Phase Transitions and the Dielectric and Piezoelectric Properties of Ceramic Solid Solutions Based on BiScO₃-PbTiO₃

E. D. Politova^{*a*}, B. V. Egorova^{*b*}, G. M. Kaleva^{*a*}, A. V. Mosunov^{*a*}, S. Yu. Stefanovich^{*a*, *b*}, A. G. Segalla^{*c*}, and J. Zeng^{*d*}

^aKarpov Institute of Physical Chemistry, Moscow, 105064 Russia ^bMoscow State University, Moscow, 119991 Russia ^cOAO ELPA, Zelenograd, Moscow, 124460 Russia ^d Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai, 200050 China

e-mail: politova@cc.nifhi.ac.ru

Abstract—The ferroelectric and piezoelectric properties of ceramic solid solutions having a composition of $(1-x)(Bi_{0.9}Nd_{0.1})(Sc_{0.9}B_{0.1})O_3 - xPbTiO_3$ (x = 0.60-0.66; B = Lu, Yb, Er, Y) and obtained by solid state reaction were studied. An increase in the Curie temperature was found upon an increase in the concentration of lead titanate, while a drop occured upon the doping of the *A* and *B* sublattices. It was shown that at high temperatures, MnO_2 and Bi_2O_3 additives lead to a reduction in the total conductivity and a dielectric loss of less than one order of magnitude. In modified ceramics, an increase in the d_{33} and k_t piezoelectric coefficients was observed as well. The effects of dielectric relaxation that are determined by the composition of the ceramics were revealed.

Keywords: BiScO₃–PbTiO₃ ceramics, ferroelectrics, piezoelectric properties. **DOI:** 10.3103/S1062873811050418

INTRODUCTION

Piezoelectric ceramic materials based on oxides of the lead zirconate-titanate system, PbZrO₃-PbTiO₃, are widely used in present-day technology. The relatively low temperature of the transition from the ferroelectric to paraelectric state (the Curie temperature, $T_{\rm C}$) limits the working temperature range of ceramics based on the lead zirconate-titanate system to 620 K. The need to use materials whose working temperatures are above 650–900 K makes the development of new piezoelectric materials with higher $T_{\rm C}$ values an issue of great importance.

Ceramic solid $(1 - x)BiScO_3 - xPbTiO_3$ solutions are now being studied intensively, since these materials could be used at temperatures above 600 K [1-17]. It has been established that compounds whose compositions correspond to the morphotropic boundary region with $x \sim 0.64$ found between compounds with rhombohedral and tetragonal structures have a $T_{\rm C}$ value above 700 K and show good piezoelectric properties [1-4]. This allows us to consider these types of compounds as a basis for developing new piezoelectric materials appropriate for high-temperature applications. In addition to high piezoelectric activity, the piezoelectric ceramic materials used for high-temperature applications should have reduced dielectric loss at high temperatures. Piezoceramic samples having low dielectric loss at high temperatures and improved ferroelectric characteristics were shown to have been obtained by using bismuth oxides and manganese oxide additives [6, 13]. In this work, the properties of solid solutions based on BiScO₃-PbTiO₃ and having a composition of $(1 - x)(Bi_{0.9}Nd_{0.1})(Sc_{0.9}B_{0.1})O_3 - xPbTiO_3$ (x = 0.60 - 0.66; $B^{3+} - Lu^{3+}$, Yb³⁺, Er³⁺, Y³⁺) were investigated. In addition, a number of samples containing bismuth and manganese oxides additives were obtained with the purpose of improving the sintering process of ceramics and to raise their resistance. The effects of doping and additives on the phase composition, microstructure, phasetransition temperature, and ferro- and piezoelectric properties were studied.

EXPERIMENTAL

Ceramic solid solutions having a composition of $(1-x) \cdot (Bi_{0.9}Nd_{0.1})(Sc_{0.9}B_{0.1})O_3 - xPbTiO_3 (x = 0.60 - 0.66; B = Lu, Tb, Er, Y)$ were obtained by solid state reaction from the following oxides: Bi₂O₃ (pure grade), Sc₂O₃ (pure grade), Nd₂O₃ (chemically pure grade), Lu₂O₃ (chemically pure grade), Y₂O₃ (chemically pure grade), Yb₂O₃ (chemically pure grade), Er₂O₃ (chemically pure grade), Stochemically pure grade), Stochemically pure grade), Stochemically pure grade), Stochemically pure grade), and TiO₂ (pure for analysis). Stoichiometric mixtures of oxides homogenized in an ethanol medium were synthesized at $T_1 = 970$ K (8.5 h), grinded, pressed, and sintered at 1420 K (2 h) with an additional intermediate annealing at 1030 K (3 h) followed by slow cooling to room



Fig. 1. Diffraction pattern of the 0.37Bi(Sc_{0.9}Lu_{0.1})O₃– 0.63PbTiO₃ sample (an ~2.5 at % excess of Bi₂O₃) obtained at $T_1 = 700^{\circ}$ C (8.5 h), and $T_2 = 1150^{\circ}$ C (2 h). The regions of the diffraction patterns for the 0.37Bi(Sc_{0.9}B_{0.1})O₃–0.63PbTiO₃ samples (an ~2.5 at % excess of Bi₂O₃) with B =Sc (1), B =Y (2), B =Lu (3), B =Er (4), B = Yb (5) are shown in the inset.

temperature. Bi_2O_3 and MnO_2 additives were introduced over and above the stoichiometry in quantities of 2.5 at % and 0.17–0.51 wt %, respectively.

The phase composition and structure of the ceramics were studied by X-ray powder diffraction analysis (DRON-3M, CuK_{α} -radiation); the microstructure was monitored by high-resolution scanning electron microscopy (Supra 50 VP, LEO, Germany). The second harmonic generation of laser radiation (Nd laser, $\lambda_{\omega} = 1.064 \ \mu m$) and dielectric spectroscopy (Agilent 4284 A LCR meter, 1 V; the temperature range, 300-1000 K; frequency range, 100 Hz-1 MHz) were used to study phase transitions. The d_{33} piezoelectric coefficients for ceramic samples prepolarized in an electric field with strengths of up to 50 kV cm^{-1} for 15 min at 400 K and cooled in the presence of a field were measured using an APC YE 2730A d_{33} meter (APC Products, United States). The piezoelectric coupling coefficient $k_{\rm t}$ was measured by the standard resonance– antiresonance method.

RESULTS AND DISCUSSION

A tetragonal phase is the main phase in the studied samples having a composition of $(1 - x)BiScO_3 - xPbTiO_3$ with x = 0.60 - 0.66 and modified with Nd₂O₃, Lu₂O₃, Y₂O₃, Er₂O₃, and Yb₂O₃ oxides (Fig. 1). The composites modified with manganese and bismuth oxides crystallize in a rhombohedral space group. A number of samples were found to be a mixture of the tetragonal and rhombohedral phases (inset in Fig. 1). Due to the partial evaporation of bismuth oxide, an oriented layer of a high-temperature modification of bismuth oxide was observed on the surface of a number of samples (Fig. 1, dotted line). Upon replacing 10 at % of scandium oxide with oxides having a larger ionic radius ($R(Bi^{3+}) = 1.31$ Å; $R(Nd^{3+}) = 1.41$ Å; $R(Sc^{3+}) =$ 0.89 Å; $R(Lu^{3+}) = 1.00$ Å; $R(Yb^{3+}) = 1.01$ Å,



Fig. 2. Images of the $0.35Bi(Sc_{0.9}Yb_{0.1})O_3-0.65PbTiO_3$ sample, obtained at $T_1 = 700^{\circ}C$ (8.5 h) and $T_2 = 1150^{\circ}C$ (2 h).

 $R(Er^{3+}) = 1.03 \text{ Å}; R(Y^{3+}) = 1.04 \text{ Å})$, a regular increase in the *c* parameter and the volume *V* of the tetragonal lattice was observed.

In Fig. 2, an image of the surface of the $0.35Bi(Sc_{0.9}Yb_{0.1})O_3-0.65PbTiO_3$ sample is shown; homogeneous grains with a diameter of $2-5 \mu m$ form the microstructure of this sample.

Ferroelectric phase transitions of the first order were revealed in the temperature range of 550–750 K using the second harmonic generation of laser radiation. These transitions are also responsible for the pronounced maxima observed in the temperature dependences of the permittivity and dielectric loss (Fig. 3). An increase in the content of lead titanate leads to a regular increase in temperature of the ferroelectric phase transition, but the $T_{\rm C}$ value declined by 125 K $(B = {\rm Nd})$, 10 K $(B = {\rm Lu})$, 12 K $(B = {\rm Yb})$, 27 K (B =Er), 47 K $(B = {\rm Y})$ in the samples containing doped *A* or *B* sublattices.

In addition to the maxima that correspond to the transitions from the ferroelectric to paraelectric phase, peaks of a relaxation nature were found; the temperature that corresponds to these additional maxima depends on the frequency of measurements (Fig. 3). In the modified samples, the effects of dielectric relaxation were suppressed. The nature of the high-temperature relaxation anomalies is most likely related to the presence of vacancies in the oxygen sublattice; these vacancies occur due to the loss of lead oxide during high-temperature synthesis. During oxygen-ion transport, dipoles relaxing in an alternating electric field appear [18].

A reduction in the value of the dielectric loss tangent by more than an order of magnitude is observed for the ceramic samples modified with bismuth and manganese oxides at temperatures above 600 K. The decrease in the total conductivity by more than an order of magnitude observed in the modified samples



Fig. 3. Temperature dependences of the permittivity (a, c) and dielectric loss tangent (b, d) for the following samples: $0.34BiScO_3-0.66PbTiO_3$ (a, b); $0.36BiScO_3-0.64PbTiO_3$ (c, d). Measurements were performed at frequencies of 100 Hz (*1*), 1 kHz (*2*), 10 kHz (*3*), and 100 kHz (*4*).



Fig. 4. Temperature dependences, $\log \sigma (1/T)$, for the following ceramic samples: $0.37\text{Bi}(\text{Sc}_{0.9}\text{Yb}_{0.1})\text{O}_3$ -0.63PbTiO₃ (*I*), $0.37(\text{Bi}_{0.9}\text{Nd}_{0.1})(\text{Sc}_{0.9}\text{Yb}_{0.1})\text{O}_3$ -0.63PbTiO₃ (*2*), $0.37\text{Bi}(\text{Sc}_{0.9}\text{Y}_{0.1})\text{O}_3$ -0.63PbTiO₃ (*2*), $0.37\text{Bi}(\text{Sc}_{0.9}\text{Y}_{0.1})\text{O}_3$ -0.63PbTiO₃ (an ~2.5 at % excess of Bi₂O₃) (*4*), 0.37BiSCYO₃-0.63PbTiO₃ (0.25 wt % of MnO₂) (*5*), 0.37BiSCYO₃-0.63PbTiO₃ (0.5 wt % of MnO₂) (*6*). The $\ln (f/T^{0.5}) (1000/T)$ (*I*) and $\ln f(1000/T)$ (*2*) dependences constructed in accordance with the $\varepsilon(T)$ and $\tan \delta(T)$ dependences for the 0.37BiSCO₃-0.63PbTiO₃ are shown in the inset.

at high temperatures confirms the assumption about the nature of the dielectric relaxation mentioned above (Fig. 4). High values of the piezoelectric coefficient d_{33} and the piezoelectric coupling coefficient k_t (which reach 350 pC/N and 0.68, respectively) were found for the ceramics modified with neodymium oxide. These results are in agreement with the conclusion that domain walls make a significant contribution to the formation of the electromechanical properties [19, 20]. A reduction in the concentration of oxygen vacancies leads to an increase in the mobility of domain walls, and consequently to an improvement in the piezoelectric properties.

CONCLUSIONS

An increase in the Curie temperature upon increasing the concentration of lead titanate in the solid $(1 - x)BiScO_3 - xPbTiO_3$ solution was revealed. Upon doping in solid $(1 - x)(Bi_{0.9}Nd_{0.1})(Sc_{0.9}B_{0.1})O_3 - xPbTiO_3$ solutions, however, a reduction in the Curie temperature values was observed. It was shown that introducing MnO₂ and Bi₂O₃ additives into compounds leads to a decrease in the total conductivity and dielectric loss by more than an order of magnitude at high temperatures. An increase in the values of the piezoelectric coefficients d_{33} and k_t was observed in ceramics modified with neodymium oxide.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research, project no. 10-03-91161.

REFERENCES

- 1. Tomashpol'skii, Yu.Ya., Zubova, E.V., Burdina, K.P., and Venevtsev, Yu.N., *Kristallogr.*, 1968, vol. 13, p. 987.
- Eitel, R.E., Randall, C.A., Shrout, T.R., and Park, S.-E., Jpn. J. Appl. Phys., 2002, vol. 41, p. 2099.
- 3. Iniguez, J., Vanderbilt, D., and Bellaiche, L., *Phys. Rev. B*, 2003, vol. 67, p. 224107.
- Eitel, R.E., Zhang, S.J., Shrout, T.R., et al., J. Appl. Phys., 2004, vol. 96, p. 2828.
- Maeder, V.D., Damjanovic, D., and Setter, N., J. Electroceram., 2004, vol. 13, p. 385.
- 6. Zhang, Sh., Eitel, R.E., Randall, C.A., and Shrout, Th.R., *Appl. Phys. Lett.*, 2005, vol. 86, p. 262904.
- Wen, X., Wang, X., and Li, L., J. Appl. Phys., 2006, vol. 100, p. 084315.
- Zhao, W., Wang, X., Hao, J., et al., J. Am. Ceram. Soc., 2006, vol. 89, p. 1200.

- 9. Chen, S., Dong, X., Mao, Ch., and Cao, F., J. Am. Ceram. Soc., 2006, vol. 89, p. 3270.
- Wen, X., Wang, X., Deng, X., et al., J. Appl. Phys., 2007, vol. 101, p. 016103.
- 11. Zou, T., Wang, X., Zhao, W., and Li, L., *J. Am. Ceram. Soc.*, 2008, vol. 91, p. 121.
- 12. Zhang, L. Xu, Zh., Li Zh., et al., J. Electroceram., 2008, vol. 21, p. 605.
- 13. Sehirlioglu, A., Sayir, A., and Dynys, F., *J. Appl. Phys.*, 2009, vol. 105, p. 114102.
- 14. Alguero, M., Amorin, H., Hungria, T., et al., *Appl. Phys. Lett.*, 2009, vol. 94, p. 012902.
- 15. Kim, B., Tong, P., Kwon, D., et al., *J. Appl. Phys.*, 2009, vol. 105, p. 114101.
- 16. Amorin, H., Jimenez, R., Ricote, J., et al., *J. Phys. D: Appl. Phys.*, 2010, vol. 43, p. 285401.
- 17. Gotmare, S.W., Leontsev, Sh.O., and Eitel, R.E., *J. Amer. Ceram. Soc.*, 2010, vol. 93, p. 1965.
- 18. Mosunov, A.V., Venskovskii, N.U., and Kaleva, G.M., *Ferroelectrics*, 2004, vol. 299, p. 149.
- 19. Morozov, M.I. and Damjanovic, D., J. Appl. Phys., 2010, vol. 107, p. 034106.
- 20. Damjanovic, D., *IEEE Trans. Ultrasonics, Ferroelectrics, Frequency Control*, 2009, vol. 56, p. 1574.