RELAXOR PROPERTIES OF THE CERAMIC SOLID SOLUTIONS IN SrTiO₃-BiScO₃ SYSTEM

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1 Introduction

Relaxor ferroelectrics can be considered as natural nanocomposites consisting of polar nanoclusters distributed inside nonpolar matrix [1]. It was recently found that SrTiO₃-BiScO₃ system is new system with relaxor properties [2, 3]. In this system, strontium titanate, SrTiO₃, is known to be an incipient ferroelectric lying near the limit of its paraelectric phase stability [4]. Various ions substituted for the host ions both in the A- and B-positions in ABO₃ perovskite structure can induce a ferroelectric phase transition in SrTiO₃. BiScO₃ is an interesting end member for fabrication of new ceramic solid solutions [5]. Despite its utility in solid solutions, there is little knowledge about the BiScO₃ member itself. In particular, it is not known at present whether BiScO₃ is ferroelectric [6]. Although it has been speculated that it may be ferroelectric, no experimental confirmations were reported.

SrTiO₃-BiScO₃ system is new and attractive system in a family of ceramic solid solutions with BiScO₃ as one of the end members. At room temperature SrTiO₃ has a cubic Pm3n structure, while BiScO₃ is a monoclinic C2/c compound. Therefore, change of symmetry from cubic to monoclinic should be observed as the mole fraction of BiScO₃ increased. Moreover, taking into account a considerable difference in structures of the end members in SrTiO₃-BiScO₃ system, intermediate phases with other symmetries including polar structures may be expected to be formed for some compositions. The calcined powders were then cold isostatically pressed at 400 MPa. The pressed samples were sintered at 1623 K for 5 h. The weight loss during sintering was confirmed to be < 1% for all samples. An additional 3 mol% Bi₂O₃ was added as a sintering aid before pressing the samples for compositions with x=0, 0.05 and 0.1. It is known that the excess Bi₂O₃ can improve the densities of the samples during the sintering, because Bi₂O₃ has a melting temperature of about 1100 K, which is lower than the sintering temperatures used in this study. The densities of all samples were higher than 90% value of theoretical density.

X-ray diffraction analysis (XRD) was performed at room temperature for phase determination using a Rigaku Ultima IV diffractometer with CuKα radiation. EBSD method (scanning electron microscope Quanta 200 3D) was used to estimate a distribution of phases with various crystal structures. Dielectric properties of the samples were measured using BR2876 LRC-meter.

3 Experimental results and discussion

Analysis of the XRD patterns taken at room temperature allows us to conclude that all compositions under study (excepting pure SrTiO₃) consist of mixture of nonpolar cubic Pm3m phase and polar tetragonal P4/mmm phase. Concentration dependences of lattice parameters for tetragonal, a and b, and cubic, a, phases extracted from XRD patterns are presented in Fig. 1 (a) and (b). Tetragonal structures can be formally reduced to cubic structures with unit-cell parameter calculated as \( a = (a^2 b^3)^{1/6} \), where \( a \) and \( b \) are tetragonal cell parameters derived experimentally. The \( a, x \) dependence is also shown in Fig. 1 (c). All of lattice parameters in Fig.1 arise with \( x \) increasing. However, in contrast with Vegard’s law prediction all of the concentration dependences of lattice parameters are nonlinear.
In order to get an additional evidence of two-phase coexisting in the samples under study, EBSD mapping was applied. Imaging a few phases with various structures can be done by this method. As an example, Fig. 2 shows EBSD images for the samples with $x=0.2$ and 0.45 taken at room temperature. In this figure the red color is corresponding to the cubic phase, while the green color presents the tetragonal phase. It can be seen that the cubic phase is predominant for the composition with $x=0.2$, but composition with $x=0.45$ is enriched by the tetragonal phase. The dependencies of the cubic and tetragonal phase fractions, $V_m$, are presented in Fig. 3. It was found that fraction of the cubic phase decreases and fraction of the tetragonal phase increases when $x$ arises.

It is known [1] that the phase coexisting of polar and nonpolar phases at some temperature range is one of specific signs of relaxor ferroelectrics. It is important that almost all of models of relaxor state consider relaxor as a nonpolar paraelectric matrix containing the polar nanoregions. Each of these nanoregions may have its own Curie temperature. The polar nanoregions with the suitable Curie temperatures will take part at phase transition at cooling from paraelectric phase to relaxor state consisting of polar nanoregions distributed within a nonpolar matrix. So, diffusing the ferroelectric phase transition is originated from distribution of the Curie temperatures in inhomogeneous material.

Relaxors are characterized by anomalous behavior of dielectric properties. Figure 4 shows the dielectric permittivity $\varepsilon$ and $\varepsilon'$ versus temperature for the samples with $x=0.2$, 0.25, 0.3, 0.4 and 0.45 (the measurement frequency is 1 MHz). Broad peaks of $\varepsilon$ are observed in the $\varepsilon(T)$ dependences. It was found that temperature of the $\varepsilon(T)$ peak, $T_m$, increased with increasing BiScO$_3$ content. In addition, increasing the dielectric losses $\varepsilon''$ was observed at cooling the samples below $T_m$. Such kind of anomalous behavior of the dielectric properties is typical for ferroelectrics at the ferroelectric phase transitions.

For ferroelectrics with sharp phase transition the temperature dependence of $\varepsilon$ for high-temperature part of the $\varepsilon(T)$ peak obeys the Curie-Weiss law. In this case the dependence of $1/\varepsilon$ versus temperature should be linear. It was found that experimental $\varepsilon(T)$ curves in Fig. 4 start to deviate from the Curie-Weiss behavior just below some temperature $T_d$ [7]. This feature can be taken as an evidence of diffusing the phase transition under study. The temperature $T_d$ called as the Burns temperature is corresponding to appearance of polar nanoregions inside a nonpolar matrix during diffuse phase transition.

Temperatures $T_m$ and $T_d$, and the temperature Curie, $\theta$, and the Curie-Weiss constant, $C_{CW}$, for the samples $(1-x)$SrTiO$_3$-$x$BiScO$_3$ with various $x$ are listed in Table 1.

For diffuse phase transition, the dependence $\varepsilon(T)$ between $T_d$ and $T_m$ can be fitted by expression [8]

$$\frac{\varepsilon_m}{\varepsilon(T)} = 1 + \frac{(T - T_m)^{\gamma}}{2\sigma^2} \quad (1)$$

where $\sigma$ is the degree of diffuseness of a phase transition and $\gamma$ is degree of dielectric relaxation. For sharp ferroelectric phase transition $\gamma = 1$ and consequent diffusing the phase transition leads to $\gamma$ increasing up to 2 at that larger values of $\gamma$ express more relaxor behavior of ferroelectric. By analyzing of dielectric properties between $T_d$ and $T_m$ of the samples with $x=0.2$, 0.25, 0.3, 0.4 and 0.5 it was found that expression (1) reproduces experimental data very well (Fig. 5). Both $\gamma$ and $\sigma$ were determined from the slope and intercept of lines in linear parts of dependences of $\ln((\varepsilon_m/\varepsilon))=1$ versus $\ln(T-T_m)$.

Let us analyze the concentration dependence of $\sigma$ within the framework of the Smolenskii-Isupov model [9] developed for two-component systems $A(B'_{1-x}B''_{x})O_3$ or $(A'_{1-x}A''_{x})BO_3$. This model gives the following expression for the degree of diffuseness

$$\sigma = \frac{\delta^2 x(1-x)^{\gamma/2}}{n} \quad (2)$$

where $n$ is the number of units cells in the critical nucleus and $\delta$ is parameter characterizing the concentration dependence of the Curie temperature. According to expression (2), the degree of diffuseness should be increased with increase of a disorder degree in the system under study. The disorder degree can be approximately expressed as a product of $x(1-x)$. It was found that experimental dependence of $\sigma$ versus $x(1-x)$ for the samples under study is in qualitative agreement with expression (1) (Fig. 6). A higher degree of diffuseness in the samples with a greater percentage of BiScO$_3$ can be explained by the increased cation disorder due to the substitution on the A-site by Bi and on the B-site by Sc in the SrTiO$_3$ structure.

Temperature dependence of dielectric permittivity $\varepsilon$ for relaxors can be analyzed in the spherical random field-random bond model [10]. The
SRFRB model predicts a transition to the ferroelectric phase, the dipolar glass state or mixed ferroelectric-dipolar glass state at various values of model parameters. One can find the parameters of the SRFRB model using data of dielectric measurements.

The order parameter q of the transition to the dipolar glass state above Tm can be calculated from the corresponding ε(T) curve using the following relationship

\[ q(T) = 1 - \frac{T \varepsilon(T)}{C_{cw} + (J_0/k) \varepsilon(T)} \]  

(3)

Here \( J_0 \) is the mean energy of polar cluster interaction and \( k \) is the Boltzmann constant. If \( q = 0 \), then expression (3) is transformed to the Curie-Weiss law, where the temperature \( \theta = J_0/k \). As an example, the temperature dependence of \( q \) for the sample with \( x = 0.2 \) is shown as scattered curve in Fig. 7.

At the same time parameter \( q \) can be expressed through microscopic model parameters

\[ q = \beta^2 J^2 \left( q + \frac{\Delta}{J} \right) (1-q)^2 + P^2 \]  

(4)

where \( \beta = 1/kT \), \( P \) is a polarization, \( \Delta \) and \( J^2 \) are variances of the random field strength and energy interaction, correspondingly. The \( q(T) \) dependence, calculated using the formula (4) for temperatures \( T > T_m \), where \( P = 0 \), satisfactorily agrees with experimental \( q(T) \) curve (solid line in Fig. 7).

The SRFRB model parameters extracted from the best fitting for all compositions under dielectric measurements are listed in Table 2. The SRFRB model predicts a transition to the spherical glass state when the following condition is fulfilled

\[ \frac{J_0}{k} \theta < \left[ \left( \frac{J}{k} \right) + \frac{\Delta}{k^2} \right]^{\frac{1}{2}} \]  

(5)

Taking into account expression (5) one can conclude from data of Tables 1 and 2 that the samples of the (1-x)SrTiO\(_3\)-xBiScO\(_3\) system should undergo a transition to the spherical glass state.

X-ray data and EBSD mapping results can be taken as evidences of glass state in the samples under study. Nonpolar cubic phase can be attributed to this state. However, the polar tetragonal phase was also found to co-exist with the cubic phase. So, the mixed ferroelectric-dipolar glass state can be realized in the ceramic of (1-x)SrTiO\(_3\)-xBiScO\(_3\) materials.

It is known [11] that simultaneous substitution of the host Sr\(^{2+}\) and Ti\(^{4+}\) ions in SrTiO\(_3\) structure by impurity ions by fabrication of solid solutions give some specific effects. For example, in SrTiO\(_3\)-PbMg\(_{1/3}\)Nb\(_{2/3}\)O\(_3\) the diffuse ferroelectric phase transition was observed only at \( x > 0.2 \) with a linear dependence of the transition temperature on composition which was associated with random fields due to disordered Mg\(^{2+}\) and Nb\(^{5+}\) distribution. Peculiarities of properties of SrTiO\(_3\)-BiScO\(_3\) system found in our research are similar to the same peculiarities of SrTiO\(_3\)-PbMg\(_{1/3}\)Nb\(_{2/3}\)O\(_3\) system and can be attributed to the diffuse ferroelectric phase transition. But in contrast with SrTiO\(_3\)-PbMg\(_{1/3}\)Nb\(_{2/3}\)O\(_3\) system where PbMg\(_{1/3}\)Nb\(_{2/3}\)O\(_3\) is relaxor ferroelectric, in SrTiO\(_3\)-BiScO\(_3\) both of the end members are not ferroelectrics.

4 Conclusion

Ceramic solid solutions of (1-x)SrTiO\(_3\)-xBiScO\(_3\) system with \( x = 0.05, 0.1, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45 \) and 0.5 were synthesized via solid-state processing techniques. End members in this system are not ferroelectrics. XRD analysis revealed that at room temperature all compositions under study (excepting pure SrTiO\(_3\)) consist of mixture of nonpolar cubic \( \text{Pm3m} \) phase and polar tetragonal \( \text{P4mm} \) phase. EBSD mapping was applied to image a two-phase structure. It was found that fraction of the cubic phase decreases and fraction of the tetragonal phase increases when \( x \) arises.

Dielectric anomalies associated with a diffuse ferroelectric phase transition were found and analyzed for these compositions.

The relaxor ferroelectric behavior was likely due to complex processes of cation substitution and ordering on the A-site and on the B-site.

Acknowledgements

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Fig. 1. Concentration dependences of the lattice parameters for various phases for the ceramic \((1-x)\text{SrTiO}_3-x\text{BiScO}_3\) materials.

Fig. 2. EBSD images for the samples with \(x=0.2\) (a) and 0.45 (b).

Fig. 3. Concentration dependences of the cubic and tetragonal fractions for the ceramic \((1-x)\text{SrTiO}_3-x\text{BiScO}_3\) materials.

Fig. 4. Temperature dependences of \(\varepsilon'\) (a) and \(\varepsilon''\) (b) for of \((1-x)\text{SrTiO}_3-x\text{BiScO}_3\) solid solutions: 1 - \(x=0.2\), 2 - 0.25, 3 - 0.3, 4 - 0.4 and 5 – 0.45.
Fig. 5. The dependences of $\ln\left(\frac{(\varepsilon_m' - \varepsilon')}{\varepsilon'}\right)$ versus $\ln(T - T_m)$ for the samples with $x=0.2$ (a), 0.25 (b), 0.3 (c), 0.4 (d) and 0.45 (e).

Fig. 6. The dependence of $\sigma$ versus $x(1-x)$ for the ceramic $(1-x)\text{SrTiO}_3-x\text{BiScO}_3$ materials.

Fig. 7. The $q(T)$ dependence for the sample with $x=0.2$. Solid line is the SFRFB model curve.

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Table 2. SFRRB model parameters

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References


