

Formation of Ceramic Solid Solutions in a $\text{SrTiO}_3\text{--BiScO}_3$ System

O. N. Ivanov, E. P. Dan'shina, V. V. Sirota, and I. D. Tarasova

Belgorod State University, Diagnostics of the Structure and Properties of Nanomaterials
Joint Research Center, ul. Pobedy 85, Belgorod, 308015 Russia
e-mail: Ivanov.Oleg@bsu.edu.ru

Abstract—X-ray structural, X-ray phase, and dilatometric analyses were used to explore specific features of the formation of solid solutions in the $(1-x)\text{SrTiO}_3\text{--}x\text{BiScO}_3$ system with $x = 0.0, 0.1, 0.2, 0.3, 0.4,$ and 0.5 . It was found that the synthesis of solid solutions from the initial Bi_2O_3 , Sc_2O_3 , TiO_2 , and SrCO_3 components is accompanied by a considerable increase in the linear dimensions of the samples, depending on their composition. Solid solutions with $x > 0.1$ are formed through intermediate phases ($\text{Sr}_5\text{Bi}_6\text{O}_{14}$ at $x = 0.2$; $\text{Sr}_{0.78}\text{Bi}_{2.22}\text{O}_4$ at $x = 0.3$; and $\text{Sr}_{2.25}\text{Bi}_{6.75}\text{O}_{12.38}$ at $x = 0.4$ and 0.5). It was shown that the samples with $x = 0.2, 0.3, 0.4,$ and 0.5 have two phases: one with a cubic $Pm\bar{3}m$ structure and one with a tetragonal $I4/mcm$ structure.

INTRODUCTION

A problem of great interest to physical materials science is the development of lead-free ceramic materials [1–3]. Lead-free ceramic systems are sought among solid solutions whose phase equilibrium diagrams include a morphotropic interface at which the physical properties of the system can reach their extreme values [4, 5]. The $\text{SrTiO}_3\text{--BiScO}_3$ system is a new system of great interest for investigations regarding the development of future functional materials with ferroelastic and ferroelectric properties.

In this system, SrTiO_3 is a virtual ferroelectric with a cubic structure at room temperature [6]. As the temperature decreases, a series of phase transitions (a ferroelastic transition from a cubic to a tetragonal structure at 110 K; a transition to a rhombic phase at 65 K; and the final formation of a rhombohedral structure below 10 K) takes place in the strontium titanate. None of these transitions is ferroelectric. Unlike SrTiO_3 , the BiScO_3 compound has been studied poorly since it is difficult to produce. Because of the large difference between the ionic radii of Bi and Sc, BiScO_3 compound is formed only under the conditions of high-temperature synthesis at high pressures of ~ 6 GPa [7]. At room temperature, BiScO_3 has a monoclinic structure. The question as to the presence of any structural phase transitions in this compound remains open. Since the edge components in the $\text{SrTiO}_3\text{--BiScO}_3$ system have different structures at room temperature, it may be expected that at some concentrations, a transition from one structure to another will take place in solid solutions based on this system. In other words, the phase diagram will have a region of morphotropic solid solutions.

The aim of this work was to experimentally determine and study the specific features of the formation of lead-free ceramic solid solutions based on the $\text{SrTiO}_3\text{--BiScO}_3$ system.

EXPERIMENTAL

Standard ceramic technology was used to synthesize $(1-x)\text{SrTiO}_3\text{--}x\text{BiScO}_3$ compounds with concentrations $x = 0.0, 0.1, 0.2, 0.3, 0.4,$ and 0.5 . The initial components were Bi_2O_3 , Sc_2O_3 , TiO_2 , and SrCO_3 powders taken in a stoichiometric ratio. The billets were formed as cylinders 25 mm long and 5 mm in diameter via cold isostatic pressing (400 MPa). The billets were synthesized at a temperature of 800°C , and sintering was performed at 1300°C .

The synthesized materials were studied by dilatometry on a NETZSCH DIL 402 C high-temperature dilatometer, and by X-ray structural and X-ray phase analyses on a Rigaku Ultima IV powder diffractometer (CuK_α radiation).

The results from the dilatometric analysis are shown in Fig. 1. As can be seen from this figure, the length of all test samples with $x = 0.1, 0.2, 0.3,$ and 0.4 changed monotonically with growing temperature. The temperature dependences of relative deformation were qualitatively similar for all the compositions studied. For example, the elongation of the samples was negligible during heating to a temperature of $\sim 850^\circ\text{C}$; the samples then elongated considerably at temperatures from ~ 850 to $\sim 1050^\circ\text{C}$; and a section with a weak temperature dependence of relative deformation was observed above $\sim 1050^\circ\text{C}$. The maximum elongation of the samples depended on their composi-

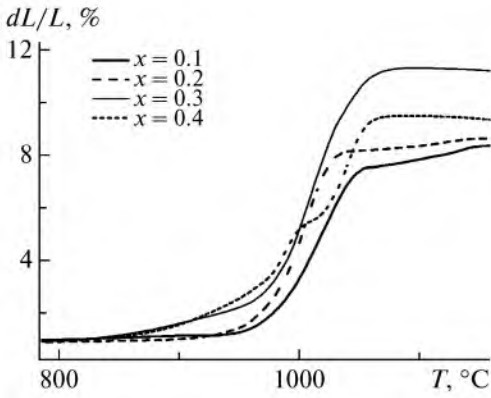


Fig. 1. Temperature dependence of the relative deformation of samples of solid solutions in the $(1-x)\text{SrTiO}_3-x\text{BiScO}_3$ system.

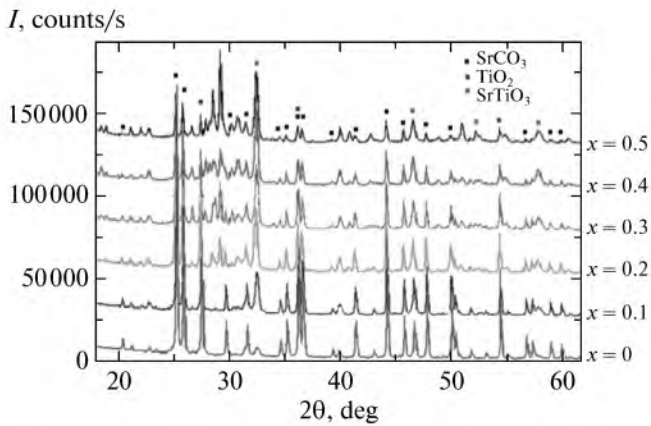


Fig. 2. Diffraction patterns of samples of solid solutions in the $(1-x)\text{SrTiO}_3-x\text{BiScO}_3$ system after annealing at a temperature of 800°C .

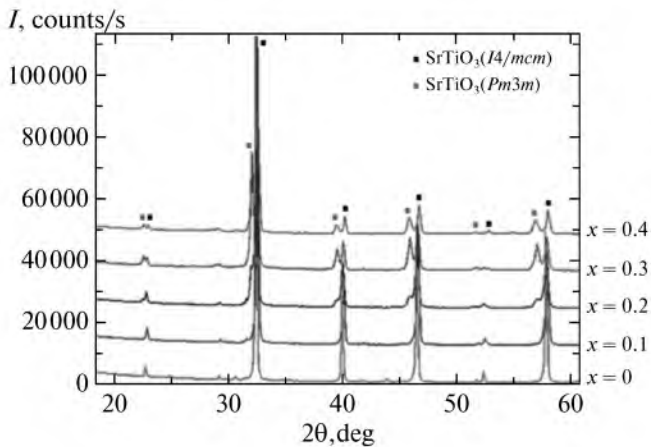
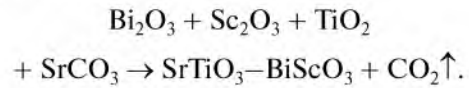


Fig. 3. Diffraction patterns of samples of solid solutions in the $(1-x)\text{SrTiO}_3-x\text{BiScO}_3$ system after annealing at a temperature of 1300°C .

tion. For samples with $x = 0.1, 0.2,$ and $0.3,$ the maximum elongation increased monotonically with growing concentration of BiScO_3 in the solid solutions (from $\sim 8\%$ at $x = 0.1$ to $\sim 11\%$ at $x = 0.3$). For the sample with $x = 0.4,$ the maximum elongation was $\sim 9\%$; i.e., it was less than in the sample with $x = 0.3,$ but greater than in the samples with $x = 0.1$ and $0.2.$

The observed complex change in the relative deformation of the samples, which were a mixture of $\text{Bi}_2\text{O}_3,$ $\text{Sc}_2\text{O}_3,$ $\text{TiO}_2,$ and SrCO_3 in the initial state, could be related to specific features of the formation of solid solutions from the initial components during high-temperature treatment.

The formation of $(1-x)\text{SrTiO}_3-x\text{BiScO}_3$ solid solutions can formally be presented as the following chemical reaction:



In actual fact, however, the process of the formation of solid solutions could be more complicated and might involve the formation of intermediate phases.

The specific features of the formation of $(1-x)\text{SrTiO}_3-x\text{BiScO}_3$ solid solutions were studied further by X-ray structural and X-ray phase analyses.

Figure 2 presents the diffraction patterns of samples with $x = 0.0, 0.1, 0.2, 0.3, 0.4,$ and 0.5 after annealing at a temperature of 800°C for 4 h in air.

The X-ray phase analysis demonstrated that the diffraction patterns of the samples with $x = 0.0$ and 0.1 included reflections corresponding to three basic phases: strontium carbonate, rutile, and strontium titanate. As concentration x increased ($x = 0.2-0.5$), phases of complex strontium-bismuth oxides $\text{Sr}_5\text{Bi}_6\text{O}_{14}$ ($x = 0.2$), $\text{Sr}_{0.78}\text{Bi}_{2.22}\text{O}_4$ ($x = 0.3$), and $\text{Sr}_{2.25}\text{Bi}_{6.75}\text{O}_{12.38}$ ($x = 0.4$ and 0.5) were formed in the solid solutions.

At the sintering stage, the samples were calcined in air at a temperature of 1300°C for 2 h. The diffraction patterns of the samples after this treatment are shown in Fig. 3. The samples with concentrations $x = 0.0$ and 0.1 had a cubic $Pm3m$ structure. When the concentration of BiScO_3 increased, they turned into two-phase samples as their diffraction patterns had reflections apparently from a phase with a tetragonal $I4/mcm$ structure, in addition to those characteristic of the cubic phase.

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