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IMPEDANCE RELAXATION IN $Na_{0.5}Bi_{0.5}TiO_3$ CERAMICS

Spectra of complex impedance $Z^*(\omega)$ are investigated in sodium bismuth titanate $Na_{0.5}Bi_{0.5}TiO_3$ ceramics, which is considered as promising ecologically friendly material for piezoelectric devices and electro- mechanical transducers. Measurements are performed in frequency range 5 Hz-1.3 10^7 Hz of AC field, temperature was varied in the interval 773-1123 K. Experimental spectra are presented as diagrams in (Z'-Z'') complex plane and discussed within equivalent circuit approach. It is shown that for studied temperatures experimental hodographs contain two arcs and can be described by impedance of two serially connected parallel RC circuits. Down shift of the arcs centers from Z' axis is attributed to relaxation times τ distribution and described by replacing of usual capacities by generalized ones. The high frequency arc corresponds to charge transfer within $Na_{0.5}Bi_{0.5}TiO_3$ grains, which are considered as isolated and surrounded by continuous intergrain medium. The low frequency arc reflects conduction within intergrain regions. It is supposed that arcs of the experimental hodographs are contributed by both ionic and electronic hopping transport. Ionic motion can be realized through mobility of Na^+ cations and O^{2-} vacancies. Electrons can hop via traps such as F^+ centers.

Keywords: sodium bismuth titanate, impedance spectroscopy.

Спектри комплексного імпедансу $Z^*(\omega)$ вивчені для кераміки натрій-вісмутового титанату $Na_{0.5}Bi_{0.5}TiO_3$, який є перспективним матеріалом для п'єзоелектричних пристроїв й електромеханічних перетворювачів. Виміри виконані в частотному діапазоні 5 Гц - 1.3·10^7 Гц, температура змінювалася в інтервалі 773-1123 К. Експериментальні спектри представлені у вигляді діаграм в комплексній площині (Z'-Z'') і обговорюються на основі методу еквівалентних схем. Показано, що для вивчених температур експериментальні годографи містять дві дуги і можуть бути описані імпедансом двох послідовно з'єднаних паралельних RC ланцюжків. Зміщення центрів дуг вниз від осі Z' приписано розподілу часів релаксації τ і описано заміною звичайних ємностей узагальненими. Високочастотна дуга на годографах відповідає переносу заряду в зернах $Na_{0.5}Bi_{0.5}TiO$, які передбачаються ізольованими і оточеними безперервним міжзеренним простором. Низькочастотна дуга відображує провідність в міжзеренних областях. Обґрунтовується, що дуги на експериментальних годографах містять вклади іонної і електронної стрибкової провідності. Іонний рух може здійснюватися за рахунок мобільних катіонів Na^+ і вакансій O^{2-}. Електрони можуть здійснювати стрибки по пастках, таких як F^+ центри.

Ключові слова: натрій-вісмутовий титанат, імпедансна спектроскопія.

Спектры комплексного импеданса $Z^*(\omega)$ изучены для керамики натрий-висмутового титаната $Na_{0.5}Bi_{0.5}TiO_3$, который является перспективным материалом для пьезоэлектрических устройств и электромеханических преобразователей. Измерения выполнены в частотном диапазоне 5 Гц - 1.3·10^7 Гц, температура изменялась в интервале 773-1123 К. Экспериментальные спектры представлены в виде диаграмм на комплексной плоскости (Z'-Z'') и обсуждаются на основании метода эквивалентных схем. Показано, что для изученных температур экспериментальные годографы содержат две дуги и могут быть описаны импедансом двух последовательно соединенных параллельных RC цепочек. Смещение центров дуг вниз от оси Z' приписано распределению времен релаксации τ и описано заменой обычных емкостей обобщенными. Высокочастотная дуга на годографах соответствует переносу заряда в зернах $Na_{0.5}Bi_{0.5}TiO_3$, которые предполагаются изолированными и окруженными непрерывным межзёренным пространством. Низкочастотная дуга отражает проводимость в межзёреных областях. Обосновывается, что дуги на экспериментальных годографах содержат вклады ионной и электронной прыжковой проводимости. Движение ионов может осуществляться посредством мобильных катионов Na^+ и вакансий O^{2-}. Электроны могут совершать прыжки по ловушкам, таким как F^+ центры.

Ключевые слова: натрий-висмутовый титанат, импедансная спектроскопия.

1. 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. 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.

2. Experimental results and discussion

It is known that valuable information on charge transfer processes can be obtained by impedance spectroscopy [3,4]. In this paper we study the spectra of complex impedance $Z^*(\omega)$ in NBT ceramics synthesized by usual technology. The samples were cut as $9\times9\times0.5$ mm^3 plates; Pt electrodes were fired on main faces at 923 K during 15 hours. The data were measured in AC field by HP4192LF impedance meter operating in a frequency range 5 Hz-1.3 10^7 Hz. The measurements were carried out in the interval 773-1123 K in order to reveal charge transfer phenomena, which were hardly detectable at lower temperatures. Experiment was performed on cooling run in dry nitrogen atmosphere, the thermostatic regime was used. For each measuring cycle temperature of the sample was stabilized during 40 min.

The impedance spectra $Z^*(\omega)$ are presented as diagrams in (Z''-Z') complex plane in Fig.1. Preliminary visual examination shows that for all temperatures the experimental hodographs represent semicircle. Such spectra are usually simulated on the basis of equivalent circuit approach by complex impedance of parallel *RC* circuit [3, 4]

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

where ω – cyclic frequency of measuring field, $\tau = RC$ – relaxation time connected with rate of charge transfer. More detailed examination demonstrates that experimental data on Fig.1 can not be described by impedance of simple parallel RC circuit. Two evident discrepancies with this simple model can be distinguished. First, the center of arc is shifted down from Z' axis. Second, the experimental points sufficiently deviate from ideal semicircle in the low- frequency part.

The first contradiction is usual feature for inhomogeneous media. As a rule, down shift of the arc center is explained as consequence of the relaxation time $\tau=RC$ distribution in the samples volume. Within equivalent circuit approach such behavior is simulated by parallel connection of ordinary resistor R with frequency dependent generalized capacitance $C^*=A\cdot(i\omega)^{n-1}$ $(0 \le n \le 1)$ [4].

The second mismatch of the experimental hodographs with ideal semicircle is visible in low- frequency part of the spectra (Fig.1). Such deviation can be understood by taking into account that NBT ceramics represents two-phase system and consists of NBT crystallites and interfacial space. It is natural to assume, that grains of NBT phase are isolated one from another and surrounded by intergrains, which create continuous medium. For such system impedance spectrum can be simulated by equivalent circuit consisting of two serially connected parallel $R_gC_g^*$ (grains) and $R_{ig}C_{ig}^*$ (intergrains) circuits [4]. The complex impedance of such circuit is given by expression

$$Z^*(\omega)=\left[\left(R_g^{-1}+i\omega C_g^*\right)^{-1}+\left(R_{ig}^{-1}+i\omega C_{ig}^*\right)^{-1}\right]. \quad (2)$$

The hodographs, computed with the help of relation (2), are drawn in Fig.1 by the solid lines.

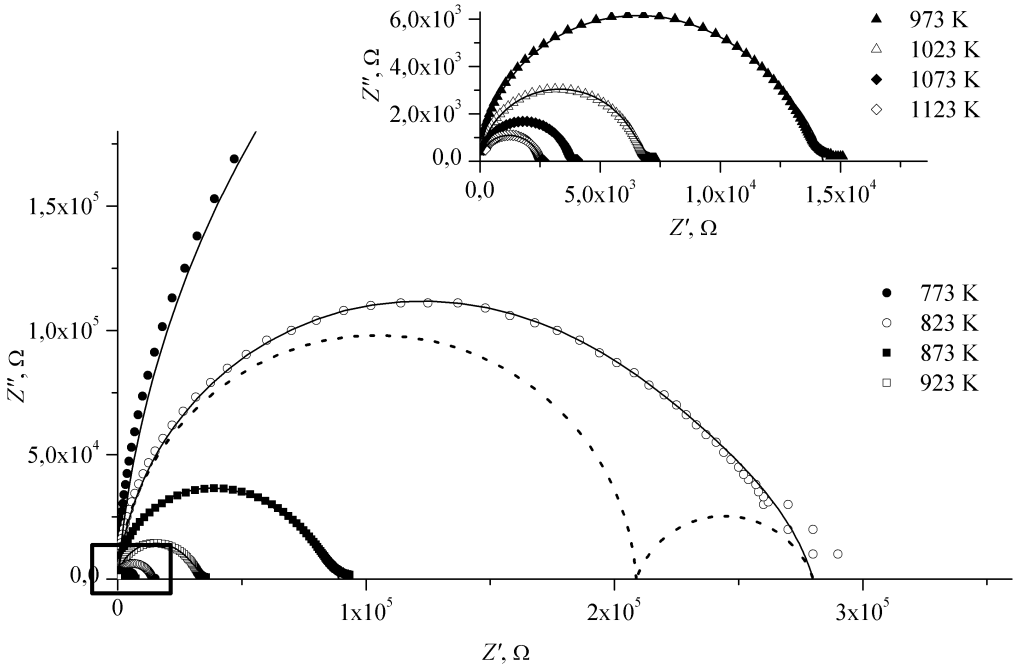

Fig.1. Impedance spectra of NBT ceramics at various temperatures. Symbols represent experimental data, solid lines are calculated by using impedance of two serially connected parallel $R_gC_g^*$ and $R_{ig}C_{ig}^*$ circuits. Dashed lines represent hodographs for separated $R_gC_g^*$, $R_{ig}C_{ig}^*$ circuits at 823 K. Fragment with the spectra measured at $T\geq973$ K are enlarged in the insert above.

Crossing points of arcs with abscissa axis in Fig.1 makes it possible to determine impedance $Z'(\omega=0)$, and, consequently, conduction $G'(\omega=0)=[Z'(\omega=0)]^{-1}$ in DC field [4]. These data, obtained for grains $G_g(0)$ and intergrains $G_{ig}(0)$, are plotted in Fig.2 in Arrhenius scale. One can see that conduction $G_{ig}(0)$ for intregrains exceeds $G_g(0)$ values of crystallites and is characterized by more high activation energy. Also in the insert to Fig.2 the exponents n of generalized capacity C^* are compared for grains (n_g) and intergrains (n_{ig}). Lower values of n_{ig} with respect to n_g demonstrate more sufficient dispersion of relaxation times $\tau=[A\cdot Z'(\omega=0)]^{1/n}$ within intergrain space relative to volume of crystallites. More high conduction and values of exponent n (Fig.2) testify an increased content of charge carriers and structural disorder within intergrain regions.

3. Conclusions

The available data [1, 2, 5] makes it possible to suppose that conductance in NBT crystal combines ionic and electronic components. Ionic motion can be contributed by relatively light Na^+ cations and typical for complex oxides mobile oxygen O^{2-} vacancies.

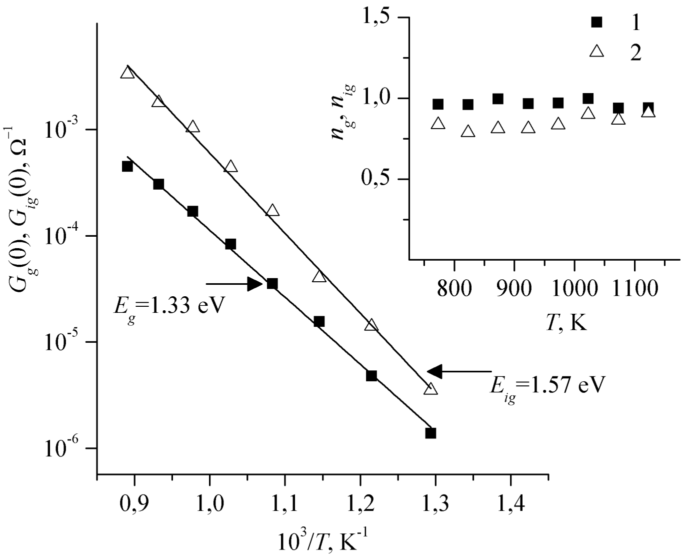

Fig. 2. Dependences of conduction in DC field vs 1/*T*, obtained from hodographs (Fig.1): 1 - grains, 2 – intergrains. The values of the exponent *n* in generalized capacity *C are in the insert.**

For both types of ionic carriers Pt-electrodes are blocking or partially permeable at high enough temperatures [4]. Therefore, nearly horizontal lines in low frequency region visible for hodographs at $T \geq 873$ K (Fig.1), can be connected with near electrode ionic transport. On the other hand, electronic conductance in NBT is expected too via hopping motion through the defects like F^+ centers. At that combination of ionic hopping with electronic one can be simulated by parallel connection of two parallel RC circuits. It is easy to show, that parallel connection of a few parallel RC circuits is equivalent to a single parallel RC circuit with parameters averaged over the existing conductance mechanisms. Thus, one can suppose, that the superimposed arcs in the experimental hodographs (Fig.1) include both ionic and electronic contributions to the total conductance of NBT ceramics.

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