Structural and dielectric properties of ceramic and thin film multiferroics based on $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$

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Abstract. This paper presents the results of a study of the structural and dielectric properties of barium-strontium titanate ($\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$) with a high concentration of doped manganese ions. It was found that upon the addition of manganese ions, the phase transition point shifts toward lower temperatures. A graph of the dependence of the ceramic lattice parameters on the concentration of manganese ions is presented. It is shown that with an increase in the sintering temperature of ceramics, the dielectric constant of the samples increases.

1. Introduction
Multiferroics have great potential for the development of magnetoelectric [1], magneto-optical [2] and multicaloric [3] devices for solid-state cooling systems. The coupling between the magnetic and electrical subsystems opens up wide possibilities for the use of the material. The control of ferroelectric properties by a magnetic field and vice versa, the control of ferromagnetic properties by an electric field is a distinctive feature of multiferroics. This allows their use in a large number of devices.

One method of preparing artificial multiferroics is doped ferroelectric with ferromagnetic or metal ions.

BST-based ceramics are widely known ferroelectric materials. Doping ceramics with manganese with a high concentration of (5-30) mol % opens up new possibilities for using these materials due to the magnetic properties of manganese (Mn). At a certain concentration of Mn, the studied structures can exhibit the properties of multiferroics. [3,4].

The purpose of the current work is to study the dielectric and structural properties of the ceramic and film samples based on BST solid solution with a high concentration of magnetic ions. Ceramic samples are being investigated to produce planar multiferroic structures based on them.

2. Sample preparation
BST ceramics were made using thermal synthesis in an air atmosphere. $\text{BaCO}_3$, $\text{TiO}_2$ and $\text{MnO}_2$ were mixed in a stoichiometric ratio $\text{Ba}/\text{Sr} = 0.5$ (BST0.5). The synthesis temperature was 1350 °C, 1400 °C, and 1450 °C. The ceramics made had a high density (up to 98%).

BST thin films were deposited by RF magnetron sputtering from a ceramic powder target. The film thickness was $h = 0.5–1.5$ μm [5]. Various substrates were used: sapphire ($\alpha$-$\text{Al}_2\text{O}_3$), lanthanum aluminate (LAO), alumina, gadolinium-gallium garnet (GGG).
Copper electrodes were applied to the samples to form capacitor structures and measure dielectric properties.

Temperature measurements of the sample capacitance were performed with an Agilent E4980A precision LCR meter (Keysight Technologies, USA). A sample in the form of a plate with electrodes was fixed in a special holder placed in a climatic chamber. The measurements were performed in the temperature range from 90 to about 400 K. Measurements were carried out in the frequency range from 100 Hz to 1 MHz. The capacitance measurement precision was 0.05%. XRD was carried out in the Ioffe Institute.

3. Experiment

Figure 1 shows the dependence of the maximum of the dielectric constant vs. frequency for ceramic plane-parallel capacitors. The measurements were carried out for samples with a manganese content of 5% and 10% for all sintering temperatures.

![Figure 1](image_url)

**Figure 1.** Dependence $\varepsilon_{\text{max}}(f)$ for BST0.5 ceramics with 5% Mn and 10% Mn sintered at 1350 °C, 1400 °C and 1450 °C.

It can be seen that the investigated compositions exhibit little dispersion of permittivity in the range from 100 Hz to 1 MHz frequencies [6,7]. Thus, we will consider the dependences $\varepsilon(T)$ only for a frequency of 1 kHz.

Figures 2 (a) and 2 (b) show the temperature dependences of the dielectric constant for compositions BST0.5 + 5% Mn and BST0.5 + 10% Mn, respectively.
The dielectric constant for both compounds takes maximum values at a sintering temperature 1450 °C. Moreover, the $\varepsilon_{\text{max}}$ values for 5% and 10% are close at sintering temperatures of 1400 °C and 1450 °C, and at 1350 °C the dielectric constant is much lower (Figure 2 (a)). Figure 3 shows the temperature dependence of the dielectric constant for samples with a Mn concentration from 0% to 15%.

The addition of Mn to pure BST leads to a strong decrease permittivity, smearing of the phase transition, and a shift of the Curie point more than 50 degrees to the low temperature region. Subsequent doping leads to a further decrease the phase transition temperature. The peak value of the dielectric constant varies slightly.

The dependence of the lattice parameters $a$ vs. the sintering temperature was plotted by the XRD results (Figure 4).
The samples have a cubic lattice with a constant independent of the synthesis temperature. However, it is clearly seen that the lattice constant depends on the concentration of Mn. An increase in the impurity content leads to a decrease in the lattice constant.

At the first stage of the fabrication of thin films, we investigated the effect of various substrates on the properties of the structure.

An analysis of the capacitance temperature dependences of structures grown on various substrates (Figure 2) allows us to conclude that the substrate affects the maximum temperature $T_{\text{max}}$.

![Figure 4](image1.png)

**Figure 4.** The dependence of the lattice parameters $a$ vs. the sintering temperature for BST0.5 + 5%, 10%, 15% Mn.

![Figure 5](image2.png)

**Figure 5.** Dependence $C(T)$ for BST0.5 thin films grown on various substrates.
Depending on the sign and magnitude of the relative deformations, the direction of maximum displacement $T_{\text{max}}$ changes (Figure 5). The sample on the alumina substrate is practically free of stresses and the temperature of maximum $T_{\text{max}} = 260 \text{ K}$. For samples with tensile stresses - BST/LAO - $T_{\text{m}}$ was shifted toward lower temperatures by 20 - 40 K.

Table 1 shows the results of studies of the structures Cu/BST/$\alpha$-Al$_2$O$_3$ with a Mn content of 10% and 15%. X-ray diffraction analysis of the structure of Cu/BST/$\alpha$-Al$_2$O$_3$ with 15% Mn shows the main phase $\text{Ba/Sr} = 0.5/0.5$ with a lattice constant $a = 3.947 \text{ Å}$. The tensile stresses of the substrate and the stresses of the manganese-containing phases affect on the BST film. Therefore, the maximum of temperature dependence of the capacitance of BST (Mn) - $T_{\text{max}}$ samples shifts toward lower temperatures by more than 50 K compared to pure BST samples (Figure 6).

| Composition | Substrate | $T_{\text{max}}, \text{K}$ | Lattice parameter $a$, Å | $\tan$ |
|-------------|-----------|---------------------------|--------------------------|--------|
| $\text{Ba}_0.5\text{Sr}_0.5\text{TiO}_3$ | Ceramics | - | 240 | 3.954 | 0.0005 |
| $\text{Ba}_0.5\text{Sr}_0.5\text{TiO}_3$ | Thin film $\alpha$-Al$_2$O$_3$ | - | 260 | 3.947 | 0.01 |
| $\text{Ba}_0.5\text{Sr}_0.5\text{TiO}_3 + 5\% \text{ Mn}$ | Ceramics | - | 186 | 3.950 | 0.0052 |
| $\text{Ba}_0.5\text{Sr}_0.5\text{TiO}_3 + 10\% \text{ Mn}$ | Ceramics | - | 128 | 3.945 | 0.0827 |
| $\text{Ba}_0.5\text{Sr}_0.5\text{TiO}_3 + 10\% \text{ Mn}$ | Thin film $\alpha$-Al$_2$O$_3$ | - | 166 | - | 0.003 |
| $\text{Ba}_0.5\text{Sr}_0.5\text{TiO}_3 + 15\% \text{ Mn}$ | Ceramics | - | - | 3.937 | 0.022 |
| $\text{Ba}_0.5\text{Sr}_0.5\text{TiO}_3 + 15\% \text{ Mn}$ | Thin film GGG | - | 190 | - | 0.001 |
| $\text{Ba}_0.5\text{Sr}_0.5\text{TiO}_3 + 15\% \text{ Mn}$ | Thin film GGG | - | 180 | 3.947 | - |

The tensile stresses of the substrate and the stresses of the manganese-containing phases affect on the BST film. Therefore, the maximum of temperature dependence of the capacitance of BST (Mn) - $T_{\text{max}}$ samples shifts toward lower temperatures by more than 50 K compared to pure BST samples (Figure 6).

**Figure 6.** Temperature dependences of the capacitance of the pure BST and BST+Mn thin films on various substrates.

4. Discussion

It is known that dopants such as Mn usually occupy the B-site in the perovskite structure ABO$_3$. The ionic radius of Mn$^{2+}$ is 0.8 Å. This is larger than the ionic radius of Ti$^{4+}$ (0.68 Å). As shown by Zhao and Semenov, the substitution of Ti$^{4+}$ ions by Mn$^{2+}$ ions leads to a decrease dielectric losses [8,9].
Mn can replace Ba or Sr ions with partial substitution of titanium positions. The ionic radii of Ba$^{2+}$ and Sr$^{2+}$ are 1.12 Å and 1.34 Å, respectively. This leads to a decrease in the lattice constant, as demonstrated by Huang and Fan [10,11].

Table 1 shows that with an increase in the Mn concentration, the structural and dielectric characteristics of the films and ceramics differ. In ceramics, with increasing impurity concentration, tan increases and the lattice constant decreases. In films, tan decreases, and the lattice constant does not change. The maximum temperature shifts to lower temperatures for both films and ceramics.

Based on the measurement results of the structural and dielectric properties of the samples, as well as from an analysis of the literature, the following conclusions can be drawn.

In films, Mn mainly occupies Ti positions, as evidenced by the shift of $T_{\text{max}}$ and a decrease in tan. Mn also occupies the A-site of ABO$_3$ structure, but the resulting compression strains are compensated by tensile strains from the substrate. The lattice constant does not change.

In ceramics, Mn mainly occupies the A-site, as evidenced by decrease in the lattice constant. Mn partially occupies the Ti positions, as can be seen from the shift $T_{\text{max}}$.

5. Conclusions
Mn additive shifts the phase transition point by more than 50 K both in ceramic and film samples.

The lattice constant is the same for pure BST and for BST + 15 Mn in films. The lattice constant is maximum for pure BST and becomes smaller with increasing concentration of Mn in ceramics.

The influence of tensile and compressive stresses from the side of the substrate and from the side of manganese ions is shown on the dielectric characteristics.

The best sintering mode of multiferroic ceramics at a temperature of 1450 °C makes it possible to obtain samples with high values of dielectric constant.

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