The surface piezoresponse of tetragonal tungsten bronze oxides with different ordering of cations in A-sublattice

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Abstract. The piezoresponse (PR) images of microsized surface areas of the hot-pressed ceramics samples $K_xBi_xNb_{10}O_{30}$, $K_xSr_xNb_{10}O_{30}$, and $Na_xSr_xNb_{10}O_{30}$, presenting different types of the inter-octahedral cations ordering, were obtained. The Fourier analysis of the PR data showed that the mesoscale regions form subsystems responsible for the electrical activity of the sample, the contribution of which manifests itself depending on the type of cation ordering.

1. Introduction

Tetragonal tungsten bronze–type (TTB) oxides are known as perspective materials for applications in modern electronic industries due to the large flexibility of their ferroelectric, dielectric, piezoelectric and mechanical properties [1].

The wide possibilities of varying the ferro-piezoelectric properties of TTB oxides are due to the presence in this structure of three nonequivalent inter-octahedral positions A1, A2, C [1-4] (Figure 1).

The most interesting are the structural modifications with substitutions at the A1 and A2 positions in the four- and pentagonal channels (Figure 1), which may be filled completely or partially with identical cations.

To reveal the common regularities caused by the cation distribution peculiarities over the A-positions structure, the most informative are the filled-type oxides, which these positions do not have vacancies in these positions. These include the compositions $M_1M_2B_{10}O_{30}$, in which two M1 cations and four M2 cations completely occupy two A1 positions in the quadrangular channels and four A2 positions in...

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the pentagonal channels of the structure (Figure 1). The C positions in the triangular channels (Figure 1) are vacant. For such compounds, three “limiting” cases of structural ordering [7] are considered:

- (1) a completely ordered structure in which each of the A1 and A2 sublattices is occupied by cations of the same type;
- (2) a partially ordered structure in which the M1 cations fill two positions in quadrangular channels, and four positions in pentagonal channels are statistically filled with M1 and M2 cations;
- (3) a disordered structure of TTB, in which six cations M1 and M2 are statistically distributed over six positions A1 and A2.

These three configurations (except for the completely ordered (1) structure), are clearly possible to form locally inhomogeneous regions of different composition.

The electrical activity of textured TTB ceramics can largely be due to the peculiarities of the properties of the crystallites forming it. To study how the structural order in TTB can affect these properties, we chose three model compositions representing the above types of ordering, respectively: $K_2Bi_2Nb_{10}O_{30}$ [8, 9], $K_2Sr_2Nb_{10}O_{30}$ [7, 10-13] and $Na_2Sr_2Nb_{10}O_{30}$ [14].

Observing of such weak details on a large piezoresponse background is not an easy problem. In [15-17], a method is proposed based on measurements of surface displacements in piezoresponse force microscopy (PFM) accompanied with subsequent Fourier analysis and Fourier filtering of piezoresponse (PR) images, to reveal small details that are poorly or not distinguishable in the source image. The possibility of studying their changes depending on the experimental conditions can provide disordering parameters when simulating random polarization with sub-micron resolution. It turned out to be possible to estimate the amplitude, correlation radius and width of the spectrum of spatial correlations in [16-18]. This approach can be applied to grain boundaries, to electric fields of charged defects, etc. In [7] the Fourier filtering of surface piezoresponse image for $K_2Sr_2Nb_{10}O_{30}$ allowed to extract electrically active objects with approximately ten nm size. Later, a giant piezoresponse [10] was found in that compound.

The scope of this work is to apply the Fourier filtering analysis of the piezoresponse images to verify the possibility of electrically active regions revealing in a textured TTB ceramics: $K_4Bi_2Nb_{10}O_{30}$, $K_2Sr_2Nb_{10}O_{30}$, and $Na_2Sr_2Nb_{10}O_{30}$, presenting three abovementioned types of the cations ordering in A-sublattices of filled TTBs.

2. Experiment. Methods of preparing materials and equipment

Samples of high-density textured ceramics $K_4Bi_2Nb_{10}O_{30}$, $K_2Sr_2Nb_{10}O_{30}$, and $Na_2Sr_2Nb_{10}O_{30}$ were prepared by uniaxial hot pressing at a pressure of $P = 40$ MPa at a temperature of 1150 °C. Oxides of the tetragonal tungsten bronze (TTB) type have acicular crystallites elongated along the c- axis. Therefore, in the process of hot pressing, a texture is often formed in these samples, which is associated with the predominant orientation of the crystallite c- axes in the direction perpendicular to the hot pressing pressure axis [1, 2].

X-ray phase analysis and determination of the samples crystallographic characteristics were carried out on a DRON 7 diffractometer, filtered Co-Kα radiation, and standard Bragg-Brentano geometry.

Piezoresponse images were obtained with SPM Veeco Multimode VS. The surface of the samples is mirror polished. The sample back surface is a silver electrode. Topography, piezoelectric response, and the phase signals were registered simultaneously. MESP conductive probe, $k \approx 3.8$ N / m, $V_{ac} = 4$ V, $f_{ac} = 50$ kHz, force of pressing the probe to the surface $\sim 100$-180 nN, bias values at the probe: $\pm 2000$ mV or $\pm 8000$ mV. For the piezoresponse images scale 20 mV corresponds to $\sim 1$ nm in a surface displacement. Scan sizes: 1.5×1.5 μm² and 5×5 μm².
3. Results and discussion
The results of X-ray and dielectric studies are described in detail in [1] and indicate the formation in the hot-pressed sample of a texture characteristic of the TTB type oxides, which is accompanied by a significant anisotropy of the dielectric constant and a decrease in the Curie temperature in comparison with the anisotropic sample.

According to X-ray phase analysis, the $K_4Bi_2Nb_{10}O_{30}$ и $Na_2Sr_4Nb_{10}O_{30}$ samples have the TTB structure and do not contain impurity phases. As a result of the structural parameters refinement, it was found that the composition of the $Na_2Sr_4Nb_{10}O_{30}$ sample corresponds to the stoichiometric one. The distribution of sodium and bismuth cations over the A-positions of the structure corresponds to the disordered type of the filled structure of the TTB (3). In the $K_4Bi_2Nb_{10}O_{30}$ sample, the cations are distributed according mainly to the ordered type of structural ordering (1), in which bismuth ions are predominantly located in the A1 channel, and potassium ions - in the A2 channel. This sample contains two types of structural defects: violation of the stoichiometry of the $K_3.96Bi_{1.86}Nb_{10}O_{30}$ compound, which leads to the appearance of vacancies in the A1 position and structural disordering, manifested by the presence of cations in “foreign positions”: $(K_{0.009}Bi_{0.886})(K_{0.986}Bi_{0.801})Na_{10}O_{30}$. The structure of the partially ordered, (2), $K_2Sr_4Nb_{10}O_{30}$ is described in detail in [7, 10], where the PFM method was applied to study the possibility of the charged nano-regions existence arising from the distribution peculiarities for $K^+$ and $Sr^{2+}$ cations in A2 channels. Small charged regions are selected using Fourier filtering, which is also used in this work for three model compounds. The results are shown in Figure 2. Since Figure 2 is intended to analyze the contributions of small meso/nano scale elements in piezoresponse images, the PR source images are not shown here. Some examples of those images are in Figure 3.

Fourier filtering made it possible to distinguish two types of meso/ nanoscale structures and their response to an external electric field (Figure 2). For each compound: the upper row is the PR Fourier transform, on which the areas with a characteristic pattern of one of two types are highlighted by frames (examples of selection are shown on an enlarged scale in the inset at the bottom right). The bottom row is the PR images after applying the inverse Fourier transform. The white line, which combines areas of the same type at the bottom of the figure is drawn for ease of perception. The symmetry of the Fourier image allows not to draw this line in the upper half of the figure. The arrows show the correspondence of the image to the type of the selected areas.

On the Fourier images, different frames highlight areas with a characteristic pattern of one of two types: thin lines (rectangles), or "stars" (squares). An example of selection are shown on an enlarged scale in the inset at the bottom right in Figure 2. Despite their low contrast and sharply uneven background, they stand out quite clearly. An example of such a selection is shown at the bottom right. Below are the piezoresponse images after applying the inverse Fourier transform, and the arrows indicate the correspondence of the image to the type of the selected area. White lines on the Fourier transform unite selected areas of the same type (lines), and are shown only for half of the figure, which is symmetrical about the origin.

For a completely ordered (1) A-sublattice of $K_4Bi_2Nb_{10}O_{30}$ (Figure 2, top), Fourier filtering shows only one type of mesoscale structure - spots of ~(30-40) nm width, forming into curved stripes. Comparison of their position with the relief of the whole piezoresponse image showed that they are located at the boundaries of regions with sharply varying contrast, both in the amplitude and in the phase images. When change the bias polarity, the position of the selected elements is inverted. Considering that $K_4Bi_2Nb_{10}O_{30}$ is a uniaxial ferroelectric, and only $180^\circ$ switching is possible, it can be assumed that the regions selected by Fourier filtering may correspond to domain boundaries. At zero bias, the response from the highlighted area is more than 10 times weaker than when the bias is applied to sample surface (0.15 mV and ~ 2.2 mV, respectively), but is still visible (center of the upper part in Figure 2).
A possible reason for the presence of a response at zero bias is the small sample nonstoichiometry described above, which creates defect areas.

The result of Fourier filtering for $K_2Sr_2Nb_{10}O_{30}$ (partial ordering, (2)) is described in [7] and is shown in the middle panel of Figure 2. In our case, it is important that the filtered image contains only elements of a type different from that in $K_4Bi_2Nb_{10}O_{30}$, corresponding to the sizes of several nm in the piezoresponse image.

For completely disordered $Na_2Sr_4Nb_{10}O_{30}$ (Figure 2, bottom), both types of structures (both “stars” and stripes) appear on the Fourier transform image, which react to an external field, which can be seen by comparing images obtained at different displacement biases. When its polarity is changed, the position of the selected elements is inverted. The corresponding filtered images are shown below. Belonging to different subsystems is confirmed by the piezoresponse magnitude corresponding to these elements: $\sim 2$ mV for “stars”, and $\sim 12$ mV for “stripes”. The reason, possibly, lies in the complex phase composition of the sample.

Generally, the analysis of the images in Figure 2 shows that the Fourier filtering of the piezoresponse images makes it possible to extract the contribution of meso / nanoscale PR elements, which details (shape, response value, and distribution over the sample surface) depend on the cation ordering in A-sublattices of model TTBs. However, before making conclusions, one should take into account the effect of texture, which creates a preferential orientation of the crystallite axes in the direction perpendicular...
to the hot pressing axis [1, 20]. For this purpose, we chose $K_4\text{Bi}_2\text{Nb}_{10}O_{30}$, since its piezoresponse can be influenced by the imperfections found above (low nonstoichiometry and defectiveness). We studied samples cut from the same block in two different orientations relative to $P$ - the hot pressing pressure axis: $N \parallel P$ (a-oriented) - the normal $N$ to the sample surface is parallel to $P$; $N \perp P$ (c-oriented) - the normal of $N$ to the sample surface is perpendicular to $P$. The results for a polarized sample with $N \perp P$ are shown in Figure 3. The bias values are: $+ 2000$ mV and $-2000$ mV. The piezoresponse images are in the top (Piezoresponse); in the middle there are the Fourier images where the red squares highlight areas for which the inverse Fourier transform is performed (Fourier), and its results are shown at the bottom of Figure 3 (Filtered Fourier).

It is clearly seen that the piezoresponse images change their contrast to the opposite one when changes the bias polarity changes (top row in Figure 3). This manifests itself in the PR Fourier images as a change in the position of the areas highlighted with red squares. In the filtered image (bottom row in Figure 3), they look like stripes one to two tens of nm wide, corresponding to the boundaries of PR regions with opposite contrast, i.e., most likely, to the domain boundaries.

None of the images shown in Figure 3, does not contain elements that are inherent in the nanoscale structures arising from partial or complete disordering (they look like narrow stripes, see Figure 2), and their corresponding nanoscale elements in the filtered piezoresponse image. Histograms of the source piezoresponse image (in the middle of the lower part in Figure 3), correspond to the concept of 180° switching and changings in the piezoresponse images contrast in the top row in Fig. 3. When switching a bias, the histogram distributions changes their shape.

The same result was obtained for the sample with $N \parallel P$, which allows not to present the figure.

On the whole, the results presented in Figure 3 do not change the main conclusion about the dependence of the manifestation of the elements of the meso/nano-scale electrically active subsystems in the sample piezoresponse on the degree of the cations ordering in A-sublattice.

4. Conclusions

The surface piezoresponse of the model samples of high-density textured ceramics $K_4\text{Bi}_2\text{Nb}_{10}O_{30}$, $K_2\text{Sr}_4\text{Nb}_{10}O_{30}$, and $\text{Na}_2\text{Sr}_4\text{Nb}_{10}O_{30}$ having different types of the of the cations ordering in A-sublattice in the TTB structure, has been studied.

Fourier filtering of piezoresponse images makes it possible to extract the contributions of electrically active nano/mesoscale regions, which manifest itself depending on the type of ordering of the cations ordering in A-sublattice: at complete ordering these may be domain boundaries, at partial ordering - nanoscale structures, and at complete disordering, both types appear. Ceramic texturing does not affect this result.

![Figure 3](image-url) Piezoresponse dependence from bias for textured for $1.5 \times 1.5$ μm² scans of ceramic $K_4\text{Bi}_2\text{Nb}_{10}O_{30}$ surface. In the frame in the bottom row there are the surface piezoresponse histograms for images in the upper row of this figure.
5. References

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