Anomalous dielectric relaxation in $Na_{0.5}Bi_{0.5}TiO_3$

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Introduction

Structural defects strongly influence physical properties and efficiency of solid state materials applied in functional electronics. For active dielectrics this fact is of special importance, since lattice imperfections increase electronic and ionic conductance at working temperatures and therefore result in material degradation and worsening of the electrophysical properties. Among other substances of perovskite family, sodium bismuth titanate $Na_{0.5}Bi_{0.5}TiO_3$ (NBT) is most promising compound for piezoelectric devices and electro- mechanical transducers. NBT belongs to the family of ferroelectric relaxors which specific properties are determined by the presence of nanometer scaled polar regions. Recently it was found that electrical properties of NBT single crystal were dependent on atmosphere and temperature of thermal treating [1, 2]. The results obtained in [1, 2] show presence of associated defects, which include oxygen vacancies and demonstrate electrical activity. In particular, slow relaxing dipolar complexes give rise to high dielectric anomaly around 670 K, whereas mobile defects increase samples capacitance and conductivity at high temperatures.

Methods

$Na_{0.5}Bi_{0.5}TiO_3$ single crystals were grown from the melt by the Czochralski method. In order to control the concentration of oxygen vacancies V_O the NBT samples were heat treated in atmospheres with different oxygen partial pressure. The samples prepared from as-grown crystal were annealed in air at 1070 K for 1 hour, then under vacuum at 1070 K for 2 hours. After each heat treatment step permittivity, conductivity and transmittance spectra were measured. Platinum electrodes were deposited by magnetron sputtering in an argon atmosphere. Dielectric permittivity ε was measured at 1 kHz in the temperature range 300-800 and in frequency diapason 0.5–100 kHz by using of AC current bridge P5083.

In order to elucidate the processes that affect the temperature behavior of the relaxation maximum Δε (T), we studied kinetics of thermal decay of the dielectric constant at the temperature of the ε maximum. The samples were heated to a temperature corresponding to the maximum, and the dielectric constant of the sample was measured every 20 s using an automatic program unit.

Results

As previously reported [1-3], temperature dependence of ε for the as-grown NBT sample showed existence of low-frequency relaxation maximum near 670K and nonlinear ε growth at T>750K. Low frequency anomaly of ε disappeared after heat treatment in air and could be partially recovered by heat treatment in vacuum. Fig. 1 shows the temperature dependences ε(T), measured in the heating mode of the NBT samples annealed in air and subsequently annealed in vacuum. It is seen that ε significantly depends on the frequency f in the whole investigated temperature range and especially around 670 K. To analyze the slow dielectric relaxation, we subtracted from ε(T) dependences the curve measured at high-frequency (100 kHz). The latter is determined only by the anomalous behavior connected with structural phase transformations and does not contain dipole defects dielectric response. Fig.1 shows the relaxation anomaly of ε obtained from the experimental data by subtraction of the other contributions.
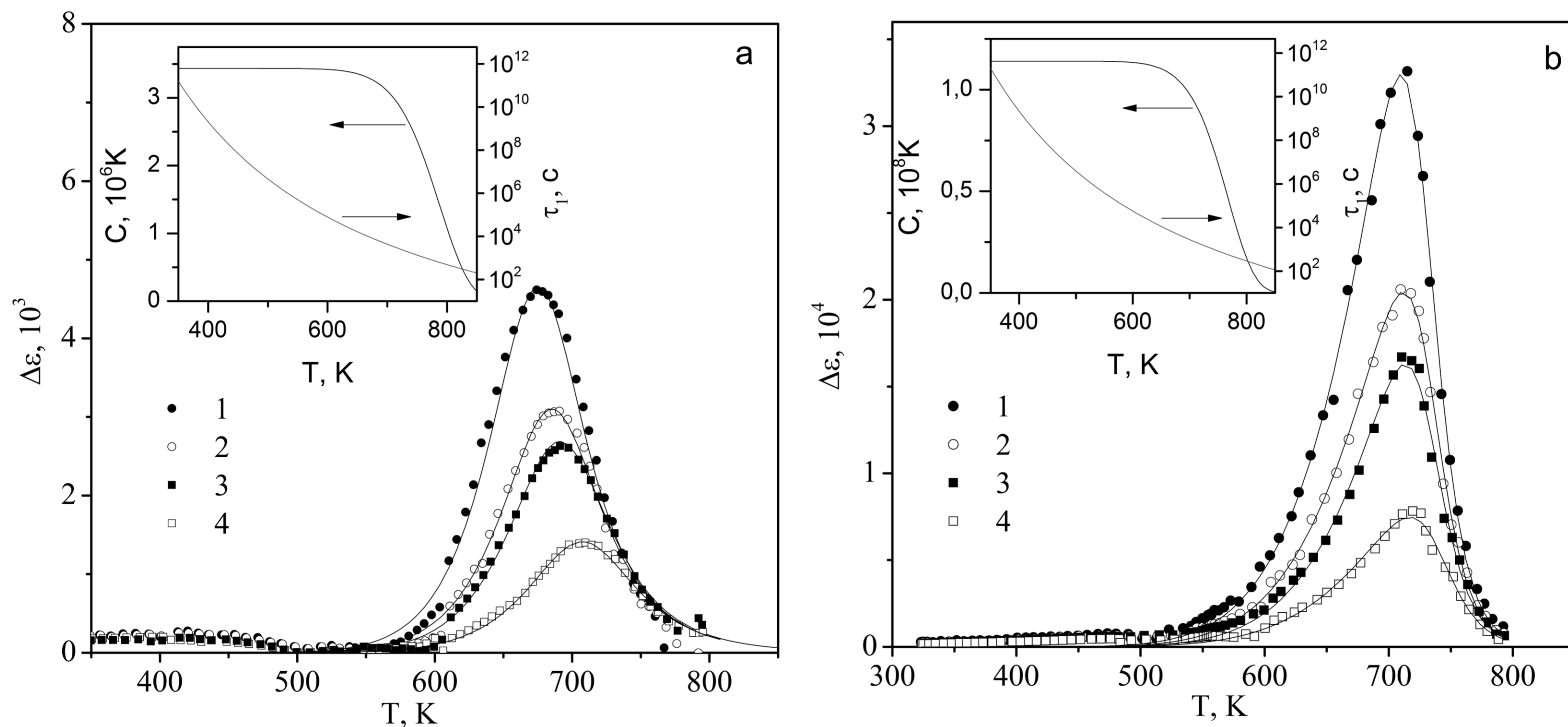

Fig. 1 Dependencies of permittivity Δε(T) for NBT crystal: as-grown sample (a); the sample annealed in air (1070 K) and subsequently annealed in vacuum (1070 K) (b). Field frequencies: $1 - 0.5$ kHz, $2 - 0.8$ kHz, $3 - 1$ kHz, $4 - 2$ kHz, $5 - 5$ kHz, $6 - 10$ kHz The solid lines are calculated. In the inset: the temperature dependences of relaxation time $\tau_1(T)$ and Curie constant C(T).

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

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

depends on high-frequency dielectric constant ε_∞, relaxation time $\tau(T) = \tau_0 exp(E/kT)$, 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:

$$C(T) = C_0 exp\left[-\frac{1}{\gamma}\int_{T_0}^{T}\frac{1}{\tau_1(T)}dT\right],$$

where γ is heating rate, $\tau_1(T) = \tau_0 exp(U/kT)$, 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.

Conclusion

To explain the experimental data, the thermal decay of the dipole centers contributing to permittivity, was considered. The specific dispersion of ε was observed if the characteristic time of the dipole defects decay became comparable with the time of temperature cycling in the experiment. Analysis of the data obtained for un-treated and heat-treated samples [2] made it possible to propose that the dipole defects responsible for permittivity relaxation were formed by Ti ions captured an electron and located nearby oxygen vacancy V_O.

References

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Acknowledgments