Space-charge polarization phenomena in single crystal and ceramics of bismuth sodium titanate

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Introduction

Electrically and optically active defects can significantly enhance electronic and ionic conductivity, affect dielectric susceptibility, optical transmission and absorption, give rise to luminescence. Recently the strong dielectric anomaly (~10^4) was observed near 670 – 690 K in NBT single crystal [1-3] and solid solutions $Na_{0.5}Bi_{0.5}TiO_3$ – $BaTiO_3$ (NBT–BT). The ε(*T*) dependence showed anomalous temperature behavior and unusual frequency dispersion. In addition, permittivity peak disappeared after heat treatment in air (~800K) and could be restored by heat treating in vacuum (~1070 K).

Experimental results

The NBT ceramics were prepared by usual sintering technique, single crystals were grown from the melt by the Czochralski method. The samples for electrical properties measurements were cut off as the plane-parallel plates. The Pt electrodes were deposited on the main planes of the samples by cathode sputtering method. Electrical properties were measured by using AC bridge P 5083 in the temperature interval 300 – 800 K for the frequency range 0.5 – 100 kHz. Two types of the samples were used: i) prepared from as sintered ceramics and ii) heat treated in vacuum. The regimes of heat treating were the same as those previously used for single crystals (*T*= 1070 K, *t*= 2 h, p ~ 1 Pa) . The data obtained are shown in Fig. 1 and Fig. 2 . One can see that after heat treating, in the range 700 – 780 K ε(*T*) demonstrates intense maximum (ε_{max} ~ 10^4, *f* = 0.5 kHz) which is strongly dependent on frequency *f*.

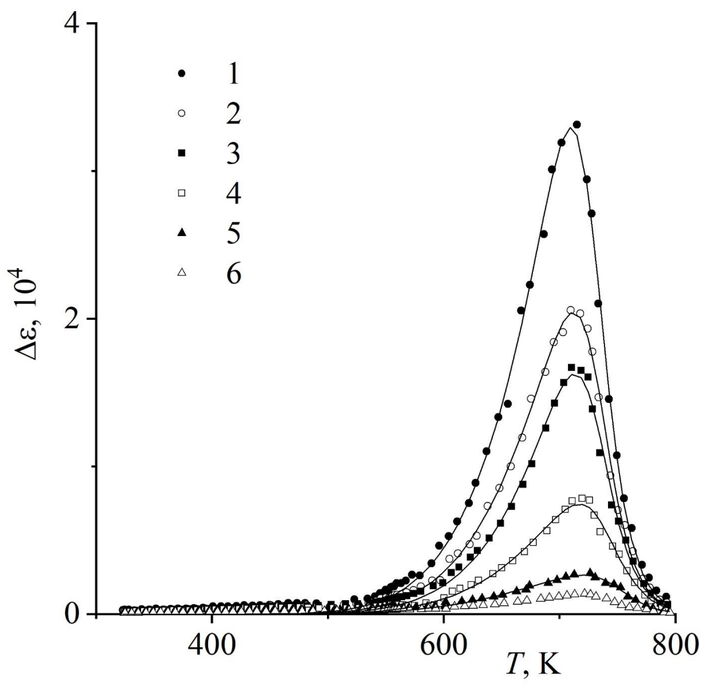

Fig. 1 The dependencies ε(*T*) measured in the first heating run of NBT single crystals previously heat treated in vacuum (1070 K, 2 h). The AC field frequency was *f* = 0.5 (1); 0.8 (2); 1 (3); 2 (4); 5 (5); 10 (6) kHz.

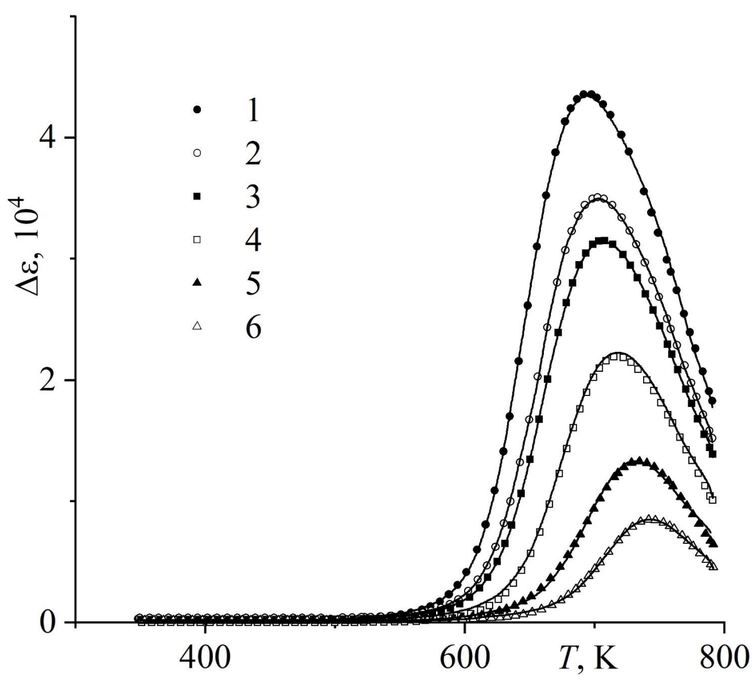

Fig. 2 The dependencies ε(*T*) measured in the first heating run of NBT ceramics previously heat treated in vacuum (1070 K, 2 h). The AC field frequencies are indicated in the caption to Fig.1.

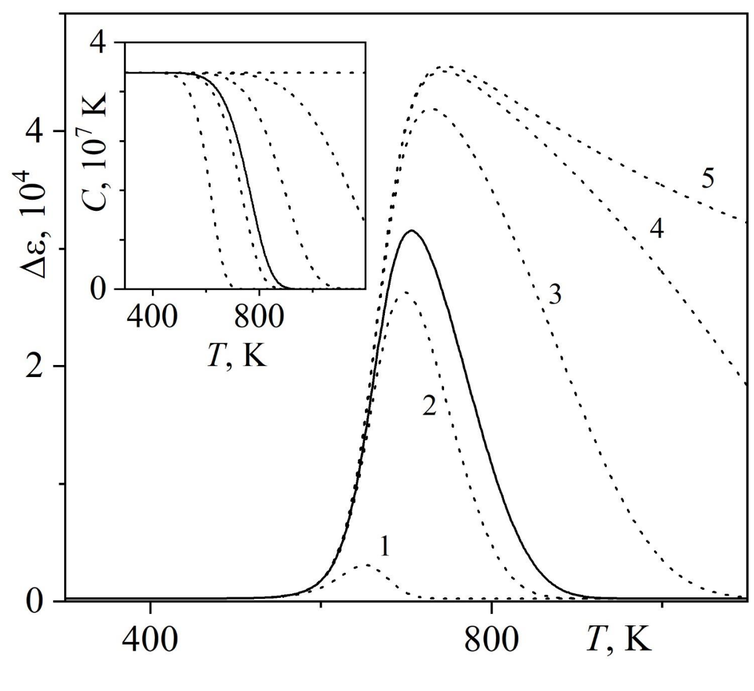

Fig. 2 The contribution from non-stable polarization to dielectric anomaly Δε(*T*). The dashed curves are calculated by using the following heating rates γ = 0.1 (1); 1 (2); 10 (3); 10^2 (4); 10^6 (5) K/min. The solid line is calculated for the experimental data in Fig. 3 (γ = 1.7 K/min, f=1 kHz). The inset shows the corresponding dependencies of Curie constant C(*T*).

Discussion

One can see, that the observed nearly symmetrical dielectric maximums differ significantly from the step-like ε(*T*) behavior, predicted by Cole-Cole model. Debye spectral function

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

depends on high-frequency dielectric constant ε_∞, relaxation time $\tau_R(T) = \tau_{R0}exp(E/kT)$, and Curie constant C(*T*) which is proportional to the concentration of relaxing particles. Analysis of the experimental data shows that on heating dipole complexes are thermally disassociated and their concentration decreases:

$$C(T) = C_0 exp\left[-\frac{1}{\gamma}\int_{T_0}^{T}\frac{1}{\tau_D(T)}dT\right],$$

where γ is heating rate, $\tau_D(T)$=$\tau_{D0}exp(U/kT)$, U is the binding energy of dipole complexes. Therefore, it can be assumed that the concentration of relaxing particles decreases significantly during the experiment, which leads to a strong temperature dependence *C*(*T*). 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 ε(*T*) anomaly as compared with Debye-like behavior. Fig. 3 shows the ε(*T*) anomaly calculated for different γ values. One can see how significantly variations of γ can change the ε(*T*) behavior. In the limit high heating rate the behavior of ε(*T*) approaches a classic behavior of Debye relaxator (Fig. 3) At infinitely low heating rate non-equilibrium polarization has enough time to decay totally before the permittivity peak can be detected. As a result, on lowering γ permittivity peak decreases in amplitude and finally disappears (Fig. 3). On heating C(*T*) shows step-like decrease manifesting decay of non-equilibrium polarization. For high rates γ, Curie constant possesses maximal possible value and practically temperature independent in whole studied interval. For low values of γ Curie constant on heating decreases to zero before the dielectric relaxation can be detected. Temperature and frequency dependencies of ε were described on the basis of Cole-Cole formulae and kinetic equation determining thermal decay of the non-equilibrium polarization. It is supposed that the observed dielectric relaxation is determined by space charge polarization mechanism, driven by oxygen vacancies and electrons localized on titanium ions. Assuming that intense ε(*T*) peak (Fig. 1-2) is determined by space charge polarization effects, for NBT ceramics one can consider the same typical defects such as oxygen vacancies , electrons localized on titanium and probably associated complexes based on them. The mobile charge defects can accumulate near the following inhomogeneities in NBT ceramics: i) intergrain boundaries; ii) ferroelectric or ferroelastic domains boundaries; iii) near-electrode regions. More information on the nature of the inhomogeneities which can cause space charge polarization in NBT can be obtained from comparison the experimental data measured for ceramic and single crystalline NBT. Now this work is in progress.

References

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2. *Sidak V.M., Trubitsyn M.P.* Dielectric relaxation and the dipole defects in $Na_{0.5}Bi_{0.5}TiO_3$ single crystal *// Appl Nanosci.* – 2022. – Vol. 12. – P. 775– 780.
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