down the *b*-axis (pure shear wave, quasilongitudinal wave and quasishear wave):

$$\rho v_{\mathrm{S1}}^2 = C_{66} \tag{4}$$

$$\rho\left(v_{\mathrm{QL2}}^2 + v_{\mathrm{QS3}}^2\right) = C_{11} + C_{44} \tag{5}$$

$$\rho^2 v_{\mathrm{QL2}}^2 v_{\mathrm{QS3}}^2 = C_{11}C_{44} - C_{14}^2 \tag{6}$$

Propagation down the *c*-axis (pure longitudinal wave and two pure schear waves):

$$\rho v_{\mathrm{L1}}^2 = C_{33} \tag{7}$$

$$\rho\left(v_{\mathrm{S2}}^2 + v_{\mathrm{S3}}^2\right) = 2C_{44} \tag{8}$$

$$\rho^2 v_{\mathrm{S2}}^2 v_{\mathrm{S3}}^2 = C_{44}^2 \tag{9}$$

Propagation in *bc* plane (pure shear wave, quasilongitudinal wave and quasishear wave):

$$\rho v_{\mathrm{S3}}^2 = \frac{1}{2}(C_{66} + C_{44}) + C_{14} \tag{10}$$

$$\rho\left(v_{\mathrm{QL2}}^2 + v_{\mathrm{QS1}}^2\right) = \frac{1}{2}(C_{11} + C_{33}) + C_{44} - C_{14} \tag{11}$$

$$\rho^2 v_{\mathrm{QL2}}^2 v_{\mathrm{QS1}}^2 = \frac{1}{4}(C_{11} + C_{44} - 2C_{14})(C_{33} + C_{44}) - \frac{1}{4}(C_{13} - C_{14} + C_{44})^2 \tag{12}$$

TABLE I Elastic properties of NBT single crystal at room temperature

Elastic stiffness constants ($\times 10^{10}$ Nm^{-2})	
C_{11}	15.39
C_{12}	1.87
C_{13}	5.21
C_{14}	−0.17
C_{33}	16.81
C_{44}	8.23
$C_{66} = 1/2(C_{11} - C_{12})$	6.76
Elastic compliance constants ($\times 10^{-11}$ N^{-1} m^2)	
S_{11}	0.74
S_{12}	−0.14
S_{13}	−0.22
S_{14}	0.02
S_{33}	0.73
S_{44}	1.22
$S_{66} = 2(S_{11} - S_{12})$	0.88
Young's modulus ($\times 10^{10}$ Nm^{-2})	
Along *a*-axis	13.8
Along *b*-axis	13.8
Along *c*-axis	13.7
Volume compressibility ($\times 10^{-12}$ N^{-1} m^2)	10.5

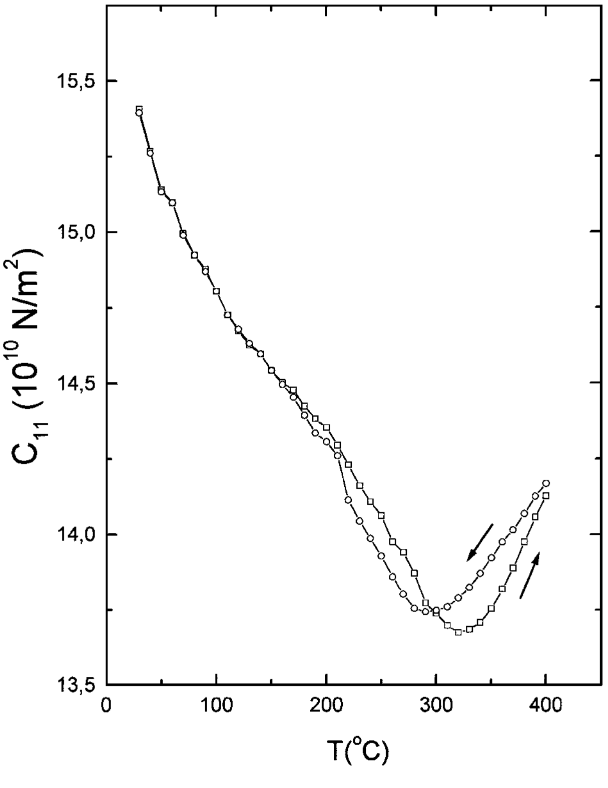

Figure 1 Temperature dependence of the elastic stiffness constant C_{11} for NBT single crystal. The lines are quides for the eyes.

The fundamental room temperature values of C_{ij} are listed in Table I (C_{66} is listed for completness). Close values of constants: C_{11} with C_{33} and C_{44} with C_{66} can be the evidence of small rhombohedral distortion in NBT. This result is in accordance with X-ray data (corner angles depart from 90° by a few min.) [4, 10]. The elastic compliances S_{ij}, Young's modulus and volume compressibility were computed from the room temperature elastic constants by using the relations for rhombohedral crystals [16], and the results are also listed in Table I. Temperature dependence of the elastic constant C_{11} is shown in Fig. 1. As it can be seen from this Figure, the elastic constant exibits anomaly near 200°C and broad minimum near 300–320°C. The anomaly near 200°C is connected with ferroelectric phase formation occurence. The broad minimum in C_{11} occurs in the same temperature range where broad maximum of electric permittivity occurs. As it has been mentioned in introduction, X-ray, neutron and Raman scattering measurements do not show any structural phase transition in this temperature range. But, as it has been indicated in Ref. [17], anomalies in ultrasonic data sometimes occur for dynamic reasons that do not involve phase transitions. And even when they do signal a phase transition, its nature is not revealed in any direct way. Thus the broad minimum in C_{11} about 320°C is probably connected with relaxation processes suggested to be a response to electrical and mechanical interactions between the polar regions and the nonpolar matrix. Also for, for example, SrTiO$_3$ some anomalies of dielectric properties can be connected with polarization clusters [18], with oxygen-vacancy-mediated relaxation process [19] or with domain-wall dynamics [19]. When sample is heated and cooled, a large thermal hysteresis is observed (Fig. 1). Similar thermal hysteresis was observed for electric permittivity, birefringence, electrostrictive strain etc. of this material.

The strain energy density (energy per unit mass), which deliver an actuator, should be as high as possible. This strain energy density is given by $1/2(s_{\max}^2 E/\rho)$, where $s_{\max}$ is the maximum field induced strain, E is Young's modulus, and ρ is the material density. The single crystal NBT has lower density than PZT ($\sim$6 g/cm^3 comparable to $\sim$8 g/cm^3) and higher Young's modulus ($\sim$140 GPa comparable to $\sim$65 GPa). Present crystal exibits about 0.15% free strain [20]. Strain energy density for NBT is $\sim$26 J/kg comparable to $\sim$7 J/kg for PZT. Present crystal exibits also high piezoelectric coefficient ($d_{33} \approx 230$ pC/N), high electromechanical coupling coefficient ($k \approx 85\%$) [20], and is capable of sustaining large mechanical stresses without any mechanical degradation [21]. The decrease of hysteresis in field-polarization and field-strain dependencies is also possible by application of compressive stress [21]. These characteristics make this material very interesting for applications.

Some from the above mentioned properties of NBT can be improved in NBT-based systems [1, 22–24]. A noticeable feature of these systems is the occurence of a morphotropic phase boundary (MPB) between rhombohedral and tetragonal symmetries. Materials with compositions close to the MPB usually present the best electromechanical properties.

4. Conclusions

The room temperature elastic constant matrix and the temperature dependence of C_{11} constant of NBT single crystal were reported for the first time. It seems that broad dip of elastic constant C_{11} in temperature range, which corresponds to maximum of electric permittivity ($\sim$320°C) is not connected with structural phase transition (i.e. it is dynamic). The most widely used parameter (strain energy density), performance of describing devices, was evaluated. Aside from reduced toxicity in processing and use, NBT single crystals and NBT-based materials can be promising candidates for, for example, high performance solid state actuators.

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