

УДК 54.057

## RELAXOR PROPERTIES OF CERAMIC SOLID SOLUTIONS IN SrTiO<sub>3</sub>-BiScO<sub>3</sub> SYSTEM

E.P. Danshina, O.N. Ivanov, T.I. Yurchenko

Belgorod State University,  
Pobedy St., 85, Belgorod, 308015, Russia, e-mail: [Ivanov.Oleg@bsu.edu.ru](mailto:Ivanov.Oleg@bsu.edu.ru)

**Abstract.** For the first time, ceramic solid solutions of (1-x)SrTiO<sub>3</sub>-xBiScO<sub>3</sub> system with  $x = 0, 0.05, 0.1, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45$  and 0.5 have been synthesized via solid-state processing techniques. End compounds of this system are not ferroelectric materials. The XRD analysis revealed that, at room temperature, all compositions under study (excepting pure SrTiO<sub>3</sub>) consist of mixture of the center-symmetric cubic Pm3m phase and the polar tetragonal P4mm phase. The EBSD mapping has applied to image two-phase structure. It was found that fraction of the cubic phase decreases and fraction of the tetragonal phase increases when  $x$  arises. Anomalous behavior of dielectric permittivity and dielectric losses have been found for these samples which are specific for ferroelectrics with diffuse phase transition.

**Key words:** relaxors, diffuse phase transition, dielectric properties.

### 1. Introduction

Relaxor ferroelectrics may be considered as natural nanocomposites consisting of polar nanoclusters distributed inside nonpolar matrix [1]. It was recently found that SrTiO<sub>3</sub>-BiScO<sub>3</sub> system is new system with relaxor properties [2, 3]. In this system, strontium titanate, SrTiO<sub>3</sub>, 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 the ABO<sub>3</sub> perovskite structure can induce the ferroelectric phase transition in SrTiO<sub>3</sub>.

BiScO<sub>3</sub> is an interesting end member for fabrication of new ceramic solid solutions [5]. Despite its utility in solid solutions, there is a little knowledge about the BiScO<sub>3</sub> member itself. In particular, it is not known at present is whether BiScO<sub>3</sub> ferroelectric [6]? Although it has been speculated that it may be ferroelectric, no experimental confirmations were reported.

The SrTiO<sub>3</sub>-BiScO<sub>3</sub> system is the new and attractive one in the family of ceramic solid solutions with BiScO<sub>3</sub> as one of the end members. At room temperature, SrTiO<sub>3</sub> has the cubic Pm3m structure while BiScO<sub>3</sub> is the monoclinic C2/c compound. Therefore, change of symmetry from cubic to monoclinic should be observed as the mole fraction of BiScO<sub>3</sub> increased. Moreover, taking into account the essential difference in structures of end members in the SrTiO<sub>3</sub>-BiScO<sub>3</sub> system, intermediate phases with other symmetries including polar structures may be expected to be formed for some compositions.

## 2. Experimental procedure

Ceramic solid solutions of  $(1-x)\text{SrTiO}_3-x\text{BiScO}_3$  with  $x=0, 0.05, 0.1, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45$  and  $0.5$  were synthesized via solid-state processing techniques from powders of  $\text{SrCO}_3$ ,  $\text{TiO}_2$ ,  $\text{Bi}_2\text{O}_3$  and  $\text{Sc}_2\text{O}_3$  taken as starting materials. After preliminary milling and drying, powders were calcined at  $1073\text{ K}$  for  $4\text{ h}$  and at  $1123\text{ K}$  for  $4\text{ h}$  at air atmosphere. Then, calcined powders were cold isostatically pressed at  $400\text{ MPa}$ . The pressed samples were sintered at  $1623\text{ K}$  for  $5\text{ h}$ . The weight loss during sintering was confirmed to be  $< 1\%$  for all samples. The additional  $3\text{ mol\% Bi}_2\text{O}_3$  was added as sintering aid before pressing the samples to compositions with  $x=0, 0.05$  and  $0.1$ . It is known that the excess  $\text{Bi}_2\text{O}_3$  can improve the densities of samples during the sintering because  $\text{Bi}_2\text{O}_3$  has the melting temperature near  $1100\text{ K}$  which is lower than the sintering temperatures used in this study. The densities of all samples were higher than  $90\%$  value of theoretical density.

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

## 3. Experimental results and discussion

Analysis of the XRD patterns taken at room temperature allows to conclude that all compositions under study (excepting pure  $\text{SrTiO}_3$ ) consist of mixture of nonpolar cubic Pm3m phase and polar tetragonal P4mm phase. Concentration dependences of lattice parameters for tetragonal,  $a_T$  and  $b_T$ , and cubic,  $a_C$ , phases extracted from the 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  $a_r = (a_T^2 b_T)^{1/3}$  where  $a_T$  and  $b_T$  are tetragonal cell parameters derived experimentally. The  $a_r(x)$  dependence is also shown in Fig. 1 (c). All lattice parameters in Fig. 1 arise with the  $x$  increasing. However, in contrast with Vegard's law prediction all concentration dependences of lattice parameters are nonlinear.

In order to get an additional evidence of two-phase coexisting in samples under study, the EBSD mapping was applied. Imaging of a few phases with various structures can be done by this method. As an example, Fig. 3 shows EBSD images for samples with  $x=0.2$  and  $0.45$  taken at room temperature. In this figure, the red color corresponds to cubic phase while the green color presents tetragonal phase. One can see that the cubic phase is predominant for the composition with  $x = 0.2$ , but the composition with  $x = 0.45$  is enriched by the tetragonal phase. The dependences of cubic and tetragonal phase fractions,  $V_f$  are presented in Fig. 4. It was found that the fraction of cubic phase decreases and the fraction of 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 local 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, the diffusing of ferroelectric phase transition is originated from distribution of Curie's temperatures in inhomogeneous material.

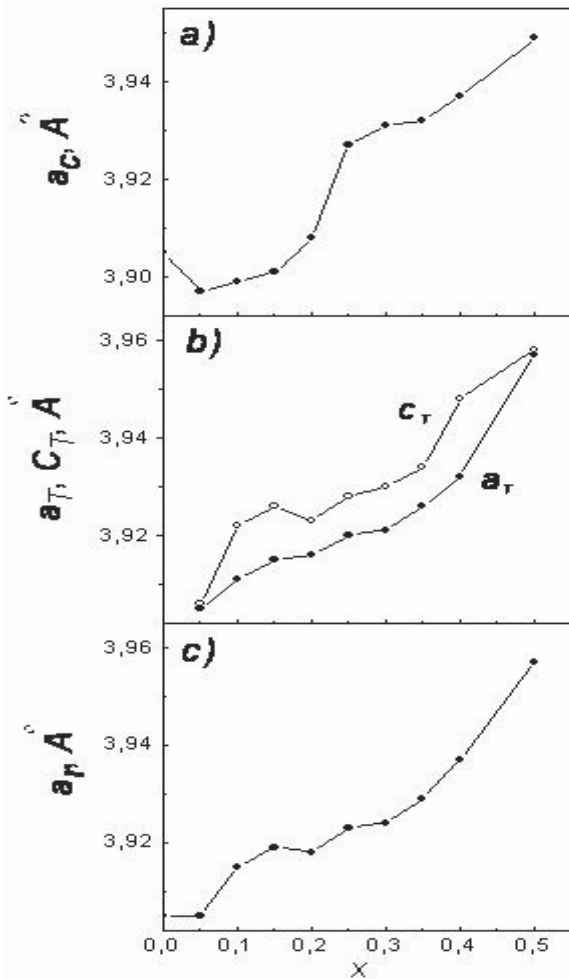


Fig. 1. Concentration dependences of lattice parameters for various phases of ceramic  $(1-x)\text{SrTiO}_3-x\text{BiScO}_3$  materials.

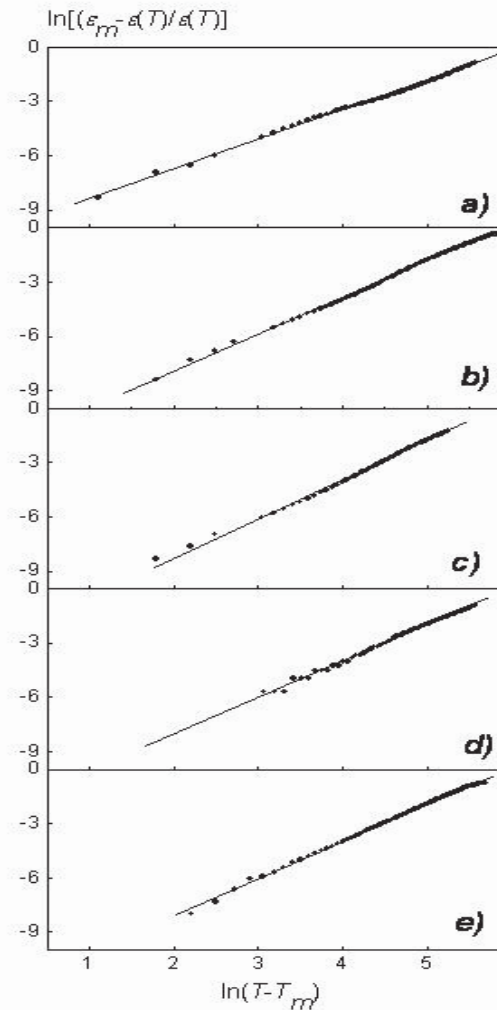


Fig. 2. Dependences of  $\ln[(\epsilon_m/\epsilon) - 1]$  versus  $\ln(T - T_m)$  for samples with  $x = 0.2$  (a),  $0.25$  (b),  $0.3$  (c),  $0.4$  (d) and  $0.45$  (e).

Relaxors are characterized by anomalous behavior of dielectric properties. Fig. 5 shows the dielectric permittivity  $\epsilon$  and  $\epsilon''$  versus temperature of samples with  $x=0.2, 0.25, 0.3, 0.4$  and  $0.45$  (the measurement frequency is 1 MHz). Broad peaks of  $\epsilon$  are observed in the  $\epsilon(T)$  dependences. It was found that the temperature  $T_m$  of the  $\epsilon(T)$  peak increases with the

increasing of  $\text{BiScO}_3$  content. In addition, the increasing of dielectric losses  $\epsilon''$  was observed at cooling of samples below  $T_m$ . Such a kind of anomalous behavior of dielectric properties is typical for ferroelectrics at ferroelectric phase transitions.

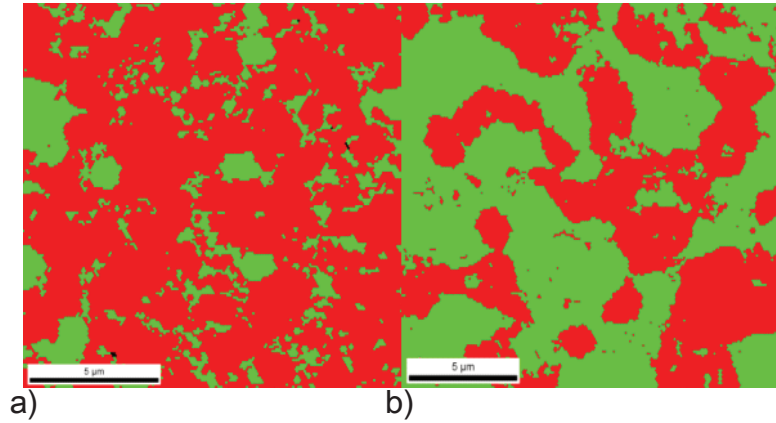


Fig. 3. EBSD images of samples with  $x = 0.2$  (a) and  $0.45$  (b).

For ferroelectrics with sharp phase transition the peak of the  $\epsilon(T)$  temperature dependence in high-temperature region obeys the Curie-Weiss law. In this case the dependence of  $1/\epsilon$  versus temperature should be linear. It was found that experimental  $\epsilon(T)$  curves in Fig. 5 start to deviate from the Curie-Weiss behavior just below some temperature  $T_d$  [7]. This feature can be taken as an evidence of the diffusing of phase transition under study. The temperature  $T_d$  called as the Burns temperature is corresponding to appearance of polar nanoregions inside nonpolar matrix during diffuse phase transition.

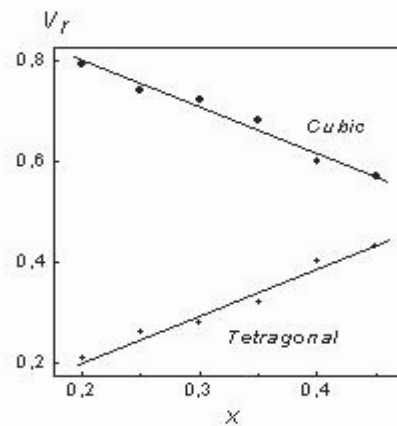


Fig. 4. Concentration dependences of the cubic and tetragonal fractions of ceramic  $(1-x)\text{SrTiO}_3-x\text{BiScO}_3$  materials.

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

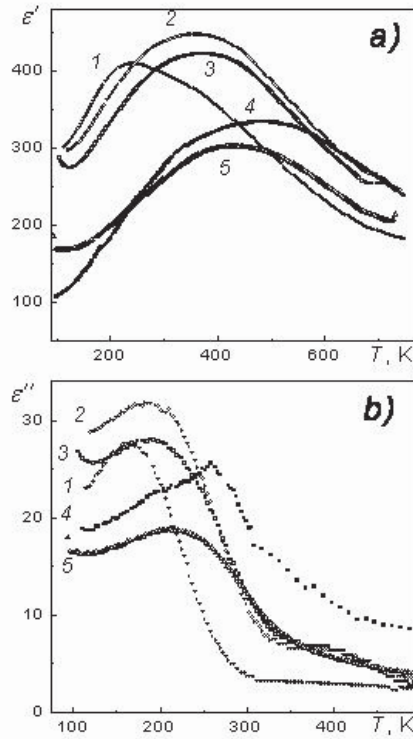


Fig. 5. Temperature dependences of  $\epsilon$  (a) and  $\epsilon$  (b) corresponding to  $(1-x)\text{SrTiO}_3-x\text{BiScO}_3$  solid solutions: 1 –  $x = 0.2$ , 2 –  $0.25$ , 3 –  $0.3$ , 4 –  $0.4$  and 5 –  $0.45$ .

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

$$\frac{\epsilon_m}{\epsilon(T)} = 1 + \frac{(T - T_m)^\gamma}{2\sigma^2} \quad (4.1)$$

where  $\sigma$  is the diffuseness degree of phase transition and  $\gamma$  is the dielectric relaxation degree.

Table 1

Dielectric data and characteristics of diffuse phase transition in  $(1-x)\text{SrTiO}_3-x\text{BiScO}_3$

x	$T_m$ , K	$T_d$ , K	$\gamma$ , K	$C_{CW}$ , $10^5$ , K
0.2	245	505	145	1.05
0.3	358	550	155	1.40
0.35	370	565	175	1.29
0.4	470	640	180	1.34
0.45	430	585	160	1.11

For sharp ferroelectric phase transition,  $\gamma = 1$  and its consequent diffusing leads to the  $\gamma$  increasing up to 2 so that at larger  $\gamma$  values it is appeared more relaxor behavior. By analyzing of dielectric properties between  $T_d$  and  $T_m$  of 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. 2). Both  $\gamma$  and  $\sigma$  were determined from linear parts of  $\ln[(\epsilon_m/\epsilon) - 1]$  versus  $\ln(T - T_m)$  dependences.

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 diffuseness degree

$$\sigma = \frac{\delta^2 x(1-x)^{1/2}}{n} \quad (4.2)$$

where  $n$  is the number of unit cells in critical nucleus and  $\delta$  is the parameter characterizing the concentration dependence of Curie's temperature.

According to the expression (2), the diffuseness degree should be increased with the increase of disorder degree in the system under study. The disorder degree can be approximately expressed as the product of  $x(1-x)$ . It was found that experimental dependence of  $\sigma$  versus  $x(1-x)$  for samples under study is in qualitative agreement with the expression (1) (Fig. 6). The higher diffuseness degree of samples with the greater percentage of  $\text{BiScO}_3$  can be explained by the increased cation disorder due to substitution on the A-site by Bi and on the B-site by Sc in the  $\text{SrTiO}_3$  structure.

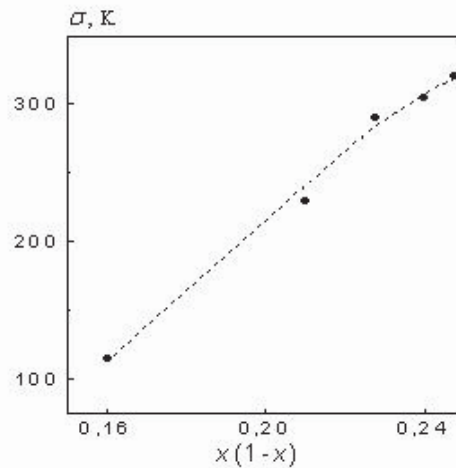


Fig. 6. Dependence of  $\sigma$  versus  $x(1-x)$  of ceramic  $(1-x)\text{SrTiO}_3-x\text{BiScO}_3$  materials.

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

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

$$q(T) = 1 - \frac{T\epsilon(T)}{C_{CW} + (J_0/k)\epsilon(T)} \quad (4.3)$$

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

At the same time, the parameter  $q$  can be expressed by microscopic model parameters

$$q = \beta^2 J^2 q + \frac{A}{J^2} (1 - q)^2 + P^2 \quad (4.4)$$

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

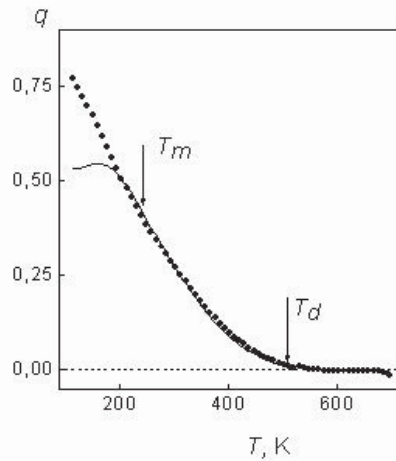


Fig. 7. The  $q(T)$  dependence for the sample with  $x=0.2$ .

Solid line is the SRFRB model curve.

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

$$\frac{J_0}{k} = \theta < \frac{8C}{k} + \frac{1}{k^2} \quad (4.5)$$

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

Table 2

SFRRB model parameters

x	$J^2, K^{-2}$	J/k, K	$J/k^2, K^2$
0.2	0.004	410	670
0.3	0.002	470	440
0.35	0.0008	480	185
0.4	0.0006	590	210
0.45	0.0006	545	180

X-ray data and results of the EBSD mapping can be taken as evidences of glass state in samples under study. Nonpolar cubic phase can be attributed to this state. However, it has been found that the polar tetragonal phase may co-exist with the cubic phase.

So, the mixed ferroelectric-dipolar glass state can be realized in the ceramic of  $(1-x)\text{SrTiO}_3-x\text{BiScO}_3$  materials.

It is known [11] that simultaneous substitution of host  $\text{Sr}^{2+}$  and  $\text{Ti}^{4+}$  ions in the  $\text{SrTiO}_3$  structure as impurity ions at the production of solid solutions leads to some specific effects. For example, the diffuse ferroelectric phase transition in  $\text{SrTiO}_3\text{-PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$  was observed only at  $x > 0.2$  with the linear dependence of transition temperature on the composition which may be associated with random fields due to the disordered  $\text{Mg}^{2+}$  and  $\text{Nb}^{5+}$  distribution.

Property peculiarities of the  $\text{SrTiO}_3\text{-BiScO}_3$  system having been found in our research are similar to the same peculiarities of the  $\text{SrTiO}_3\text{-PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$  system and they can be attributed to the diffuse ferroelectric phase transition. But in contrast with the  $\text{SrTiO}_3\text{-PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$  system where  $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$  is relaxor ferroelectric, in  $\text{SrTiO}_3\text{-BiScO}_3$  both of the end members are not ferroelectric.

### 3. Conclusion

Ceramic solid solutions of the  $(1-x)\text{SrTiO}_3-x\text{BiScO}_3$  system with  $x=0, 0.05, 0.1, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45$  and  $0.5$  were synthesized via solid-state processing techniques. End members in this system are not ferroelectric. The XRD analysis revealed that, at room temperature, all compositions under study (excepting the pure  $\text{SrTiO}_3$ ) consist of mixture of the nonpolar cubic  $\text{Pm}3\text{m}$  phase and the polar tetragonal  $\text{P}4\text{mm}$  phase. The EBSD mapping was applied to image the 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 diffuse ferroelectric phase transition were found and analyzed for compositions pointed out.

Due to complex processes of cation substitution and ordering on the A-site and on the B-site, the relaxor ferroelectric behavior was like.



## Acknowledgements

The work was performed in the framework of the federal target program "Research and Development on Priority Directions of Scientific-Technological Complex of Russia in 2007–2012" under Contract No 16.552.11.7004.

1. Lines M.E., Glass A.M. / Oxford: Clarendon Press, 1977.
2. Ivanov O., Danshina E., Tuchina Yu., Sirota V. // Phys. Status Solidi B. – 2011. – 248;4. – P.1006-1009.
3. Ivanov O., Danshina E., Tuchina Yu., Sirota V. // Advances in Science and Technology. – 2010. – 67. – P.59-63.
4. Muller K.A., Burkard H. // Phys. Rev. B. – 1979. – 9; 7. – P.3593-3602.
5. Eitel R.E., Randall C.A., Shrout T.S., Park S.-E. // Jpn. J. Appl. Phys. – 2002. – 41. – P.2099-2104.
6. Trolier-McKinstry S., Bieganski M.D., Wang J., Belik A.A., Takayama-Muromachi E., Levin I. // J. Appl. Phys. – 2008. – 104. – 044102-01-07.
7. Viehland D., Jang S.J., Cross L.E., Wuttig M. // Phys. Rev. B. – 1992. – 46. – 13. – P.8003-8006.
8. Huang C.-C., Cann D.P., Tan X., Vittayakorn N. // J. Appl. Phys. – 2007. – 102. – P.0444103-1.
9. Smolenskii G.A., Bokov V.A., Isupov V.A. / Saint-Petersburg: Nauka, 1971.
10. Pirs R., Blinc R. // Phys. Rev. B. – 1999. – 60;19. – P.13470-13478.
11. Lemanov V.V. // Ferroelectrics – 2002. – 265. – P.1-21.

SrTiO<sub>3</sub>-BiScO<sub>3</sub>

....., .....

....., 85, ....., 308015, ....., e-mail: Ivanov.Oleg@bsu.edu.ru

. Впервые синтезированы керамические твердые растворы системы (1-x)SrTiO<sub>3</sub>-xBiScO<sub>3</sub> с x = 0, 0.05, 0.1, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45 и 0.5 по керамической технологии. В данной системе оба крайних компонента не являются сегнетоэлектрическими материалами. Данные рентгеноструктурного анализа показали, что при комнатной температуре все составы (кроме чистого SrTiO<sub>3</sub>) состоят из смеси centro-симметричной кубической Pm3m фазы и полярной тетрагональной P4mm фазы. Проведен EBSD анализ для подтверждения наличия двухфазной структуры. Было обнаружено, что количество кубической фазы уменьшается, а тетрагональной фазы

увеличивается при увеличении концентрации  $x$ .

Для этих образцов на температурных зависимостях диэлектрической проницаемости и диэлектрических потерь обнаружены аномалии, характерные для сегнетоэлектриков с размытым фазовым переходом.

: релаксоры, размытый фазовый переход, диэлектрические свойства.