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ELECTRICAL AND OPTICAL PROPERTIES OF HEAT TREATED $Na_{0.5}Bi_{0.5}TiO_3$ CRYSTALS

Electrical properties in AC field (*f*=1 kHz, T=300-800 K) and optical absorption spectra (λ=400-900 nm, T=300 K) were studied in as-grown and heat treated in air and in vacuum $Na_{0.5}Bi_{0.5}TiO_3$ crystals. It was shown that permittivity ε, conductivity σ, and optical absorption α strongly depended on heat treatment atmosphere and temperature. Annealing at T_{ann}=1100 K in air resulted in the disappearance of permittivity relaxation maximum and significantly decreased conductivity. Subsequent annealing at T_{ann} in vacuum restored the low-frequency relaxation maximum of ε but practically did not change σ. Optical absorption was slightly decreased after heat treatment in air and significantly increased after annealing in vacuum. The obtained data are discussed in assumption that heat treating in air decreases the content of oxygen vacancies V_O, whereas annealing in vacuum generates an additional number of V_O. It is supposed that the observed changes of electrical and optical properties are determined by proper structural defects, such as F^{++}, F^+ and O^- centers, concentration of which can be controlled by a heat treatment in various atmospheres.

Keywords: permittivity, electrical conductivity, optical absorption spectra, sodium bismuth titanate.

Електричні властивості в змінному полі (f=1 кГц, T=300-800 К) і спектри оптичного поглинання (λ=400-900 нм, T=300 К) досліджено у необроблених і відпалених у повітрі та вакуумі кристалах $Na_{0.5}Bi_{0.5}TiO_3$. Показано, що діелектрична проникність ε, електропровідність σ та оптичне поглинання α сильно залежать від атмосфери та температури термообробки. Відпалювання при T_{ann}=1100 К у повітрі призводить до зникнення релаксаційного максимуму діелектричної проникності та помітно знижує електропровідність. Подальше відпалювання у вакуумі при T_{ann} відновлює релаксаційний максимум ε, але практично не змінює σ. Оптичне поглинання знижується після термообробки в повітрі й значно збільшується після відпалу у вакуумі. Отримані дані обговорюються в припущенні, що термічна обробка в повітрі знижує вміст кисневих вакансій V_O, тоді як відпал у вакуумі породжує додаткову кількість V_O. Передбачається, що зміни електричних та оптичних властивостей визначаються власними структурними дефектами, такими як F^{++}, F^+ та O^- центри, концентрацію яких можна контролювати шляхом термічної обробки в різних атмосферах.

Ключові слова: діелектрична проникність, електропровідність, спектри оптичного поглинання, натрій-вісмутовий титанат.

Электрические свойства в переменном поле (f=1 кГц, T=300-800 К) и спектры оптического поглощения (λ=400-900 нм, T=300 К) исследованы в необработанных и отожженных в воздухе и вакууме кристаллах $Na_{0.5}Bi_{0.5}TiO_3$. Показано, что диэлектрическая проницаемость ε, электропроводность σ и оптическое поглощение α сильно зависят от температуры и атмосферы термообработки. Отжиг при T_{ann}=1100 К в воздухе приводит к исчезновению релаксационного максимума диэлектрической проницаемости и значительно понижает электропроводность. Последующий отжиг в вакууме при T_{ann} восстанавливает релаксационный максимум ε, но практически не меняет σ. Оптическое поглощение снижается после термообработки в воздухе и значительно увеличивается после отжига в вакууме. Полученные данные обсуждаются в предположении, что термическая обработка в воздухе снижает содержание кислородных вакансий V_O, тогда как отжиг в вакууме порождает дополнительное количество V_O. Предполагается, что изменения электрических и оптических свойств определяются собственными структурными дефектами, такими как F^{++}, F^+ и O^- центры, концентрацию которых можно контролировать путем термической обработки в различных атмосферах.

Ключевые слова: диэлектрическая проницаемость, электропроводность, спектры оптического поглощения, натрий-висмутовый титанат.

1. Introduction

Structural defects noticeably influence physical properties and efficiency of solid state materials used in functional electronics. For active dielectrics this fact is of particular importance because the lattice defects determine electronic and ionic conductivity at operating temperatures. The ferroelectric-relaxor $Na_{0.5}Bi_{0.5}TiO_3$ (NBT) is the most promising material for use in functional micro-electronics due to high dielectric permittivity and piezoelectric coefficients, transparency in the visible range of wavelengths (band gap of 3.03 eV width) and environmentally safe lead-free chemical composition [1]. According to [2, 3], electrical properties of NBT crystals strongly depend on temperature and atmosphere of annealing that is explained by changing the concentrations of mobile charged and dipolar defects formed by oxygen vacancies V_O. In this paper we study electrical and optical properties of as-grown and heat treated NBT crystals in order to clarify the nature of electrically and optically active defects.

2. Experimental part

NBT single crystals were grown from the melt by the Czochralski method. In order to control the concentration of oxygen vacancies V_O, the samples were heat treated in various atmospheres. As-grown samples were annealed in air at T_{ann}=1100 K for 1 hour, then in vacuum at the same temperature T_{ann} for 2 hours. Permittivity, conductivity and transmittance spectra were measured for as-grown samples and after each heat treatment step.

Measuring ε and σ were performed in AC field (f=1 kHz) in the temperature range 300-800 K by using bridge P5083. Platinum electrodes were deposited by magnetron sputtering in argon atmosphere. The optical transmission spectra were measured by using spectrophotometer Specord M-40 in the wavelength range 400-900 nm at room temperature. The absorption spectra $\alpha(h\nu)$ were calculated by dint of relation [4]

$$t = (1-R)^2\exp(-\alpha d)/\left[1-R^2\exp(-2\alpha d)\right], \quad (1)$$

where h – Planck's constant, ν – frequency of light wave, t – transmission coefficient, $R=(1-n)^2/(1+n)^2$ – reflection coefficient, d – thickness of the sample. The spectral dependence of the refractive index $n(h\nu)$ of NBT single crystals is taken from [5].

3. Results and discussion

Temperature behavior of permittivity ε and conductivity σ are illustrated by the Fig. 1. For as-grown crystals one can see broad relaxation peak of ε(T) near 670 K and exponential growth of σ above 500 K (curves 1 in the Fig. 1). After annealing in air (T_{ann}=1100 K) the relaxation maximum of ε disappears and conductivity decreases significantly (curves 2 in the Fig. 1). Subsequent annealing in vacuum restores and sufficiently increases the relaxation maximum of ε(T), but the conductivity is practically unchanged (curves 3 in the Fig. 1). As it is argued in [2], in the range of T_{ann} oxygen atoms in NBT structure become mobile enough. Thus, two types of the structural defects connected with oxygen vacancies (V_O) could be responsible for the features observed: reorienting dipolar complexes contributing to ε relaxation peak near 670 K and mobile charged defects increasing conductivity at high temperatures. The data in the Fig. 1 demonstrate that the content of the dipolar complexes can be regulated by annealing in different atmospheres. The mobile defects disappear after annealing in air and cannot be restored by subsequent annealing in vacuum.

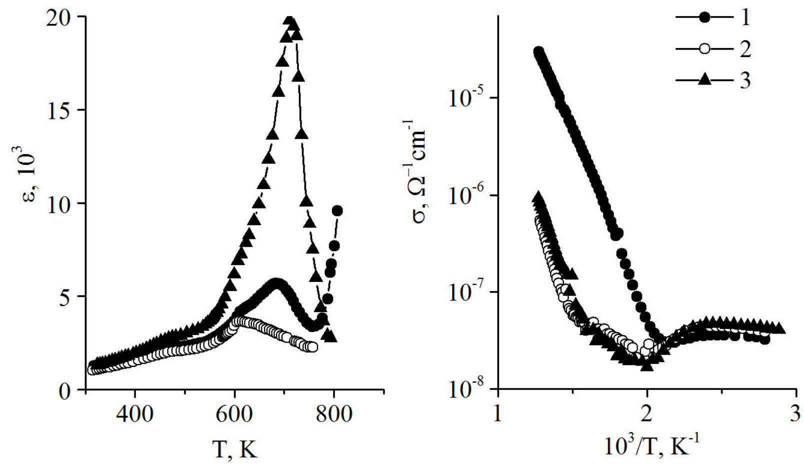

Fig. 1. Dependencies ε(*T*) and σ(1/*T*) of NBT measured in AC field (*f*=1 kHz) for: 1 - as-grown crystal; 2 - the sample after annealing in air (T_{ann}=1100 K); 3 - the sample after subsequent annealing in vacuum at the same temperature T_{ann}.

It should be noted that after annealing in vacuum, the samples changed their color and became dark. Fig. 2a shows the heat treatment effect on the optical absorption spectra α(*h*ν). One can see that annealing in air slightly decreases absorption, whereas heat treating in vacuum sufficiently increases α. Such result demonstrates optical activity of defects formed by V_O. The defects that have dipole moment and contribute to optical absorption can be associated with F-centers. Extended absorption edge indicates presence of tail impurity energy states localized near the valence band top and the conduction band bottom. Existence of electronic and hole traps evidences that electronic hopping conduction is possible in NBT structure.

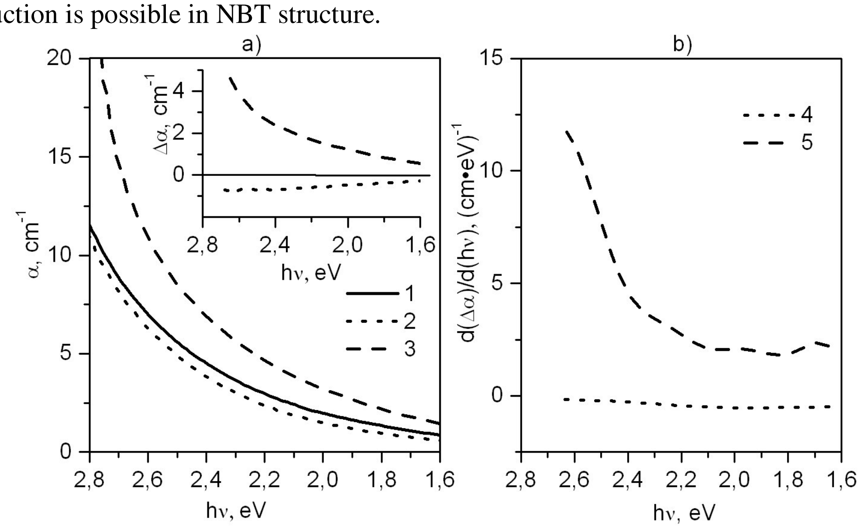

Fig. 2. (a) Absorption spectra of NBT for: 1 - as-grown crystal; 2 - sample after annealing in air (T_{ann}=1100 K); 3 - the sample after subsequent annealing in vacuum at T_{ann}. Inset shows the difference of optical absorption Δα of heat treated and as-grown samples. (b) Derivative spectra, calculated for Δα for the samples annealed in air (4) and annealed in vacuum (5).

The difference of optical absorption Δα, shown in the inset (Fig. 2a), demonstrates that annealing in air slightly decreases optical absorption, whereas heat treating in vacuum sufficiently increases α. Fig. 2b shows the derivative spectra $d\Delta\alpha/d(h\nu)$ for the samples annealed in air and in vacuum. One can see that the derivative spectra for the samples treated in air and in vacuum (curves 4 and 5 in the Fig. 2b) sufficiently differ near the absorption edge. It may evidence for the different nature of the defects, responsible for optical absorption in as-grown and heat treated in vacuum samples.

It may be assumed that F^{++}, F^{+} and hole O^{-} centers simultaneously exist in as-grown crystal. At higher temperatures the F^{+} centers are destructed due to thermal fluctuations. Electrons occupy the vacant places in the electron shells O^{-}, therefore, the holes centers disappear. Oxygen vacancies contribute to the ionic conductivity. This is confirmed by the results of [6], in which concluded that the ionic conductivity prevails in nominal stoichiometric NBT crystals.

The heat treatment in air decreases the content of oxygen vacancies $V_{\mathbf{O}}$ that can change the valence of bismuth ($Bi^{3+}\rightarrow Bi^{5+}$) or generate the hole centers ($O^{2-}\rightarrow O^{-}$). The increase of binding energy of oxygen vacancies (mobility decrease) due to charge state change of the neighboring ions causes a substantial decrease of the conductivity.

The heat treatment in vacuum generates the oxygen vacancies and negatively chargeddefects appear. Oxygen vacancies and such defects may form the F-centers.

4. Conclusions

The study of electrical properties and optical absorption of NBT crystals shows the presence of electrically and optically active defects sensitive to the oxygen content in the atmosphere. Such defects may be F^{++}, F^{+} centers and O^{-} centers, concentration of which can be controlled by heat treatment in various atmospheres.

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