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IMPEDANCE SPECTRA OF SINGLE CRYSTALLINE 0.87Na_{0.5}Bi_{0.5}TiO₃ - 0.13BaTiO₃ SOLID SOLUTIONS

The spectra of complex impedance $Z^*(\omega)$ were studied in single crystalline 0.87Na_{0.5}Bi_{0.5}TiO₃-0.13BaTiO₃ solid solutions. The experimental data measured in the frequency range 5-5·10⁵ Hz and in the temperature interval 770-870 K, were described within the equivalent circuit approach. The results obtained for 0.87Na_{0.5}Bi_{0.5}TiO₃-0.13BaTiO₃ solid solutions are compared with the impedance spectra of Na_{0.5}Bi_{0.5}TiO₃ single crystals. It is shown that electrical conductivity σ of 0.87Na_{0.5}Bi_{0.5}TiO₃-0.13BaTiO₃ decreases by more than an order of magnitude in comparison with sodium bismuth titanate. It is assumed that σ decreases due to lower mobility of oxygen vacancies.

Keywords: sodium-bismuth titanate, oxygen vacancies, impedance spectroscopy.

1. Introduction

Sodium-bismuth titanate Na_{0.5}Bi_{0.5}TiO₃ (NBT) and solid solutions based on it attract close attention owing to high values of dielectric permittivity, piezo- and pyroelectric coefficients, parameters of electromechanical coupling [1]. However, in spite of numerous studies, the influence of intrinsic structural defects on electrophysical properties in real NBT crystals remains unclear up to now. Recently, it was shown [2-5] that for as-grown NBT crystals the typical intrinsic imperfections were associated dipolar complexes and mobile charged defects based on oxygen vacancies V_O. Heat treatment at different temperatures and in various atmospheres (air, inert gas, vacuum) made it possible to regulate the content of such defects and control the valuable properties of NBT crystals. It is known that the highest permittivity and piezomodules are observed in Na_{0.5}Bi_{0.5}TiO₃-BaTiO₃ solid solutions [1]. In this paper we study the complex impedance spectra $Z^*(\omega)$ in crystalline solid solutions 0.87Na_{0.5}Bi_{0.5}TiO₃-0.13BaTiO₃ (0.87NBT-0.13BT) and compare the obtained results with the data for NBT single crystals. The composition 0.87NBT-0.13BT was chosen near but not exactly at the morphotropic phase boundary (x=0.65, [6]) in order to obtain high enough piezoelectric parameters and relatively low electrical conductivity.

2. Experimental part

0.87NBT-0.13BT single crystals were grown from the melts by the Czochralski method. Samples for impedance spectra studying were prepared as the plates with 5×5×0.5 mm dimensions and with principal surfaces parallel to (111) plane. According to the data given in [2], the annealing of NBT crystals in air at 870 K leads to dissociation of the dipole complexes, while the content of the mobile defects remains practically unchanged. In order to reveal the mobile defects contribution to charge transfer, slow relaxation of the dipole centers was eliminated by the samples annealing at temperature $T_{an}=870$ K for 1 hour. After heat treatment, platinum electrodes were deposited to the main samples planes by magnetron sputtering in Ar atmosphere. The impedance spectra were studied with the help of Tesla BM-507 impedance meter in the frequency range 5 – 5·10⁵ Hz and in the interval 600 – 900 K.

3. Results and discussion

Fig. 1 shows the impedance spectra $Z^*(\omega)$ for 0.87NBT-0.13BT plotted as the diagrams in the complex ($Z'-Z''$) plane. It can be seen that the obtained hodographs consist of a single semicircle arc, which diameter decreases significantly on heating. Such hodographs can be described by the impedance of a single parallel RC-chain with lumped elements

$$Z^*(\omega) = Z(\omega=0) \cdot [1 + i\omega\tau]^{-1} \quad (1)$$

where ω is a cyclic frequency of the field under measuring, $\tau=RC$ is the impedance relaxation time associated with the inverse rate of charge transfer. The centers of the arcs of the experimental hodographs are slightly shifted down from Z' axis. Such shift can be described by replacing the usual capacity in a parallel RC-chain with a frequency-dependent generalized capacitance $C^*=A \cdot (i\omega)^{n-1}$. The parameter $0 \leq n \leq 1$ in the exponent determines the ratio between the active and reactive components of the element C^* and takes into account the distribution of relaxation times of charge carriers within the sample bulk. The hodographs calculated with the help of expression (1) are shown in Fig. 1 by solid lines.

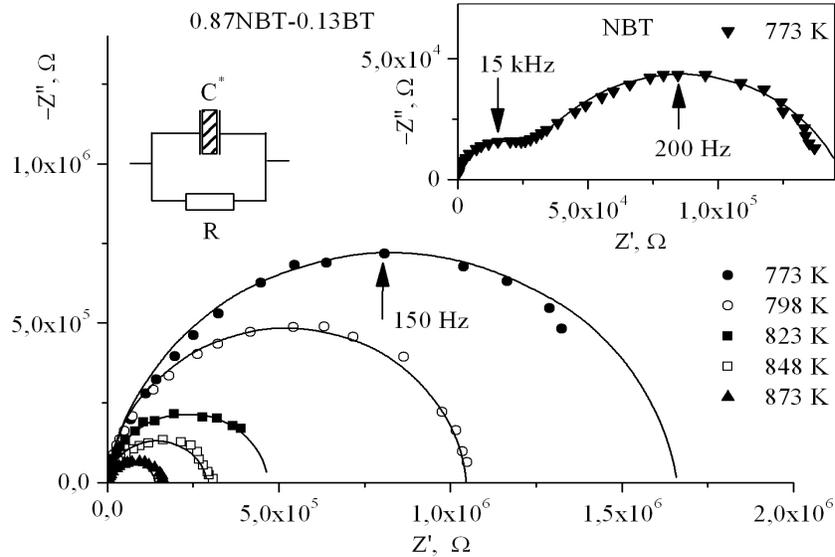


Fig. 1 ($Z'-Z''$) hodographs of 0.87NBT-0.13BT. In the inset: the hodograph for NBT crystals [4, 5]. The samples of 0.87NBT-0.13BT and NBT were preliminary annealed in air at $T_{an}=870$ K.

For comparison, the inset to Fig. 1 shows the hodograph of NBT crystal, also annealed at T_{an} . One can see that, in contrast to the diagrams of 0.87NBT-0.13BT solid solutions, the NBT hodograph contains the arcs of two semicircles. As shown in [4,5], the high frequency (hf) arc in the NBT hodograph can be associated with charge transfer in the bulk of the sample, where the concentration of V_O corresponds to the as-grown untreated crystal. The low-frequency (lf) arc in the NBT hodograph (the inset to Fig. 1), according to [4,5], is determined by charge transfer in the near-surface layers where the V_O content was significantly decreased after annealing. Comparison of the data in Fig. 1 shows that the frequency range of the single arc in the 0.87NBT-0.13BT hodographs corresponds to the lf arc in the NBT hodograph. At the same time, the diameter of the arc for 0.87NBT-0.13BT is essentially greater, that indicates lowering the electrical

conductivity of the solid solution by more than an order of magnitude in comparison with pure NBT. The hf arc, reliably detected for NBT, is not observed in the 0.87NBT-0.13BT diagrams at all (Fig. 1). From the intersections of the arcs of the experimental hodographs with the abscissa axis Z' , one can determine the electrical conductivity in DC field $\sigma(\omega=0)$. The temperature dependences of $\sigma(\omega=0)$, determined for the observed arcs (Fig. 1), are presented in the Arrhenius scale in Fig. 2. It can be seen that for NBT crystals the conductivity $\sigma(0)$ corresponding to the lf arc is noticeably lower than $\sigma(0)$ for the hf arc. At that, both dependencies in the scale used have close slopes ($E=1.0$ eV). According to [4, 5], this difference in conductivities corresponding to lf and hf arcs is due to the formation of a near-surface layer with decreased V_O content after annealing. For 0.87NBT-0.13BT, the DC conductivity $\sigma(0)$ is more than an order of magnitude lower than $\sigma(0)$ for the lf arc in the hodographs of NBT. In addition, the activation energy for charge transfer in solid solutions is almost two times higher than for NBT crystals.

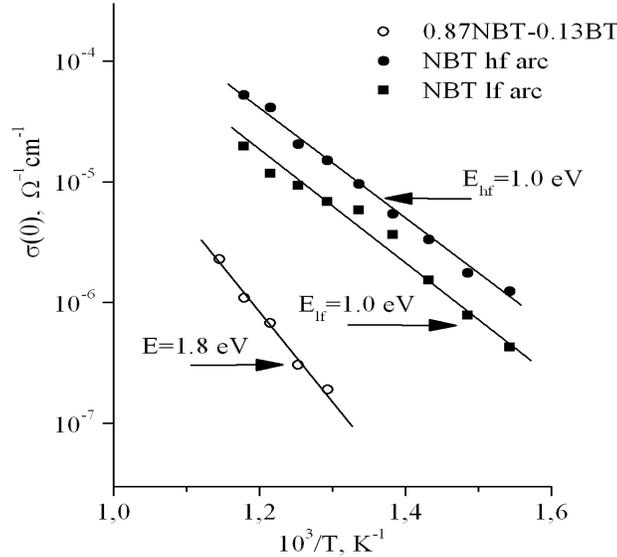


Fig. 2 Conductivity in DC field $\sigma(\omega=0)$ vs $1/T$ for 0.87NBT-0.13BT and NBT single crystals.

Electrical conductivity contributed by a certain type of carriers can be expressed as

$$\sigma = nq\mu \quad (2)$$

where n , q , and μ are the concentration, charge, and mobility of the carriers, respectively.

It is known that at high enough temperatures mobile oxygen vacancies V_O determine conduction in complex oxide dielectrics. Charge transfer in NBT crystals is associated with the presence of V_O formed as a result of Bi_2O_3 small losses during the single crystals growing. Lowering $\sigma(0)$ in 0.87NBT-0.13BT solid solution compared to NBT, can be the result of V_O concentration or mobility decrease. According to the data presented in [7], the concentration of V_O in as-grown NBT crystals is estimated as 0.25 – 0.5% that corresponds to the losses of Bi_2O_3 in the range 0.17 – 0.33%. V_O content in 0.87NBT-0.13BT solid solution can be expected of the same order as in NBT crystals with the same thermal pre-history. Hence, conductivity decrease in 0.87NBT-0.13BT should be attributed to lowering the mobility of the charge carriers. As shown in [2, 3], to reduce the V_O concentration it is necessary to perform annealing in air at much higher temperature (1070 K) than $T_{an}=870$ K, used for the samples treating in this paper. Then the difference in the activation energies of $\sigma(0)$ (Fig. 2) can be connected with the V_O

mobility that is the result of differing reliefs of the 0.87NBT-0.13BT and NBT lattice potentials experienced by carriers. The presence of single arc in the 0.87NBT-0.13BT hodographs (Fig. 1) indicates that the impedance of the sample is almost completely determined by the near-surface layer depleted of V_O after heat treatment. The relative contribution from the sample volume, where the V_O content corresponds to the untreated crystal, becomes small and cannot be distinguished in the experiment.

The stability of the perovskite family crystals with ABO_3 structure can be estimated by using the tolerance factor, which is introduced as follows [8, 9]

$$\tau = \frac{R_A + R_O}{\sqrt{2}(R_B + R_O)}. \quad (3)$$

Here R_A and R_B are the radii of cations in A and B positions, respectively, R_O is the radius of an oxygen ion. For the most stable structures, the factor τ varies from 0.75 to 1.00. As shown in [8, 9], the maximal mobility of V_O corresponds to $\tau=0.96$, and for higher values of the tolerance factor, mobility μ decreases rapidly. The evaluation of the factor τ for NBT crystals gives the value 0.982, whereas for 0.87NBT-0.13BT solid solution the value of τ is 0.993. Thus, the density of the lattice packing and degree of the structural stability lead to reduced V_O mobility and decrease electrical conductivity of NBT-BT solid solutions.

3. Conclusions

The study of complex impedance spectra showed that electrical conductivity of 0.87NBT-0.13BT solid solutions is more than an order of magnitude lower than σ of pure NBT crystals. It is assumed that the decrease of electrical conductivity in 0.87NBT-0.13BT is due to lower mobility of oxygen vacancies.

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Received 15.10.2017