Phase transformations and dielectric characteristics of FE-relaxor Sr$_{0.75}$Ba$_{0.25}$Nb$_2$O$_6$ ceramics and thin films

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Abstract. In the paper the results of a structure and dielectric properties study of ferroelectric-relaxor Sr$_{0.75}$Ba$_{0.25}$Nb$_2$O$_6$ (SBN-75) ceramics and thin films with the structure of an unfilled tetragonal tungsten bronze have been presented. The existence of orientation domains in the SBN-75 film with rotation in the interface plane only by angles of ± 18.4° relative to the axes of the MgO substrate is revealed. In the tetragonal approximation, the unit cell parameters of the film (c = 3.948 Å and a = 12.49 Å) and its strain in comparison with the cell parameters of the ceramic sample have been determined.

1. Introduction
Sr$_x$Ba$_{1-x}$Nb$_2$O$_6$ (SBNx) solid solutions (SS) with unfilled tetragonal tungsten bronze (TBB) structure are prominent representatives of uniaxial ferroelectric-relaxors (FER) [1]. They have high electro-optical and pyroelectric coefficients, that makes them promising materials for use in nonlinear optics, holography, and piezoelectric devices [2]. The crystal structure of SBNx is a three-dimensional framework formed by connected NbO$_6$ octahedra with a formation of three types of channels along the c axis [1, 3]. The five-cornered channels are statistically filled with barium and strontium atoms, the four-cornered channels are filled only with strontium atoms. Three-cornered channels are unfilled according to all structural studies. In SBNx SS, the displacement of Sr, Ba, and Nb atoms relative to the oxygen planes leads to the ferroelectric polarization appearance (at polarization switching metal atoms pass through the mirror plane). The probabilistic filling the positions by barium and strontium cations (in Sr$_{0.75}$Ba$_{0.25}$Nb$_2$O$_6$ [4], the population of five-cornered channels by Ba and Sr is 30.9 and 57.2 %, respectively, the population of four-cornered channels by Sr is 71.5 %) cause significant fluctuations in the chemical composition in the volume of the material and as a consequence the ferroelectric-relaxor properties appears [5]. It was shown that ferroelectric-relaxor properties appear also in SBNx thin films by our studies of these structures [5, 6].

In this paper the results of a structure, microstructure, and dielectric characteristics study of Sr$_{0.75}$Ba$_{0.25}$Nb$_2$O$_6$ (SBN-75) ceramics and thin films presented.
2. Methods and materials

Sr$_{0.75}$Ba$_{0.25}$Nb$_2$O$_6$ ceramics was made from Nb$_2$O$_5$, SrCO$_3$ and BaCO$_3$ by the solid-phase reaction method followed by sintering as part of conventional ceramic technology at the Research institute of physics SFU.

RF sputtering of SBN-75 films ~ 300 nm thickness at an oxygen pressure of 0.5 T on a (001) MgO substrate was performed on a Plasma-50-SE system.

The grain structure of the ceramic was studied by a FE-SEM Zeiss SUPRA 25 scanning electron microscope at the Joint Center for Scientific and Technological Equipment of the SSC RAS.

X-ray phase analysis, structural perfection of ceramics and thin films, unit cell parameters in the normal to the substrate plane direction, and also the orientation relations between the film and the substrate were established by X-ray diffraction by a modernized DRON-4-07 diffractometer (CuK$\alpha$).

Temperature dependences of the relative permittivity, $\varepsilon'/\varepsilon_0$ ($\varepsilon_0=8.75 \times 10^{-12}$ F/m is the dielectric constant), and the dielectric loss tangent, tan$\delta$, of the samples obtained using an Agilent 4980A LCR meter.

3. Results

The $\theta$-2$\theta$ X-ray diffraction patterns of the Sr$_{0.75}$Ba$_{0.25}$Nb$_2$O$_6$ ceramics contained only reflections typical for the TTB structure (Fig. 1). The calculated values of the ceramic unit cell parameters in the tetragonal unit cell approximation were $a_c=12.42$ Å and $c_c=3.908$ Å, which completely correlates with [5]. No impurity phases were found in ceramics. This is confirmed by the results of SEM analysis of the cleaved facet of studied ceramics presented in fig. 2. It can be seen that the material is quite homogeneous, impurity phase inclusions both in the form of individual grains and in the form of intragranular inclusions are not observed. The geometrical grain size of ceramics varies from 2 $\mu$m to 15 $\mu$m, their shape is mainly irregular polyhedrons with rounded borders.

The results of the $\varepsilon'/\varepsilon_0(T,f)$ and tan$\delta(T,f)$ measurements of the Sr$_{0.75}$Ba$_{0.25}$Nb$_2$O$_6$ ceramic are shown in Fig. 3. A temperature decrease from 800 to 300 K is accompanied by an increase in $\varepsilon'/\varepsilon_0$ (at $T=360$–600 K, the value of $\varepsilon'/\varepsilon_0$ is almost independent of $f$) and the formation of maximum, $T_m1$, which shifts to the high-temperature region with increasing measuring electric field frequency. Taking into account [1, 3] it is caused by the phase transition in the Sr$_{0.75}$Ba$_{0.25}$Nb$_2$O$_6$ phase from the paraelectric (PE) phase (P4b2) to the ferroelectric (FE) phase (P4bm). At $T\approx 270$–280 K, an anomaly is formed on the $\varepsilon'/\varepsilon_0(T)$ curves, which is most pronounced at low frequencies. The analysis of the $(\varepsilon'/\varepsilon_0)^{-1}(T)$ dependences (Fig. 3b) shows that the Burns temperature, $T_d$, (the temperature of the polar nano-regions appearance in the FER, above which the relaxors behave is like classical FE in the PE phase (the Curie-Weiss law is satisfied) is $\approx 520$ K.

![Figure 1. 0-20 X-ray diffraction pattern of Sr$_{0.75}$Ba$_{0.25}$Nb$_2$O$_6$ ceramic at T = 300 K](image-url)
Figure 2. SEM images of Sr$_{0.75}$Ba$_{0.25}$Nb$_2$O$_6$ cleaved facet

Figure 3. $\varepsilon'/\varepsilon_0(T)$ (1) and $\tan \delta(T)$ (2) dependencies at $T = 20$-600 K temperature range and $f = 10^2$–$10^6$ Hz frequency range, measured in the cooling mode (a) and $(\varepsilon'/\varepsilon_0)^{-1}(T)$ dependency at $T = 20$–800 K temperature range and $f = 10^6$ Hz frequency (b) of Sr$_{0.75}$Ba$_{0.25}$Nb$_2$O$_6$ ceramic.

As can be seen from fig. 4, the dependence $T_{m1}(f)$ is described by the Vogel-Fulcher law:

\[ f = f_0 \exp\left(\frac{E_{\text{act}}}{k(T_m - T_f)}\right) \]  

where $f_0$ is the frequency to overcome the potential barrier $E_{\text{act}}$, $k$ is the Boltzmann constant, $T_f$ is the Vogel-Fulcher temperature, interpreted as the temperature of the “static freezing” of electric dipoles or the transition to the state of a dipole glass. The calculated values of $E_{\text{act}}$ and $f_0$ were 0.05 eV and $10^{12}$ Hz, respectively, and are comparable with those for the SBNx ceramics in [8].

The calculated value of $T_f = 280$ K allows to connect the anomalies in the $\varepsilon'/\varepsilon_0(T)$ and $\tan \delta(T)$ dependences with the phase transformation of Sr$_{0.75}$Ba$_{0.25}$Nb$_2$O$_6$ from the relaxor (nanopolar) state to the macrodomain state, in which bulk FE domains coexist with near-surface nanoscale domains [4]. The values of $T_f$ for the studied Sr$_{0.75}$Ba$_{0.25}$Nb$_2$O$_6$ ceramics exceed those in a single crystal [9] and are close to the values in ceramics [8].

At $T < 200$ K, diffuse maximum ($T_{m2}$) are formed on $\varepsilon'/\varepsilon_0(T)$ and $\tan \delta(T)$, which shift to the high-temperature region with $f$ increasing. Taking into account the results of [10, 11] and found at $T = 77$ K the FE-like dielectric hysteresis loops, the diffuse low-temperature FE $\rightarrow$ FE phase transition from the tetragonal to monoclinic phase, characterized by the appearance of spontaneous polarization.
components in the perpendicular to the c axis direction [11], is a reason for the appearance of these hysteresis loops in Sr$_{0.75}$Ba$_{0.25}$Nb$_2$O$_6$.

Thus, we found that two diffuse ferroelectric phase transformations on the dielectric characteristics of Sr$_{0.75}$Ba$_{0.25}$Nb$_2$O$_6$ ceramics occur in the 20–800 K temperature range. The dielectric relaxation during the PE $\rightarrow$ FE transition (280–520 K) has a non-Debye character, which indicates the coexistence of the short and long polar orders in Sr$_{0.75}$Ba$_{0.25}$Nb$_2$O$_6$ [12] due to fluctuations in the chemical composition. These effects, in general, also occur in Sr$_{0.75}$Ba$_{0.25}$Nb$_2$O$_6$ polycrystalline thin films [5].

The $\theta$-2$\theta$ X-ray diffractions patterns of Sr$_{0.75}$Ba$_{0.25}$Nb$_2$O$_6$/MgO heterostructure (Fig. 5) contained only reflections corresponding to Sr$_{1-x}$Ba$_x$Nb$_2$O$_6$ solid solutions and MgO (001) substrate, which indicates the absence of impurity phases and buffer layers in the heterostructure. The $\phi$-scans of (221) Sr$_{0.75}$Ba$_{0.25}$Nb$_2$O$_6$ reflection and (113) MgO reflection (Fig. 4) have proved that the barium-strontium niobate film was heteroepitaxially grown. The presence of 8 reflections in the $\phi$-scans of Sr$_{0.75}$Ba$_{0.25}$Nb$_2$O$_6$ indicates at two types orientation domains.

Figure 4. $(\ln(f_0)-\ln(f))^{-1}$ dependence on $T_m$, demonstrating the Vogel-Fulcher law in Sr$_{0.75}$Ba$_{0.25}$Nb$_2$O$_6$

Figure 5. $\theta$-2$\theta$ X-ray diffraction pattern of Sr$_{0.75}$Ba$_{0.25}$Nb$_2$O$_6$/MgO heterostructure. Rocking curve of (002) reflection in inset.
A comparison of the positions for (221) reflections of the film and (113) reflections of a substrate demonstrate that the [110] crystallographic axes of two $\text{Sr}_{0.75}\text{Ba}_{0.25}\text{Nb}_2\text{O}_6$ orientation domains are rotated relative to the [110] axis of the MgO substrate at angles $+18.4^\circ$ and $-18.4^\circ$. The results of $\theta-2\theta$ scans proved that the [001] axis of the substrate and both $\text{Sr}_{0.75}\text{Ba}_{0.25}\text{Nb}_2\text{O}_6$ orientation domains are codirectional. The formation of various orientation domains in SBNx films heteroepitaxially grown on MgO (001) substrates takes place in most works devoted to this material and it is associated with the specificity of the film and substrate crystal structures coupling [13]. By used our technology for the synthesis of $\text{Sr}_{0.75}\text{Ba}_{0.25}\text{Nb}_2\text{O}_6$ films the structure of the films is characterized by the presence of orientation domains with a rotation of only $\pm 18.4^\circ$.

![Figure 6: (a) $\varphi$-scans of (221) film reflection and (113) substrate reflection; (b) $\theta-2\theta$ X-ray diffractogram of (313) reflection for two orientation domains $+18.4^\circ$ and $-18.4^\circ$](image)

The unit cell parameters of the $\text{Sr}_{0.75}\text{Ba}_{0.25}\text{Nb}_2\text{O}_6$ film calculated in the tetragonal approximation, were $a_f = 12.49 \pm 0.01 \, \text{Å}$, $c_f = 3.948 \pm 0.001 \, \text{Å}$. As can be seen from Fig. 6b both orientation domains have the same lattice parameters. The unit cell strains of the $\text{Sr}_{0.75}\text{Ba}_{0.25}\text{Nb}_2\text{O}_6$ film in the interface plane is $e_{11} = (a_f-a_c)/a_c = 0.006$, and in normal to surface direction is $e_{33} = (c_f-c_c)/c_c = 0.01$.

Thus, in the SBN-75 film magnitude of the unit cell strain is significant for the TTB structure, which can lead to a significant change in electrophysical and optical properties, to a temperature shift in the FE phase transitions. The effect of strain on SBN-75 film properties is the subject of our further research.

4. Conclusion

The results of the structure and dielectric characteristics studies of SBN-75 ceramics and thin films are presented. Based on the dielectric properties analysis of SBN-75 ceramics in the temperature range 20–800 K, the sequence and regions of phase transformations are determined. It found that the SBN-75/MgO heterostructure is epitaxial where only two types of orientation domains are existed. The crystallographic axes of orientation domains are rotated on $\pm 18.4^\circ$ relative to the substrate axes. It was shown that the SBN-75 film unit cell is strongly strained relative to the bulk. The results can be used in the development and manufacture of functional materials based on $\text{Sr}_{0.75}\text{Ba}_{0.25}\text{Nb}_2\text{O}_6$ ferroelectric-relaxor thin films.

Acknowledgment

This work was carried out as part of the State Task for the SSC RAS (project no. 01201354247) and was supported by the grant MK-4100.2018.2.

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