

Diffuse Ferroelectric Phase Transition in SrTiO₃–BiScO₃ System Ceramics

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Received May 7, 2010

Abstract—Ceramic samples of the $(1-x)\text{SrTiO}_3-(x)\text{BiScO}_3$ system with $x = 0, 0.05, 0.1, 0.2, 0.3, 0.4,$ and 0.5 have been synthesized for the first time. X-ray diffraction data showed that the samples with $x = 0.2, 0.3,$ and 0.4 at room temperature comprise the mixture of two phases: (i) cubic nonpolar phase with $Pm3m$ structure and (ii) tetragonal polar phase with $P4mm$ structure. The temperature dependences of permittivity and dielectric loss tangent of these samples exhibit anomalies characteristic of ferroelectrics with diffuse phase transitions.

Strontium titanate SrTiO₃ (STO) possesses a cubic structure at room temperature and exhibits phase transitions to a tetragonal phase at 110 K, then to an orthorhombic phase at 65 K, and eventually a rhombohedral phase is formed below 10 K. Although STO exhibits no ferroelectric activity, it is considered as a potential ferroelectric system in which the ferroelectric phase transition is suppressed by quantum fluctuations [1]. However, the substitution of Sr ions in sublattice A and/or Ti ions in sublattice B of the perovskite-like (ABO₃) structure of STO by other ions introduced either as impurities or as components of solid solutions with STO can initiate the ferroelectric phase transition [2]. Compound BiScO₃ (BSO) possesses a monoclinic structure at room temperature. The question concerning structural phase transitions (including ferroelectric) in this compound is still open [3].

The STO–BSO system is new and practically unstudied. Since the terminal compounds in this system possess different room-temperature structures, one can expect that the STO–BSO system at certain concentrations would exhibit transitions from one to another structure, including the transitions via intermediate phases possessing ferroelectric properties due to a partial substitution of Sr ions by Bi ions and Ti ions by Sc ions. It should be noted that BSO has been widely used in recent years for the creation of binary and ternary solid solutions such as BaTiO₃–BiScO₃ [4], (K_{0.5}Bi_{0.5})TiO₃–BiScO₃–PbTiO₃ [5], and some other.

The present study was aimed at obtaining ceramic samples of the STO–BSO system and characterizing the synthesized compounds as potential ferroelectrics.

Ceramic samples of the $(1-x)\text{STO}-(x)\text{BSO}$ system with $x = 0, 0.05, 0.1, 0.2, 0.3, 0.4,$ and 0.5 have been synthesized from mixtures of ScCO₃, TiO₂, Bi₂O₃, and Sc₂O₃ powders taken in preset stoichiometric ratios. The synthesis was performed in two stages involving the heat treatment at 1073 K (4 h) and 1123 K (4 h). Prior to sintering, the synthesized powder was compacted by means of cold isostatic pressing at 400 MPa. The compacted blanks had the shape of 25-mm-long cylinders with a diameter of 8 mm. These compacts were sintered at various temperatures depending on the composition, beginning with 1623 K for a sample with $x = 0$. As the BSO content x was increased, the sintering temperature was decreased (to 1543 K for $x = 0.5$) for the same treatment time of 5 h. The synthesis and sintering stages were carried out in air.

The structure of sample was studied by X-ray diffraction (XRD). The measurements were performed on a Rigaku Ultima IV diffractometer using Ni-filtered CuK_α radiation. The dielectric permittivity ϵ and loss tangent $\tan\delta$ were measured at a frequency of 1 MHz on an RLC meter of the BR2876 type.

Figure 1 presents the typical XRD diffractograms of ceramic samples measured at 295 K. An analysis of these patterns showed that the samples with $x = 0.05$ and 0.1 possess cubic $Pm3m$ structures (i.e., retain the structure characteristic of pure STO at room temperature). As the BSO content x increases from 0.2 to 0.4, the samples become two-phase, which is manifested by the appearance of reflections assigned to a phase with a tetragonal $P4mm$ structure in addition to the reflections typical of the cubic phase. The most pronounced evidence for the presence of a phase with a tetragonal symmetry is splitting of the (210) peak (characteristic of the cubic structure) into three peaks

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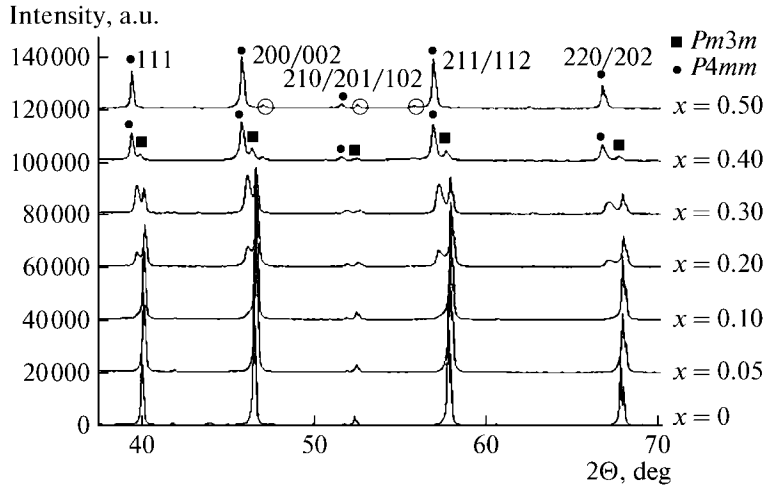


Fig. 1. Typical XRD diffractograms of ceramic samples of the $(1-x)\text{STO}-(x)\text{BSO}$ system with various compositions x . In the XRD pattern for the sample with $x = 0.5$, black circles indicate the reflections due to Bi_2O_3 and Sc_2O_3 oxide components.

corresponding to reflections from the (102), (201), and (210) planes in the tetragonal structure.

As an example, Fig. 2 compares the XRD patterns of samples with $x = 0$ and 0.3. Note that the presence of double diffraction peaks from each plane—which is most pronounced for the (210) reflection, while the (102)/(201) peaks exhibit overlap that hides their exact structure—is caused by the presence of both $\text{Cu}K_{\alpha 1}$ and $\text{Cu}K_{\alpha 2}$ radiation components rather than by some features of the crystalline structure. The peaks due to $\text{Cu}K_{\alpha 1}$ and $\text{Cu}K_{\alpha 2}$ radiation are taken into consideration during the full-profile analysis of XRD patterns so as to refine the exact peak positions. The experimental XRD patterns were processed using a Rigaku PDXL program package. The profiles were smoothed according to the Savitzky–Golay method [6] and the background was subtracted using the Sonnevild–Visser procedure [7].

The XRD pattern obtained for a sample with $x = 0.5$ displays additional reflections due to Bi_2O_3 and Sc_2O_3 oxides, which indicate that the initial components in this mixture do not completely enter into the reaction for the formation of a ceramic. For this reason, this composition was excluded from the subsequent stages of investigation.

Since the samples with $x = 0.2, 0.3,$ and 0.4 are characterized (according to the room-temperature XRD data) by the coexistence of two phases—polar phase with a tetragonal $P4mm$ structure and nonpolar phase with a cubic $Pm3m$ structure—it can be expected that the coexistence of these phases and their thermal evolution will lead to specific features in the dielectric properties, which are characteristic of the ferroelectrics with diffuse phase transitions.

Figure 3 shows the temperature dependences of permittivity ϵ and loss tangent $\tan\delta$ for the samples

with $x = 0.2, 0.3,$ and 0.4. The $\epsilon(T)$ curves exhibit broad maxima, the heights ϵ_m and temperature positions T_m of which depend on the composition. As the BSO content x increases, the peaks increase in the height and shift toward higher temperatures. It is important to note that cooling a sample below T_m is

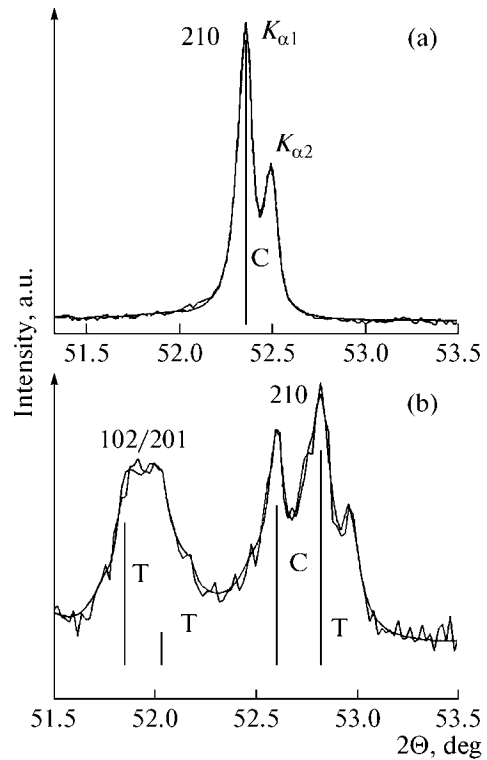


Fig. 2. XRD patterns of the ceramic samples containing (a) only a cubic phase ($x = 0$) and (b) a mixture of cubic and tetragonal phases ($x = 0.3$). Vertical bars C and T indicate peaks of the cubic and tetragonal phase, respectively.

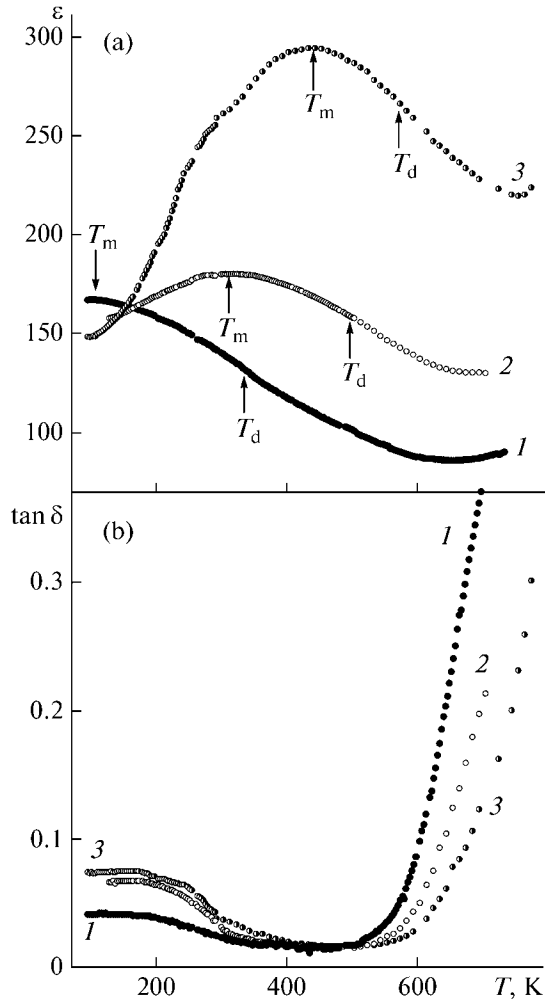


Fig. 3. Temperature dependences of (a) dielectric permittivity ϵ and (b) loss tangent $\tan \delta$ for ceramic samples of the $(1-x)\text{STO}-(x)\text{BSO}$ system with $x = 0.2$ (1), 0.3 (2), and 0.4 (3).

accompanied by an increase in the dielectric losses. This behavior is characteristic of the ferroelectrics with diffuse phase transition [2]. This character of the ferroelectric phase transition is inherent in many multicomponent ceramic systems. It can be related to composition fluctuations, which lead to disorder in

Experimental data and calculated characteristics of ceramic samples of the $(1-x)\text{STO}-(x)\text{BSO}$ system

BSO content x	T_m , K	ϵ_m	C_{CW} , 10^4 K	T_d , K
0.2	100	167	6.84	320
0.3	312	180	10.42	505
0.4	443	295	19.08	570

the ion sublattice A and/or B of the perovskite structure.

As a result, local regions with different chemical compositions and, hence, Curie temperatures appear in the crystal. When the temperature is varied, these regions (polar nanoclusters) are sequentially involved in the phase transformation process and the phase transition takes place in a certain temperature interval. The growth in $\tan \delta(T)$ on heating the samples above ~ 500 K, which can be seen in Fig. 3b, is probably related to an increase in the conductivity with the temperature.

As is known, the permittivity ϵ of the ferroelectrics with diffuse phase transition (in contrast to the usual ferroelectrics with “sharp” phase transition) obeys the Curie–Weiss law not immediately above T_m , but at a somewhat higher temperature T_d called the Burns temperature [7]. The Burns temperature corresponds to a situation where the first polar nanoclusters appear in the paraelectric matrix during the diffuse phase transition from a high-temperature (paraelectric) to low-temperature (ferroelectric) phase [8]. The T_d value is experimentally determined as a point at which the $\epsilon(T)$ curve for $T > T_m$ begins to deviate from the behavior corresponding to the Curie–Weiss law described by the formula

$$\epsilon(T) = \frac{C_{CW}}{T - T_m}, \quad (1)$$

where C_{CW} is the Curie–Weiss constant.

An analysis of the temperature dependences of the permittivity at $T > T_m$ in the samples studied allowed us to determine their Curie–Weiss constants and the Burns temperatures. Experimental data and calculated characteristics of ceramic samples of the $(1-x)\text{STO}-(x)\text{BSO}$ system with $x = 0.2, 0.3,$ and 0.4 are summarized in the table.

Thus, we have experimentally confirmed for the first time that, in the new STO–BSO binary system where both terminal compounds are not ferroelectrics, intermediate compositions can be synthesized that exhibit anomalous dielectric properties characteristic of the ferroelectrics with diffuse phase transition.

Acknowledgments. This study was supported in part by the Ministry of Education and Science of the Russian Federation within the framework of the Federal Targeted Program “Scientific and Pedagogical Staff for Innovative Russia,” project no. P415.

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Translated by P. Pozdeev