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# Microstructure features of the BST/(Mg, Ln)-ceramic

K. P. Andryushin*,§, A. V. Nagaenko†, S. V. Khasbulatov‡, L. A. Shilkina*,
E. V. Glazunova*, S. I. Dudkina*, I. N. Andryushina* and L. A. Reznichenko*
*Research Institute of Physics, Southern Federal University
194 Stachki Str., Rostov-on-Don 344090, Russia
†Institute of High Technology and Piezo Technic, Southern Federal University
10 Milchakova, Rostov-on-Don 344090, Russia
‡Faculty of Physics and Information-Communication Technologies
32 Sheripova Str., Grozny 364024, Russia
§kpandryushin@gmail.com

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Solid solutions of the composition $Ba_{1-x-y}(Mg, Ln)_xSr_yTiO_3$ ($x = 0.01$; 0.025; 0.04; $y = 0.20$; 0.50; 0.80; Ln = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tu, Yb) were prepared by two-stage solid-phase synthesis followed by sintering using conventional ceramic technology. The influence of rare-earth elements on the microstructure of the prepared ceramic samples was investigated. It was found that regardless of the type of modifiers introduced, the grain landscape of the studied solid solutions with different amounts of $SrTiO_3$ is refined (in the initial system, the average grain size, $\bar{d}$, at $x = 0.20$ is 6 $\mu$m; at $x = 0.50$ is 4 $\mu$m; at $x = 0.80$ is 18 $\mu$m) to crystallite sizes not exceeding (2–3) $\mu$m, and compacted. The using of mechanical activation procedures leads to an even greater decrease in the size and an increase in the density of ceramics. The increasing in the concentration of modifiers in each group (within the considered range of dopant variation) against the background of such a fine-grained structure has little effect on the dynamics of changes in $\bar{d}$. It is concluded that it is advisable to use the data obtained in the development of functional materials based on BST/(Mg, Ln) and devices with the participation of these compositions.

*Keywords*: Ceramics; BST; microstructure; rare-earth elements.

## 1. Introduction

In addition to densification, phase transformations and polymorphic transformations, the key points in the sintering of dispersed crystalline powders for ferroelectric ceramics are recrystallization processes. As a result, a microstructure (grain landscape) of finished products is formed. Essentially, sintered polycrystalline bodies are nothing more than a conglomerate of grains, the boundaries of which form a kind of network of intercrystalline surfaces. The latter, generally speaking, determines the main difference between ceramics and single crystals and significantly affects, along with the elemental composition and the nature of the crystal structure, on the macroscopic properties of substances. The ability to control the grain structure (the size and habit of grains and pores, the type of their packing, the state of grain boundaries and other details of the grain landscape) makes it possible to vary widely the performance characteristics of ceramics, up to the formation of their fundamentally new combinations. The levers of the directed organization of a given set of properties of ceramic ferroelectrics can be both the regulations of the technological process (temperature, duration, frequency of firing, etc.) and variations in the elemental composition of the sintered compositions.

The objects of study were solid solutions (SSs) of the binary system (Ba, Sr)$TiO_3$ (BST), modified with Mg and lanthanides (Ln) (rare-earth elements, REEs). Their choice is primarily due to the need for such materials for the design of control microwave elements of accelerating technology.[1–5] It is shown that the introduction of REE into the BST composition leads to the formation of the required set of properties: low dielectric constants and losses, high coefficients of their controllability by the electric field. Since the works in this regard are sporadic, and there is no information about the grain structure of these objects at all, it seemed expedient to fill this gap with the aim of subsequent use of the results obtained to establish a correlation relationship between the composition — crystal structure — grain landscape — macroresponses — application areas BST/(Mg, Ln) — ceramics.

## 2. Materials and Methods

The objects of study were SS of the composition $Ba_{1-x-y}(Ln, Mg)_xSr_yTiO_3$ ($x = 0.01$; 0.025; 0.04; $y = 0.20$; 0.50; 0.80;

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[§] Corresponding author.

Ln = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tu, Yb) obtained in the form of ceramics by two-stage solid-phase synthesis followed by sintering using conventional ceramic technology. Synthesis regimes: $T_{\text{synt.1}} = (1470–1620)$ K, $\tau_1 = 4$ h; $T_{\text{synt.2}} = (1520–1670)$K, $\tau_2 = 4$ h; $T_{\text{sint.}} = 1720$ K, $\tau_{\text{sint.}} = 2$ h. Variations of $T_{\text{synt.1}}$ and $T_{\text{sint.2}}$ are associated with their dependence on the qualitative–quantitative elemental composition of the SS. In some cases, mechanical activation (MA) procedures were used.

A JSM — 6390L scanning electron microscope (SEM) (Japan) with a system of microanalyzers from Oxford Instruments (Great Britain) was used to study the microstructure of cleaved samples. The microscope resolution is up to 1.2 nm at an accelerating voltage of 30 kV (image in secondary electrons), the limits of the accelerating voltage are from 0.5 to 30 kV, magnification is from × 10 to × 1,000,000, and the beam current is up to 200 nA.

## 3. Experimental Results and Discussion

Figures 1–13 show fragments of the microstructures of the SS-modified ceramics.

The analysis of the grain structure of the studied ceramics showed that regardless of the type of introduced modifiers, the grain landscape of SS with different amounts of $SrTiO_3$ is refined (in the original system, the average grain

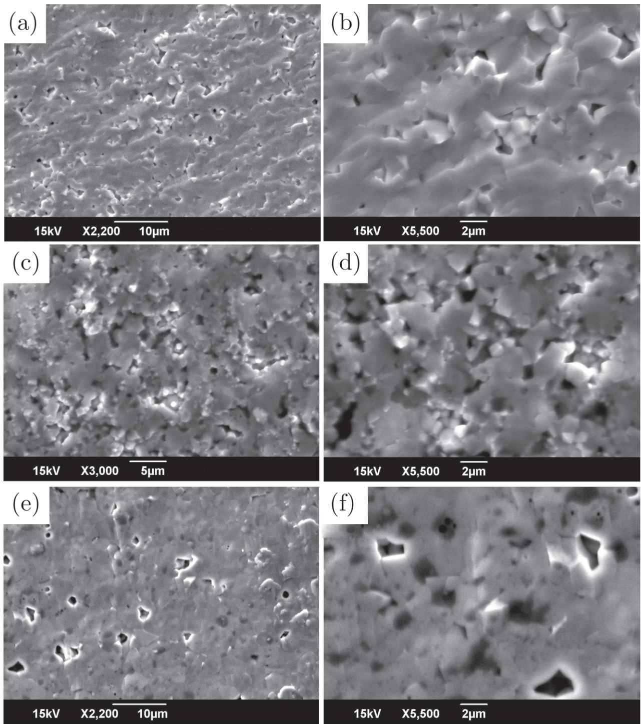

Fig. 2. Fragments of the microstructure of the SS of the modified BST system. (a, b) La 0.04, $x = 0.20$, (c, d) La 0.025, $x = 0.50$ and (e, f) La 0.01, $x = 0.80$.

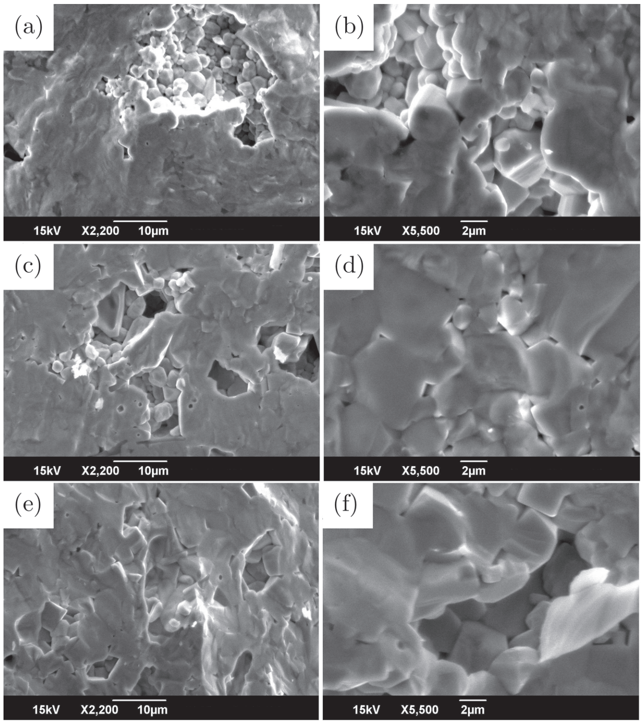

Fig. 1. Fragments of the microstructure of the SS of the modified BST system. (a, b) Mg 0.04, $x = 0.20$, (c, d) Mg 0.025, $x = 0.50$ and (e, f) Mg 0.01, $x = 0.80$.

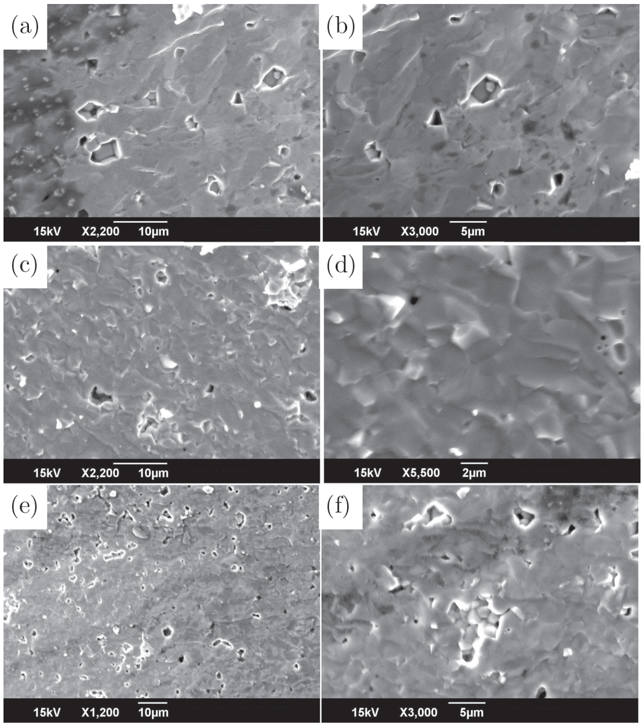

Fig. 3. Fragments of the microstructure of the SS of the modified BST system. (a, b) Gd 0.04, $x = 0.20$, (c, d) Gd 0.025, $x = 0.50$ and (e, f) Gd 0.01, $x = 0.80$.

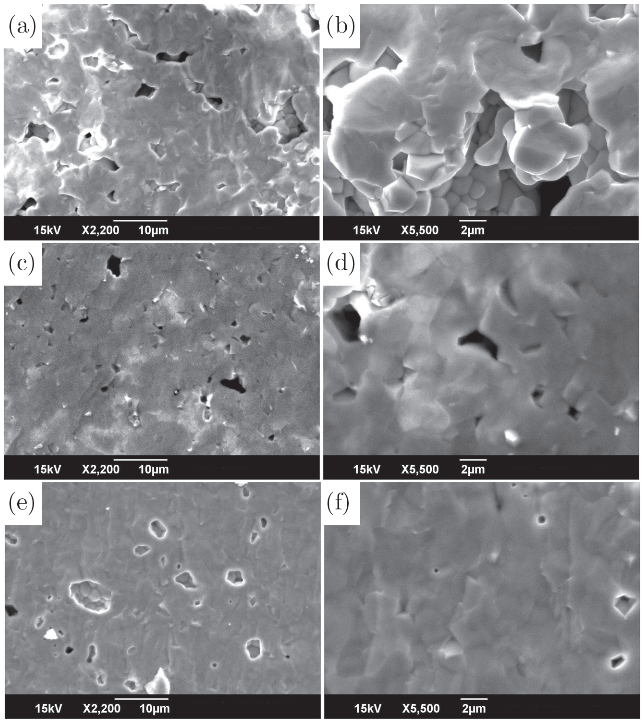

Fig. 4. Fragments of the microstructure of the SS of the modified BST system. (a, b) Tb 0.04, $x = 0.20$, (c, d) Tb 0.025, $x = 0.50$ and (e, f) Tb 0.01, $x = 0.80$.

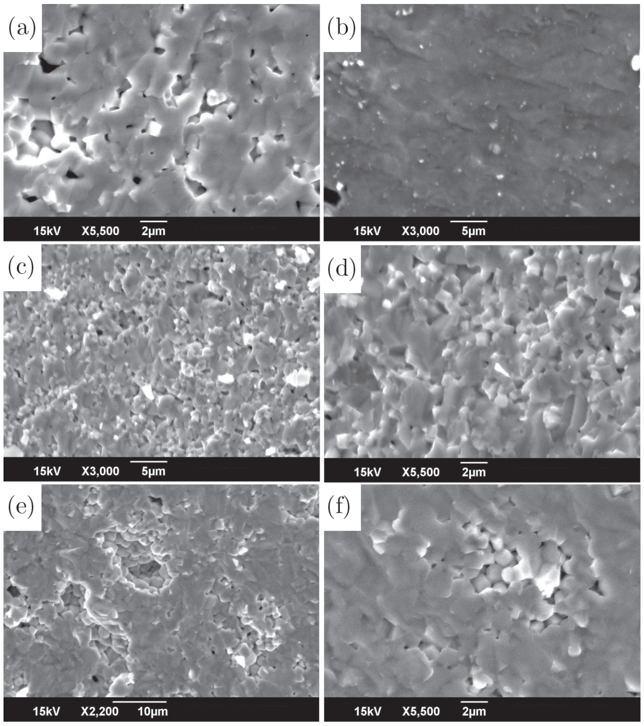

Fig. 5. Fragments of the microstructure of the SS of the modified BST system. (a, b) Pr 0.04, $x = 0.20$, (c, d) Pr 0.025, $x = 0.50$ and (e, f) Pr 0.01, $x = 0.80$.

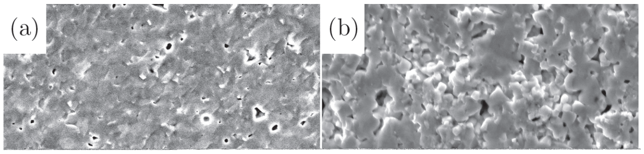

Fig. 6. Fragments of the microstructure of the SS of the modified BST system. (a) Nd 0.04, $x = 0.20$ without M.A. (b, c) Nd 0.025, $x = 0.50$ 5 min M.A. (d, e) Nd 0.025, $x = 0.50$ 10 min M.A. (f, g) Nd 0.025, $x = 0.50$ 15 min M.A. (h, i) Nd 0.01, $x = 0.80$ without M.A.

size, $\bar{d}$, at $x = 0.20$ is 6 $\mu$m; at $x = 0.50$ is 4 $\mu$m; at $x = 0.80$ is 18 $\mu$m)[6] to crystallite sizes not exceeding (2–3) $\mu$m, and is compacted. The using of MA procedures leads to an even greater decrease in the size of  and an increase in the density of ceramics. The increasing in the concentration of modifiers in each group (within the considered range of dopant variation) against the background of such a fine-grained structure has little effect on the dynamics of changes in $\bar{d}$. The observed can be explained as follows.

The introduction of Mg and large-size REEs most often leads to: the transformation of the symmetry of SS with $x =$

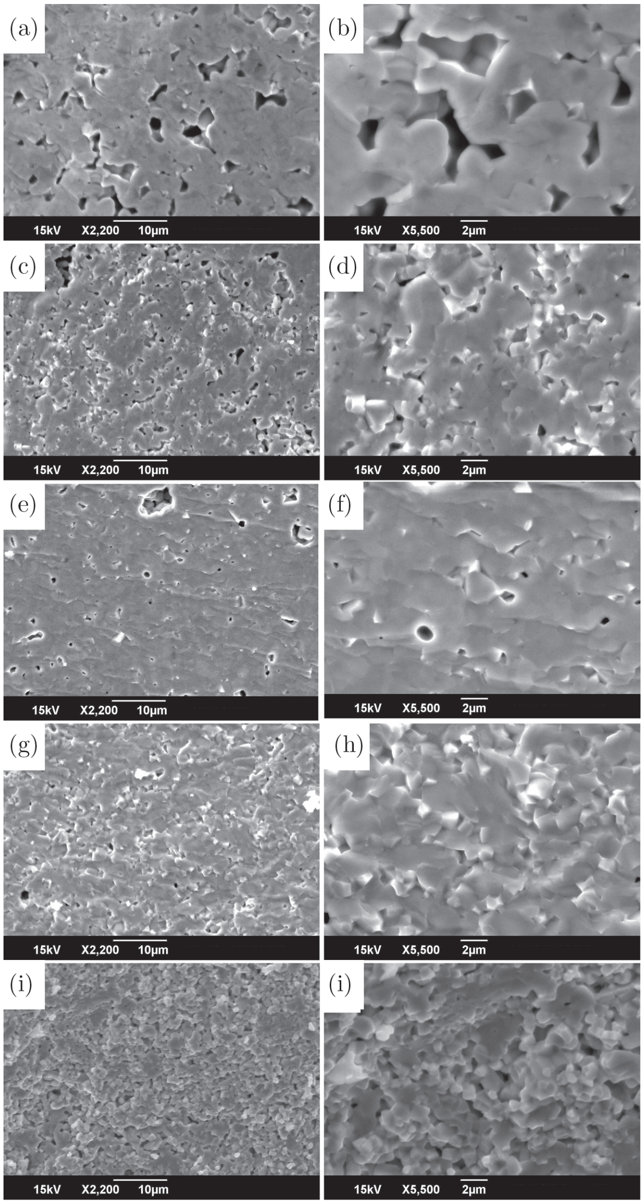

Fig. 7. Fragments of the microstructure of the SS of the modified BST system. (a, b) Sm 0.04, $x = 0.20$ without M.A. (c, d) Sm 0.025, $x = 0.50$ 5 min M.A. (e, f) Sm 0.025, $x$=0.50 10 min M.A. (g, h) Sm 0.025, $x = 0.50$ 15 min M.A. (i, j) Sm 0.01, $x = 0.80$ without M.A.

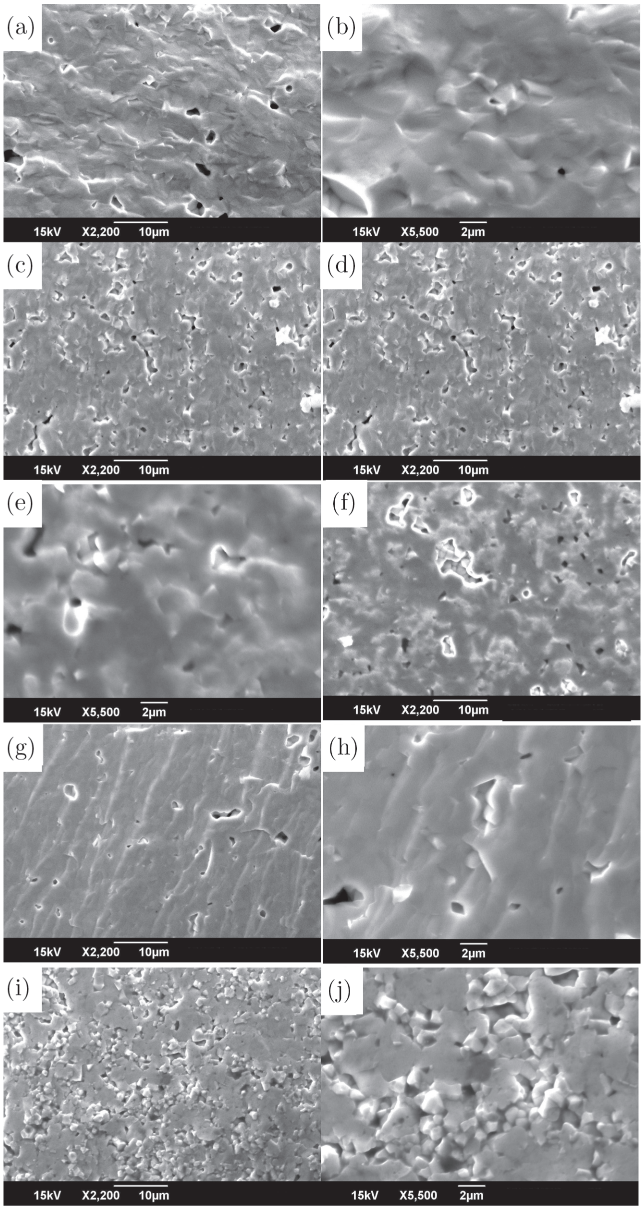

Fig. 8. Fragments of the microstructure of the SS of the modified BST system. (a, b) Eu 0.04, $x = 0.20$ without M.A. (c, d) Eu 0.025, $x = 0.50$ 5 min M.A. (e, f) Eu 0.025, $x = 0.50$ 10 min M.A. (g, h) Eu 0.025, $x = 0.50$ 15 min M.A. (i, j) Eu 0.01, $x = 0.80$ without M.A.

0.20 from tetragonal to cubic; a change in the phase state of a SS with $x = 0.50$ — a shift in the phase diagram to the initial stage of spinodal decomposition or to a metastable region; the development of a defect situation in a SS with $x =$ 0.80. All these factors contribute to a decrease in the spontaneous deformation of the cell, weakening of internal stresses in ceramics and, as a consequence, facilitation of diffusion processes and mass transfer during recrystallization. With the latter, as is known,[7] an increase in  should be observed.

However, this does not happen. In contrast to the traditional inverse dependence of $\bar{d}$ on $\delta$ (homogeneous deformation parameter),[7] we observe the symbatic behavior of these characteristics. The reason probably lies in the fact that with very small distortions of the structure or with their practical absence (in our case, cubic phases), conditions are created for the simultaneous appearance of several recrystallization centers — the nuclei of a new grain structure with a naturally reduced mass capacity, which later on the stages of grain growth are "forced" to ensure their small size.

In the case of modifying ceramics with small-sized RREs, they replace basic elements in very small amounts (limited solubility — microisomorphism) with the precipitation

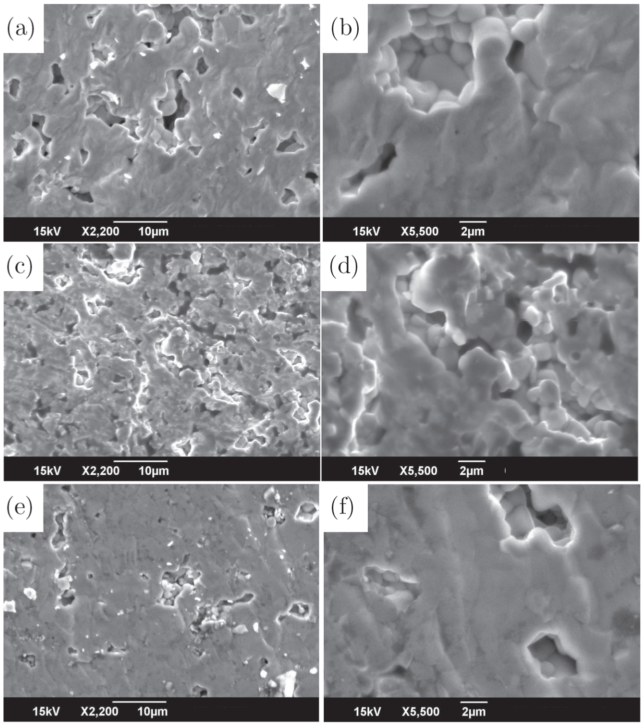

Fig. 9. Fragments of the microstructure of the SS of the modified BST system. (a, b) Dy 0.04, $x = 0.20$, (c, d) Dy 0.025, $x = 0.50$ and (e, f) Dy 0.01, $x = 0.80$.

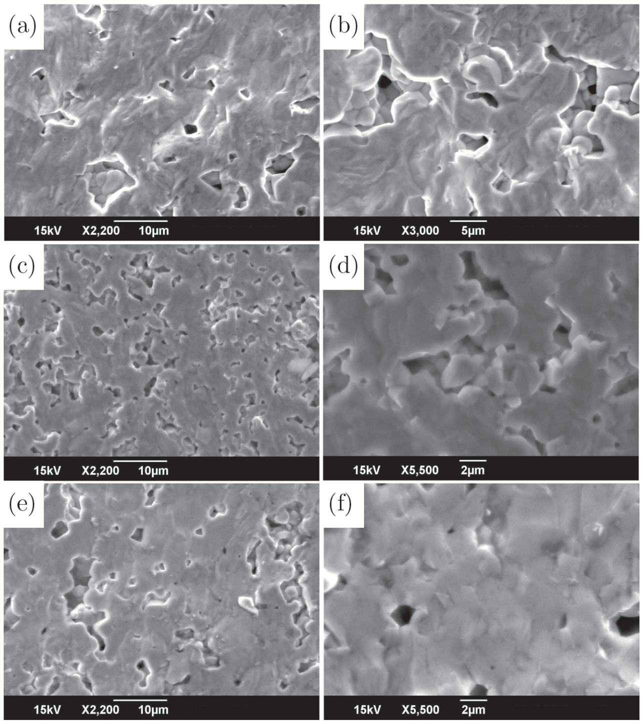

Fig. 10. Fragments of the microstructure of the SS of the modified BST system. (a, b) Ho 0.04, $x = 0.20$, (c, d) Ho 0.025, $x = 0.50$ and (e, f) Ho 0.01, $x = 0.80$.

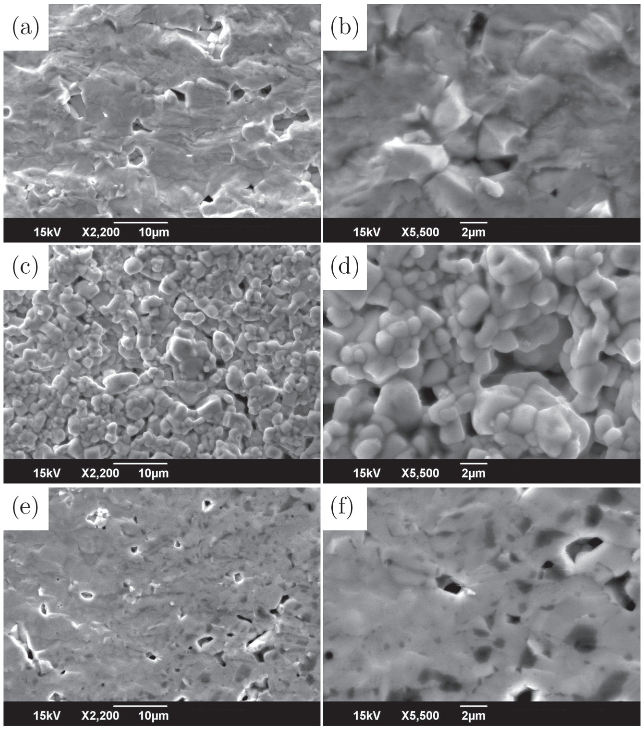

Fig. 11. Fragments of the microstructure of the SS of the modified BST system. (a, b) Er 0.04, $x = 0.20$, (c, d) Er 0.025, $x = 0.50$ and (e, f) Er 0.01, $x = 0.80$.

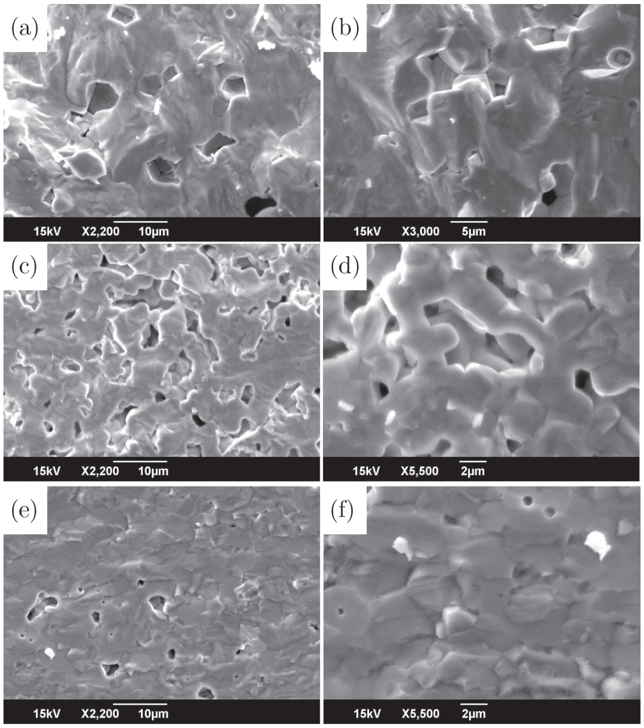

Fig. 12. Fragments of the microstructure of the SS of the modified BST system. (a, b) Tm 0.04, $x = 0.20$, (c, d) Tm 0.02, $x = 0.50$ and (e, f) Tm 0.01, $x = 0.80$.

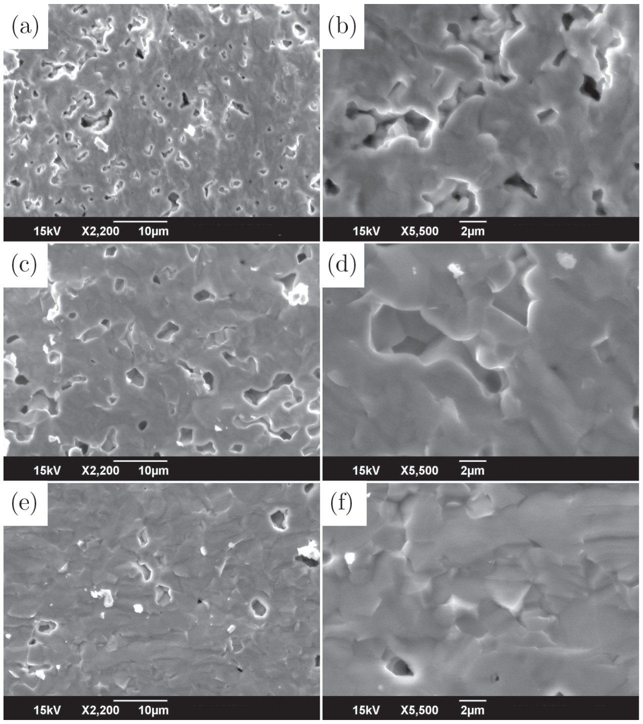

Fig. 13. Fragments of the microstructure of the SS of the modified BST system. (a, b) Yb 0.04, $x = 0.20$, (c, d) Yb 0.025, $x = 0.50$ and (e, f) Yb 0.01, $x = 0.80$.

of ballast phases. The latter act as catalysts for recrystallization processes, provoking the multicluster nature of the grain structure at the primary stage of its formation and, as described above, contributing to its refinement.

Based on the obtained pictures of the grain landscape of the studied ceramics and considering a significant decrease in the average size of crystallites in them in comparison with the basic media, we can assume a decrease in dielectric permittivities in these objects, which we have shown experimentally. This follows from the well-known direct dependence $\varepsilon \sim \bar{d}$.[8] It is this effect that is necessary in the creation of electronic devices for accelerating technology.

Thus, the experience of modifying BST media with REE can be considered successful and effective for the above applications.

## 4. Conclusion

SSs of the composition $Ba_{1-x-y}(Mg, Ln)_xSr_yTiO_3$ ($x = 0.01$; 0.025; 0.04; $y = 0.20$; 0.50; 0.80; Ln = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tu, Yb) were prepared by two-stage solid-phase synthesis followed by sintering using conventional ceramic technology. The influence of RREs on the microstructure of the prepared ceramic samples was investigated. It was found that regardless of the type of modifiers introduced, the grain landscape of the studied SSs with different amounts of $SrTiO_3$ is refined (in the initial system, the average grain size, $\bar{d}$, at $x = 0.20$ is 6 $\mu$m; at $x = 0.50$ is 4 $\mu$m; at $x = 0.80$ is 18 $\mu$m) to crystallite sizes not exceeding (2–3) $\mu$m, and compacted. The use of mechanically activating procedures leads to an even greater decrease in the size $\bar{d}$ and an increase in the density of ceramics. The increasing in the concentration of modifiers in each group (within the considered range of variation of dopants) against the background of such a fine-grained structure has little effect on the dynamics of changes in $\bar{d}$.

It is expedient to use the obtained results in the development of functional materials based on BST/(Mg, Ln) and devices with the participation of these compositions.

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