Вісник ХНУ, серія «Фізика», вип. 27, 2017. с. 44-48

PACS: 77.22.Ch, 77.84.-s
UDC: 537.226.1, 537.311.32

Electrical properties of $0.87Na_{0,5}Bi_{0,5}TiO_3$-$0.13BaTiO_3$ single crystals

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Electrical properties of as- grown and heat treated in air $0.87Na_{0,5}Bi_{0,5}TiO_3$-$0.13BaTiO_3$ single crystals were studied in AC field in the range 0.5–100 kHz from 300 to 800 K. It was shown that permittivity and conductivity strongly depend on heat treatment. Annealing at 1070 K removes slow relaxation of permittivity and decreases conductivity. It is supposed that dielectric dispersion is determined by the dipole defects formed by oxygen vacancies. The effect of $BaTiO_3$ additive on electrical properties of $Na_{0,5}Bi_{0,5}TiO_3$ crystal is discussed.

Keywords: $Na_{0.5}Bi_{0.5}TiO_3$ - $BaTiO_3$ crystal; dielectric relaxation; conductivity; oxygen vacancy.

Електричні властивості вихідних і термооброблених в повітрі монокристалів $0.87Na_{0,5}Bi_{0,5}TiO_3$-$0.13BaTiO_3$ вивчено в змінному полі в діапазоні 0.5-100 кГц від 300 до 800 К. Показано, що діелектрична проникність і електропровідність сильно залежать від термічної обробки. Відпал при 1070 К усуває повільну релаксацію діелектричної проникності і зменшує провідність. Передбачається, що діелектрична дисперсія визначається дипольними дефектами, що утворюються кисневими вакансіями. Обговорюється вплив добавки $BaTiO_3$ на електричні властивості кристала $Na_{0.5}Bi_{0.5}TiO_3$.

Ключові слова: кристали $Na_{0.5}Bi_{0.5}TiO_3$ - $BaTiO_3$; діелектрична релаксація; електропровідність; кисневі вакансії.

Электрические свойства исходных и термообработанных в воздухе монокристаллов $0.87Na_{0,5}Bi_{0,5}TiO_3$-$0.13BaTiO_3$ изучены в переменном поле в диапазоне 0,5-100 кГц от 300 до 800 К. Показано, что диэлектрическая проницаемость и электропроводность сильно зависят от термической обработки. Отжиг при 1070 К устраняет медленную релаксацию диэлектрической проницаемости и уменьшает проводимость. Предполагается, что диэлектрическая дисперсия определяется дипольными дефектами, образованными кислородными вакансиями. Обсуждается влияние добавки $BaTiO_3$ на электрические свойства кристалла $Na_{0.5}Bi_{0.5}TiO_3$.

Ключевые слова: кристаллы $Na_{0.5}Bi_{0.5}TiO_3$ - $BaTiO_3$; диэлектрическая релаксация; электропроводность; кислородные вакансии.

Introduction

Lead free ferroelectrics attract attention of researchers as the functional materials for piezoelectric and pyroelectric sensors. One of the most perspective is sodium bismuth titanate $Na_{0,5}Bi_{0,5}TiO_3$ (NBT) with $A'_{1-y}A''_yBO_3$ -type perovskite structure. At room temperature NBT is strong ferroelectric but high coercive field and conductivity hamper the polarization switching and restrain the use of pure NBT. The different A-site substitutions in NBT structure make it possible to avoid this drawback. Among the NBT- based solid solutions the $Na_{0,5}Bi_{0,5}TiO_3$-$BaTiO_3$ (NBT-BT) with morphotropic phase boundary (MPB) possesses lower coercive field, better ferroelectric properties and high electromechanical coupling coefficient. MPB for (1-x)NBT-xBT solid solutions is observed in the range x = 0.05 – 0.07 where high piezoelectric coefficients were found [1]. At the same time the authors of [2] report the high piezoelectric activity of solid solutions with x=0.13-0.14 content of $BaTiO_3$. In spite of numerous investigations of NBT-BT system, electrical properties of these solid solutions were not studied systematically. This paper is devoted to studying the effect of Ba on electrical properties of NBT crystals.

Experimental procedure

The single crystals of $0.87Na_{0,5}Bi_{0,5}TiO_3$-$0.13BaTiO_3$ (0.87NBT-0.13BT) were grown by Czhochralski method. The content of $BaTiO_3$ addition x=0.13 is given for starting materials. The samples were prepared as the plates with (001) main planes. Platinum electrodes were deposited by magnetron method in an argon atmosphere. Electrical properties were measured for as- grown and annealed samples. Heat treatment of the samples was performed in air at 1070 K for 1h. After that the samples were cooled

https://doi.org/10.26565/2222-5617-2017-2-8

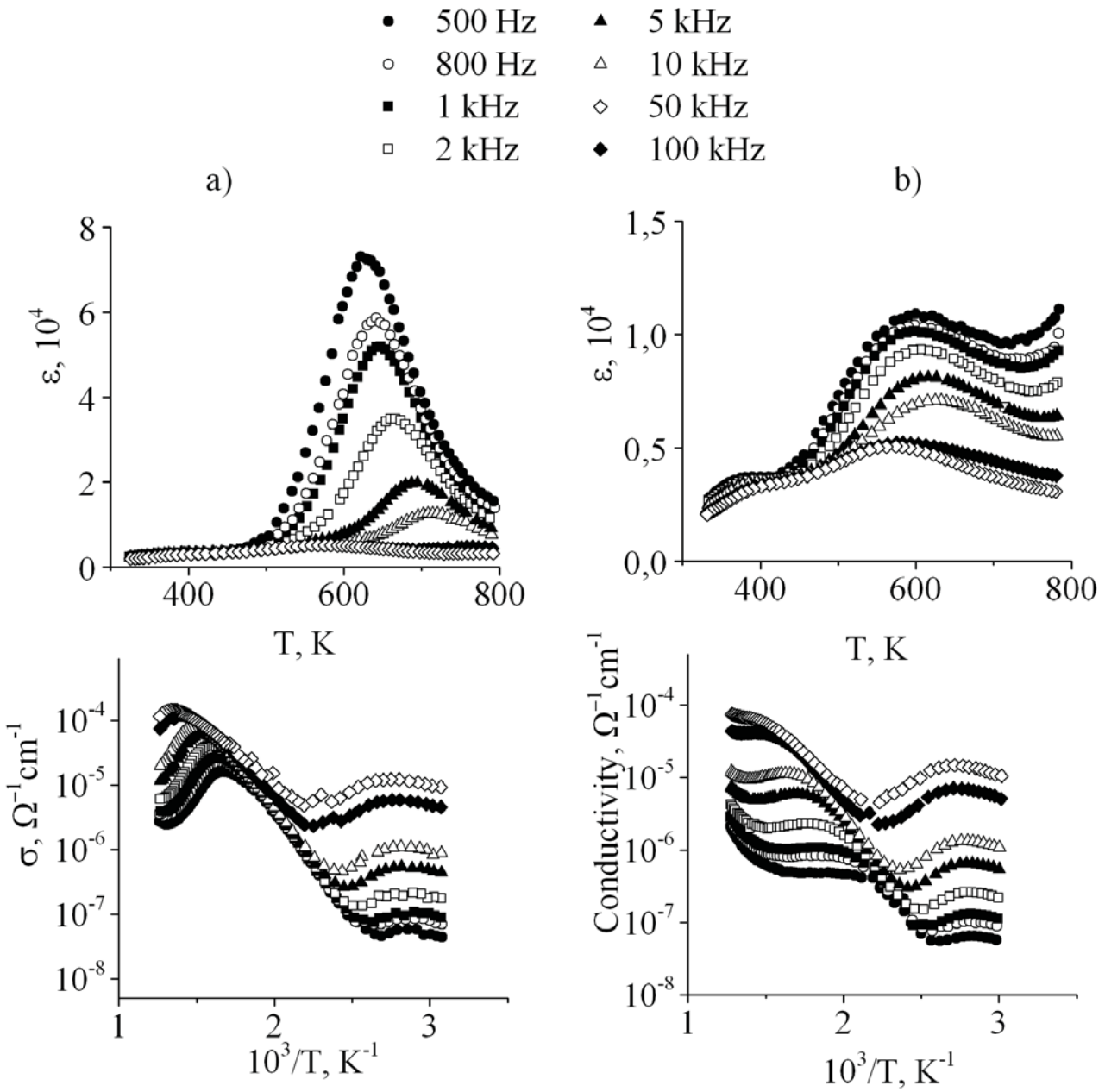

Fig.1 Dependences of permittivity ε(T) and conductivity σ(1/T) of as- grown NBT-0.13BT. a) – heating run, b) – subsequent cooling run

to room temperature. The permittivity and conductivity were measured by using AC bridge P 5083 in temperature interval 300 –800K and in frequency range 0.5–100 kHz.

Results and discussion

Fig.1a, b shows the temperature dependencies of dielectric permittivity ε and conductivity σ measured on heating and on cooling of as- grown 0.87NBT-0.13BT samples which were not heat treated previously. It can be seen that three anomalies of ε(T) behavior are observed, such as inflexion at T~420K, diffuse peak near T_m~580K (f>10 kHz) and frequency dependent maximum around 630K. Authors of [2] suggested that anomalies of ε near T~420K and 580K can be attributed to diffuse phase transitions. Permittivity dispersion is most prominent in the range of ε(T) maximum near ~630K. Dispersion is observed for low frequencies and becomes practically indistinguishable for f >10 kHz (Fig.1a). In the range 0.5–10 kHz maximum of ε shifts to high temperatures as frequency f increases.

The σ(1/T) curves plotted in Arrhenius scale (Fig. 1a) exhibit three regions with different character of temperature and frequency dependence. Weak dependence of σ on temperature and considerable frequency dispersion are observed at T<420 K. In the range 420 K–580 K σ is practically independent on f but exponentially increases on heating that indicates thermally activated charge transport. Around 630 K the σ(1/T) curves show frequency dependent peak which correspond to ε(T) relaxation maximum.

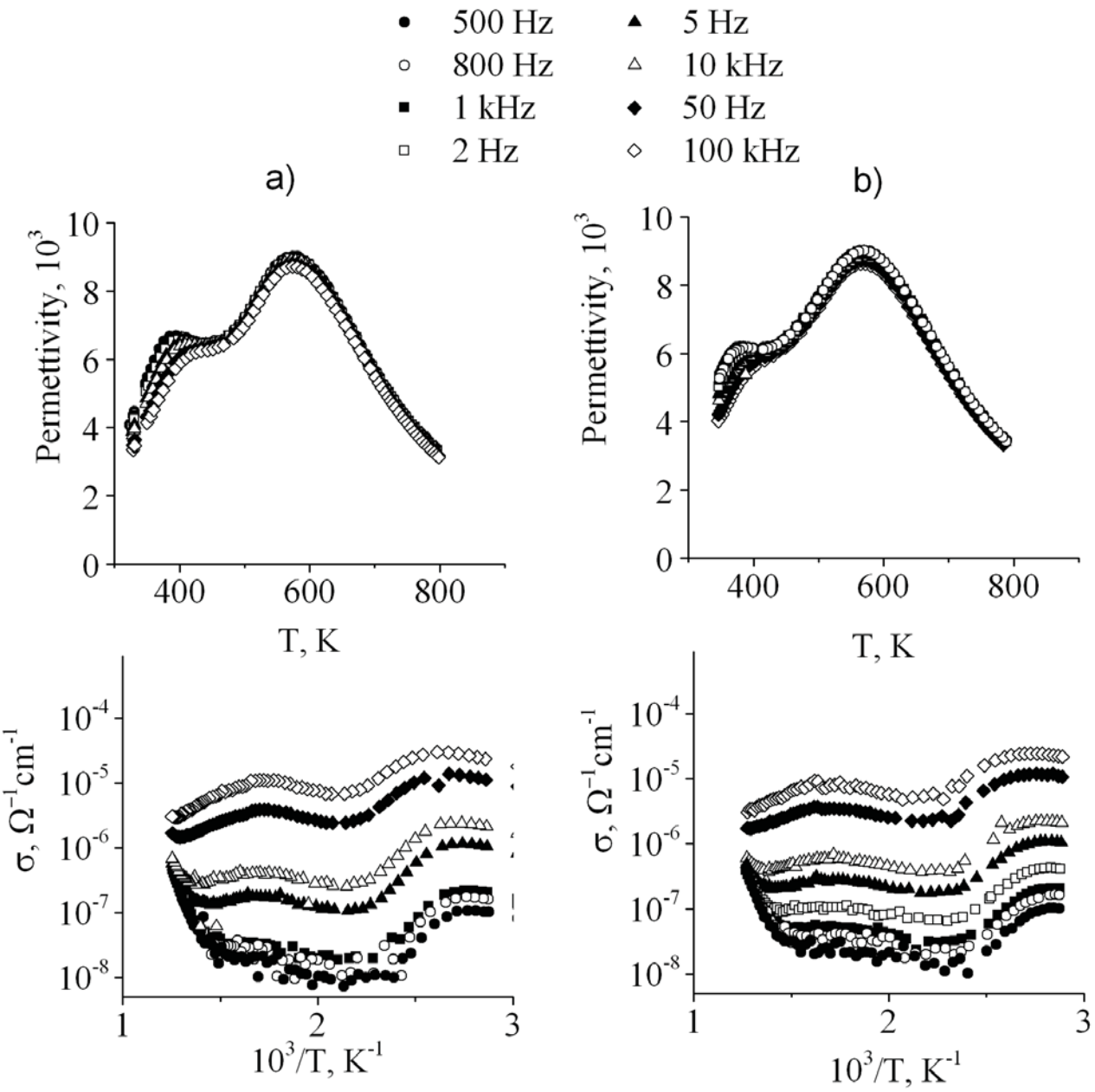

Fig.2 Dependences of permittivity ε(T) and conductivity σ(1/T) of annealed NBT-0.13BT (1070K, 1 h). a) – heating run, b) – subsequent cooling run.

The inflexion of the σ (1/T) curves corresponds to the anomalies of ε(T) discussed above.

Comparison of Fig.1a and b demonstrates that on cooling relaxation maximum of ε(T) decreases. In addition, conductivity exhibits considerable frequency dependence at T>580 K (Fig.1b). On cooling run frequency dependent peak of the σ(1/T) curves near 630 K practically disappears (Fig.1 b) The similar dielectric dispersion and temperature hysteresis were observed in NBT crystals and explained by response of slow relaxing polar defects created by oxygen vacancies [3]. One can assume that the same defects exist in as- grown 0.87NBT-0.13BT crystals. Apparently on heating up to 800K the number of such defects decreases and relaxation maximum of ε(T) at ~630 K reduces in amplitude.

Fig.2 a, b shows permittivity and conductivity temperature dependences of NBT-0.13BT samples annealed in air at 1070K for 1 h. One can see that after annealing the relaxation maximum of ε(T) near 630 K disappears. In comparison with as- grown samples σ reduces in one order at high temperatures and exponential growth of conductivity is not observed up to 800 K (Fig.1, 2). Besides permittivity and conductivity dependences measured on heating and cooling nearly coincide (Fig.2) in contrast to the data measured for as grown samples (Fig.1). Such effect of heat treatment observed earlier for NBT crystals [3, 4] shows thermal destroying the dipolar complexes contributing to slow dielectric relaxation around 630 K.

Fig.3a shows the temperature behavior of ε in annealed samples of 0.87NBT-0.13BT and NBT crystals. Curve of ε(T) of 0.87NBT-0.13BT exhibits the typical for NBT anomalies related to diffuse phase transitions [5]. It can be seen that introducing Ba^{2+} to NBT lattice increases permittivity, broadens maximum of ε, shifts ε(T) inflexion and diffuse peak to lower temperatures, decreases region in which the temperature hysteresis of electrical properties is observed.

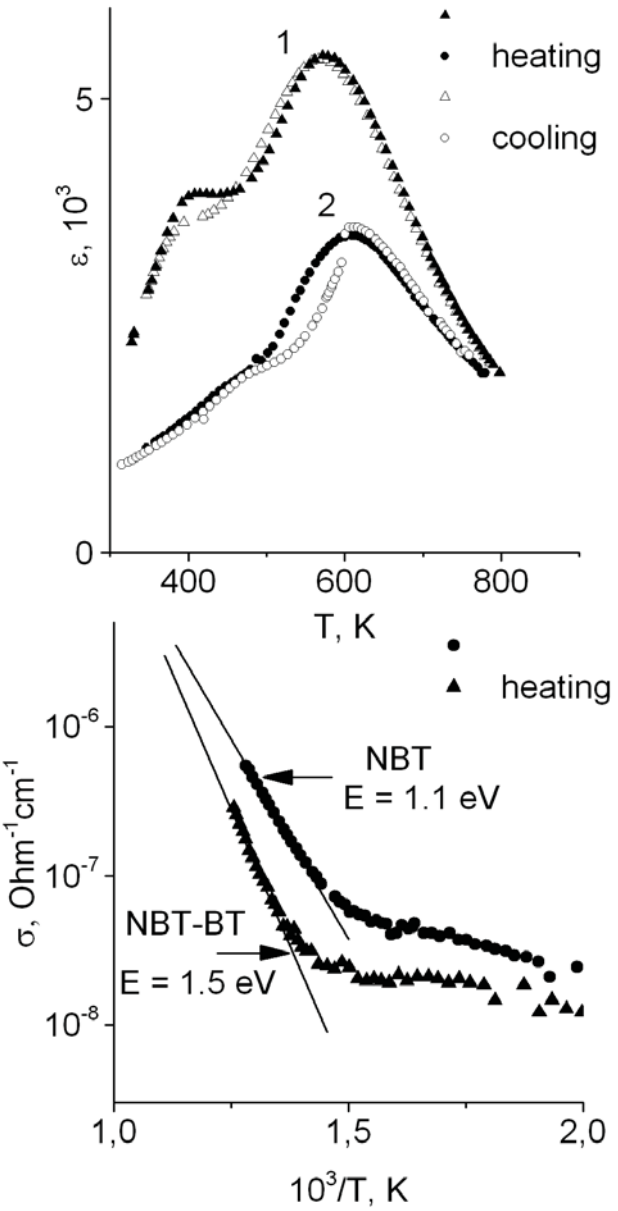

Fig. 3 Dependencies ε(T) (a) and σ(1/T) (b) of annealed NBT-0.13BT (1) and NBT (2) samples (1070K, 1 h). AC field, f=1 kHz.

It is known that distribution pattern and disordering of Na^+ and Bi^{3+} cations in the A-site and existence of oxygen vacancies affect the properties of NBT [1,3-5]. Structural and phase transformations in 0.87NBT-0.13BT are more complicated that in NBT due to disorder in the A-sites occupied by Na+, Bi3+ and Ba2+ with different valence, mass and ionic radius. The corresponding substitutions of cations in NBT lattice play a key role and significantly improve the ferroelectric properties [1,6]. The structural disordering in A-site of 0.87NBT-0.13BT structure may be the result of Bi, Na and Ba non-stoichiometry caused by oxide evaporation during ceramics synthesis and crystal growing. Excess charge, introduced by Bi, Na and Ba vacancies, is compensated by necessary amount of oxygen vacancies. Therefore, the role of oxygen vacancies is also important and strongly effect on the properties of NBT-BT system.

The relaxation maximums of ε(T) for as-grown crystals of 0.87NBT-0.13BT and NBT are observed near 630 K and 670K respectively. In [3,4] it was shown that such low-frequency dielectric dispersion in NBT was determined by intrinsic defects associated with dipole complexes formed by oxygen vacancies VO. Obviously that the similar dipole defects exist in 0.87NBT-0.13BT solid solutions and give rise to slow dielectric relaxation (Fig.1). The dipole defects disassociate after heat treatment and ε(T) relaxation peak disappears.

It should be noted that in as- grown 0.87NBT-0.13BT samples amplitude of ε(T) relaxation maximum (Fig.1a) in one order higher in comparison with ε(T) peak in as- grown NBT [3,4]. Such difference indicates higher concentration of dipole defects in 0.87NBT-0.13BT solid solutions. However high temperature growth of ε(T) typical for NBT [3,4] is not detected probably due to decreasing concentration of mobile charged defects. One can assume that association energy of the dipole centers in 0.87NBT-0.13BT is higher in comparison with NBT.

Fig.3b compares σ(1/T) behavior for annealed 0.87NBT-0.13BT and NBT samples in which slow dielectric relaxation is absent. One can see that conductivity in 0.87NBT-0.13BT is noticeably lower than in NBT. Besides charge carriers in 0.87NBT-0.13BT solid solutions overcome higher potential barriers (1.5 eV) in comparison with NBT (1.1eV). One can suppose that in the studied temperature interval oxygen vacancies V_O in 0.87NBT-0.13BT are less mobile than in NBT.

Conclusions

Low frequency dielectric relaxation was detected around 630K (f<10kHz) for as- grown NBT-0.13BT crystals. Permittivity maximum disappeared after heat treatment in air at 1070 K. It is proposed that ε peak is caused by reorientation of the dipole complexes formed by oxygen vacancies. The data obtained for NBT-0.13BT solid solutions are compared with electrical properties of NBT. It is shown that Ba^{2+} introducing to NBT lattice increases permittivity, broadens maximum of ε, shifts the dielectric anomalies to lower temperatures.

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