

DIPOLE DEFECT DECAY AND DIELECTRIC RELAXATION IN $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ SINGLE CRYSTAL

V. M. Sidak^{1*}, M. P. Trubitsyn²

¹*Dnipropetrovsk Medical Academy of Health Ministry of Ukraine, Dnipro, Ukraine*

²*Oles Honchar Dnipro National University, Dnipro, Ukraine*

*e-mail: vasylsidak@gmail.com

Electrical properties of heat treated in air and in vacuum $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ single crystals were measured in AC field ($f=1$ kHz) in the range 300–800 K. Relaxation anomaly of permittivity $\epsilon(T)$ is observed near 700 K for the crystal heat treated in vacuum. It is argued that processing in vacuum generates the defect dipoles, which give rise to the dielectric anomaly. The character of the $\epsilon(T)$ experimental dependence is quite different from the predictions of Debye model. The non-Debye behavior of $\epsilon(T)$ is explained by the concentration decrease of dipole defects due to their thermal destruction at high temperatures. In addition, the $\epsilon(T)$ anomaly could be described more precisely by taking into consideration configurational and vibrational entropy of the subsystem of dipole defects. The observed dielectric relaxation is presumably attributed to reorientations of the dipole moments of $\text{Ti}^{3+}-\text{V}_\text{O}$ centers.

Keywords: sodium bismuth titanate, permittivity, dipole moment, relaxation anomaly, non-Debye behavior.

Received 24.10.2020; Received in revised form 27.11.2020; Accepted 02.12.2020

1. Introduction

Structural defects strongly influence physical properties and efficiency of crystalline materials applied in functional electronics. For active dielectrics, this fact is of special importance since lattice imperfections increase electronic and ionic conductance at operating temperatures and therefore degrade electrophysical properties of the material. Among other substances of perovskite family, sodium bismuth titanate $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ (NBT) is the most promising compound for piezoelectric devices and electro-mechanical transducers. Earlier slow dielectric relaxation was observed in NBT crystal in the temperature range of 600 – 750 K [1, 2]. It was proposed that dielectric anomaly was contributed by associated dipole defects formed on the basis of oxygen vacancies V_O . One should note that the type of the anomaly was quite unusual and differed from typical Debye-like behavior. This paper is devoted to the analysis of the non-Debye $\epsilon(T)$ anomaly detected in NBT crystal.

2. Experimental results and discussion

NBT single crystals were grown from the melt by Czochralski method. The samples were cut off as the plane parallel plates with $5 \times 5 \times 1$ mm³ dimensions. Pt electrodes were deposited on (111) main planes of the samples by magnetron sputtering in an Ar atmosphere. Electrical properties were measured in AC field ($f=1$ kHz) by using the AC bridge P5083. The measurements were performed in the temperature range 300 – 800 K. Before the measurements, the samples were heat treated in atmospheres with different oxygen partial pressure to control the concentration of oxygen vacancies (V_O). At first the sample cut off from the as-grown NBT single crystal boule was annealed in air at 1070 K for 1 hour and after that was cooled to room temperature. Such treatment allowed to eliminate the $\epsilon(T)$ anomalies dependent on the sample prehistory [1–3]. Then the NBT sample was annealed in vacuum at 1070 K for 2 hours and was cooled to room temperature again. After each heat treatment electrical properties were measured.

Fig. 1 shows the temperature dependences $\epsilon(T)$ measured on heating the NBT sample annealed in air (dependence 1) and subsequently annealed in vacuum (dependence 2). One can see that annealing in vacuum results in appearance of strong $\epsilon(T)$ anomaly. As earlier [1–3], this peak of $\epsilon(T)$ could be detected only for the first heating run and disappeared for the next cooling run (dependence 3) and subsequent temperature cycling.

The dependences 1 and 3 are similar to each other (Fig. 1) and display only the variation of $\varepsilon(T)$ caused by the structural phase transitions in NBT [4]. It is obvious that the latter contribution is presented in the dependence 2 as well (Fig. 1). The dielectric anomaly caused by the relaxing dipole defects in pure form can be derived by subtraction the dependence 1 from the dependence 2. Such subtraction yields nearly symmetrical anomaly $\Delta\varepsilon(T)$ shown in Fig. 2.

The dielectric response due to thermal polarization mechanisms can be described by Debye function [5, 6]

$$\varepsilon^*(T, \omega) = \varepsilon_\infty + \frac{(C/T)}{1 + i\omega\tau(T)}, \quad (1)$$

where ε_∞ is high-frequency permittivity; $\tau(T) = \tau_0 \exp(E/kT)$ is the relaxation time of polarization; Curie constant C is proportional to the concentration of relaxing dipoles.

Eq. 1 predicts strongly asymmetrical anomaly of permittivity real part $\varepsilon(T)$, which is shown in Fig. 2 by the dashed line. One can see that the nearly symmetrical experimental maximum of $\Delta\varepsilon(T)$ is quite different from the stepped Debye-like anomaly. To explain such difference, one should remember that the relaxing dipole complexes disassociate on heating due to thermal excitation [1]. Hence in Eq. 1 one should account the temperature dependence of Curie constant $C(T)$. Assuming that thermal decay of the dipole complexes can be described by an exponential function, one can take Curie constant in the form $C(T) = C_0 \cdot \exp(U/kT)$, where U estimates binding energy of the dipole complexes. Substituting this expression for $C(T)$ into Eq. 1 one can obtain nearly symmetrical $\Delta\varepsilon(T)$ anomaly depicted in Fig. 2 by the dashed curve 3. Obviously, that accounting thermal decay of the dipole complexes via Curie constant temperature dependence $C(T)$ gives more sharp decrease of the high temperature wing of $\Delta\varepsilon(T)$ anomaly (curve 3 in Fig. 2) as compared with Debye-like behavior (curve 2, Fig. 2). Nevertheless, dashed curve 3 notably deviates from the experimental data.

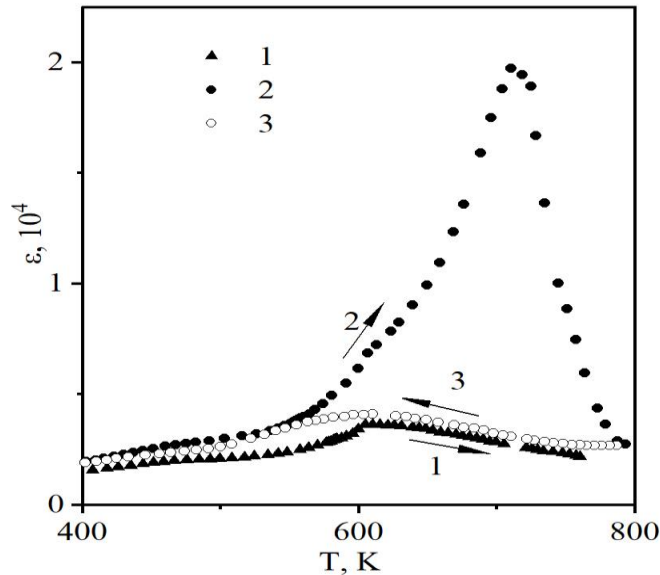


Fig. 1 Dependencies $\varepsilon(T)$ measured on heating for the NBT sample annealed in air (1) and subsequently annealed in vacuum (2). The intense peak of $\varepsilon(T)$ disappeared on the following cooling run (3).

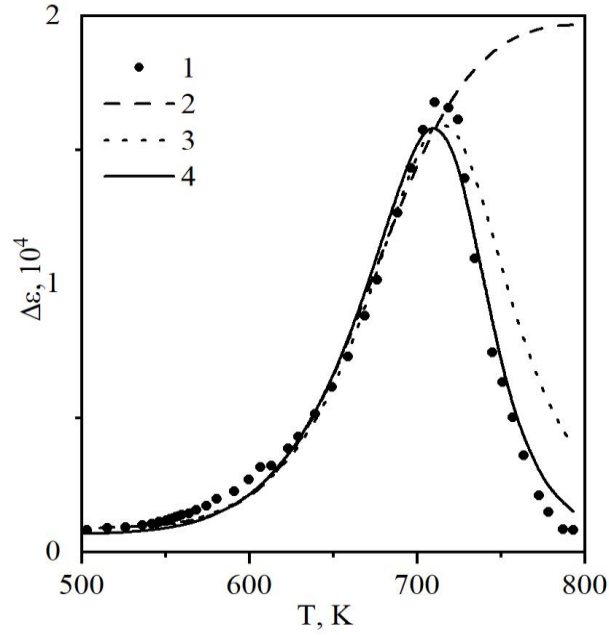


Fig. 2 $\Delta\varepsilon(T)$ anomaly caused by the relaxing dipole defects: 1 – the experimental data; 2 – Debye-like anomaly; 3 – calculations with accounting the thermal decay of dipole defects; 4 – calculations additionally accounting the configurational entropy of the defects.

To explain this discrepancy, let us write an equilibrium concentration of defects in a crystal as $n = n_0 \exp[\Delta G/kT]$ where $\Delta G = \Delta H - T\Delta S$ is free energy change, ΔH is a change of enthalpy accompanying the defect decomposition, ΔS is an entropy change [7]. ΔS can be written as a sum of configurational and vibrational entropy changes $\Delta S = \Delta S_{conf} + \Delta S_{vib}$. If the defects create certain clusters, the configurational entropy become dependent on temperature $\Delta S_{conf} \sim T^n$ [8]. In that case the parameter U should correspond to the binding energy of the dipole defect cluster. The solid line 4 in Fig. 2 is calculated based on Eq. 1 with accounting the temperature dependence of Curie constant $C(T)$ and the configurational entropy $\Delta S_{conf} \sim T^3$. One can see that these assumptions make it possible to describe the experimental data with satisfactory accuracy. It should be added that the calculations gave the value of the pre-exponential factor $\tau_0 \sim 1 \cdot 10^{-15}$ s, which was a few orders lower than the inverse lattice vibrations frequencies. Follow the authors of [8, 9, 10] one can overcome this contradiction by accounting the collective nature of dielectric relaxation and including vibrational entropy change ΔS_{vib} into the exponent in the denominator of Eq. 1. In such case the value of τ_0 is also dependent on the vibrational entropy change.

The data obtained allow to discuss the possible nature of the dipole defects giving rise to the non-Debye dielectric relaxation. Referring to [11], one can suppose that annealing in vacuum mainly increases the concentration of oxygen vacancies V_O . Besides, optical spectra studying showed that NBT crystal darkened after treatment in vacuum. Hence such treatment not only generates excess concentration of V_O but also affects the electronic subsystem of the crystal. Based on the data in [12], one can propose that the dipole defects responsible for the $\varepsilon(T)$ anomaly (Figs. 1, 2) are created by Ti ions located nearby V_O and have captured an electron. Oxygen vacancy hopping through the corners of Ti–O octahedra is accompanied by the reorientation of the dipole moment of $\text{Ti}^{3+}-V_O$ center.

3. Conclusions

Dielectric relaxation anomaly was observed around 670 K in NBT single crystal annealed in vacuum ($T_{ann}=1070$ K). The nearly symmetrical $\varepsilon(T)$ maximum was sufficiently different from the behavior predicted by Debye relaxator model. The non-Debye dielectric relaxation is described by accounting thermal decay of the dipole complexes contributing to the $\varepsilon(T)$ anomaly. It is proposed the observed dielectric relaxation is determined by reorienting dipole moments of $Ti^{3+}-V_O$ centers.

References

1. **Kruzina, T.V.** Vliyanie termicheskoy obrabotki na elektricheskie svoystva kristallov $Na_{0.5}Bi_{0.5}TiO_3$ / T.V. Kruzina, V.M. Sidak, M.P. Trubitsyn, S.A. Popov, and J. Suchanicz // *Visnyk KhNU*. – 2013. – Vol. 1076, No.19. – P. 50 – 53.
2. **Kruzina, T.V.** Thermal treatment and dielectric properties of $Na_{0.5}Bi_{0.5}TiO_3$ single crystal / T.V. Kruzina, V.M. Sidak, M.P. Trubitsyn, S.A. Popov and J. Suchanicz // *Ferroelectrics*. – 2014. – Vol. 462, No.1. – P. 140 – 144.
3. **Kruzina, T.V.** Electrical and optical properties of heat treated $Na_{0.5}Bi_{0.5}TiO_3$ crystals / T.V. Kruzina, T.V. Panchenko, V.M. Sidak, S.A. Popov, V.S. Shchetinkin // *Visnik Dnipropetrovs'kogo universitetu. Seriâ Fizika, radioelektronika*. – 2016. – Vol. 24, Issue 23, No 1. – P. 106 – 109.
4. **Trolliard, G.** Reinvestigation of phase transitions in $Na_{0.5}Bi_{0.5}TiO_3$ by TEM. Part II: Second order orthorhombic to tetragonal phase transition / G. Trolliard, V. Dorcet // *Chem. Mater.* – 2008. – Vol. 20, No 15. – P. 5074 – 5082.
5. **Poplavko, Yu.** *Functional Dielectrics for Electronics Fundamentals of Conversion Properties* / Yu. Poplavko, Yu. Yakymenko. – Woodhead Publishing, 2020. – 312 p.