

Crossover from an Ordinary Ferroelectric to a Relaxor in $\text{Sr}_{2+x}\text{Bi}_{4-x}\text{Ti}_{5-x}\text{Nb}_x\text{O}_{18}$

S. A. Gridnev, N. A. Tolstykh*, A. I. Bocharov, and N. V. Zhivotenko

Voronezh State Technical University, Voronezh, 394026 Russia

*e-mail: mad_nik@bk.ru

Abstract— $\text{Sr}_{2+x}\text{Bi}_{4-x}\text{Ti}_{5-x}\text{Nb}_x\text{O}_{18}$ materials with $x = 0.2, 0.4, 0.6, 0.8,$ and 1 are synthesized. Investigations of the dielectric constant of the samples reveal an increase in the blurring of the phase transition as the share of titanium ions substituted for niobium ions grows. The Burns temperature and the temperature corresponding to the dielectric permittivity maximum are determined for all of the above compositions. Crossover from a normal ferroelectric to a relaxor ferroelectric in $\text{Sr}_{2+x}\text{Bi}_{4-x}\text{Ti}_{5-x}\text{Nb}_x\text{O}_{18}$ samples is observed.

DOI: 10.3103/S1062873816090161

INTRODUCTION

One of the greatest problems in the physics of ferroelectrics is studying the blurring of ferroelectric phase transitions and transitions to the relaxor state. This problem has been intensively studied both theoretically and experimentally. There are now several models that more or less describe the physical properties of relaxor ferroelectrics. These are mostly for complex ferroelectrics with perovskite structure and the general formula $A'A''B'B''O_3$. Most researchers associate phase transition blurring and the transition to the relaxor state with the statistical distribution of cations in ferroelectrically active sublattices. These can be sublattice A or B, depending on the chemical composition.

We believe it would be advantageous to clarify the extent to which the models proposed for ferroelectrics with perovskite structure can be used to describe the blurring of phase transitions in ferroelectrics with other types of lattice.

A convenient material for such studies is ferroelectrics with the structure of Aurivillius phases (APs) and the general formula $(A'A'')_{m-1}\text{Bi}_2(B'B'')_m\text{O}_{3m+3}$ [1, 2]. In this structure, positions A with a cubooctahedral environment are occupied by mono-, bi-, and trivalent cations with large radii (Na, K, Ca, Sr, Ba, Pb, Bi, and Ln (Lanthanides)), while sites B inside oxygen octahedrons are occupied by highly charged cations with short radii (Al, Ti, Cr, Ga, Mn, Fe, Nb, Mo, Ta, and W). Positions A and B can be occupied by several identical or different atoms. The substituting of atoms in positions A and B considered in [3–5] has a considerable impact on the electrical characteristics of APs. Major changes in the values of the dielectric constant and electrical conductivity are observed in particular. In addition, the Curie temperature can vary widely. By

varying the composition of cations with different ionic radii and/or the valence in sublattices A and B, we can identify a ferroelectrically active sublattice and make valid assumptions about the dominant mechanism of phase transition blurring.

The aim of this work was to study the effect substituting Ti^{4+} cations for Nb^{5+} ions has on the relaxor properties of layered perovskite with AP structure ($\text{Sr}_{2+x}\text{Bi}_{4-x}\text{Ti}_{5-x}\text{Nb}_x\text{O}_{18}$), along with the blurring of the phase transition in this material.

EXPERIMENT

Specimens of $\text{Sr}_{2+x}\text{Bi}_{4-x}\text{Ti}_{5-x}\text{Nb}_x\text{O}_{18}$ with $x = 0, 0.2, 0.4, 0.6, 0.8,$ and 1 were fabricated by means of solid-phase synthesis from a composition of chemically pure $\text{Bi}_2\text{O}_3, \text{SrCO}_3, \text{TiO}_2,$ and Nb_2O_5 powders in a specific stoichiometric ratio. Prior to synthesis, the powders were mixed in a planetary mill for 30 min. Solid phase synthesis was conducted in several stages, with annealing at a temperature of 800°C and then at 1160°C . The specimens were sintered at 1170°C .

X-ray analysis of the ceramics using a Rigaku SmartLab X-ray diffractometer (CuK_α -radiation) showed that the synthesized samples belong to the orthorhombic symmetry group and were single-phase. Figure 1 shows the X-ray diffraction pattern for the $\text{Sr}_{2+x}\text{Bi}_{4-x}\text{Ti}_{5-x}\text{Nb}_x\text{O}_{18}$ composition as an example.

RESULTS AND DISCUSSION

Real and imaginary parts ϵ' and ϵ'' of the dielectric permittivity were studied for each sample in the temperature range of 100 to 500 K at different frequencies of the measuring field. Figure 2 shows the temperature

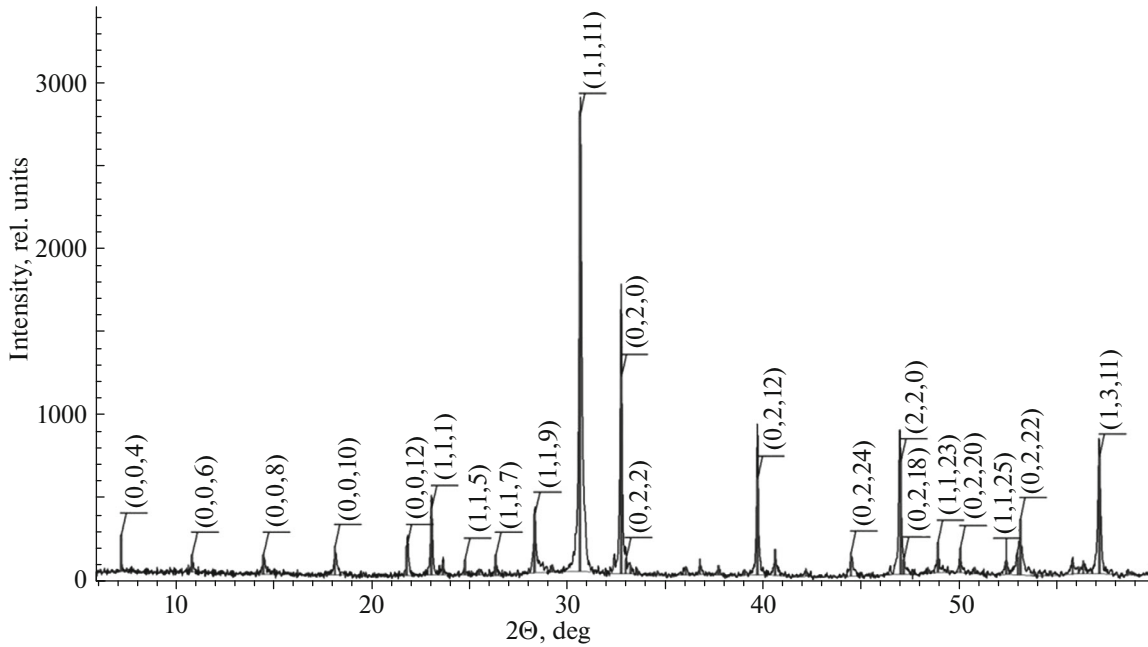


Fig. 1. X-ray pattern of ceramic sample $\text{Sr}_{2.2}\text{Bi}_{3.8}\text{Ti}_{4.8}\text{Nb}_{0.2}\text{O}_{18}$.

dependence of ϵ' for the fabricated materials at a frequency of 100 kHz.

It was found that deviation from the Curie–Weiss law is observed in the region of the permittivity maximum and at much higher temperatures. The temperature corresponding to the onset of deviation of the inverse dielectric permittivity from the linear dependence is called the Burns temperature, T_d . Anomalies in various physical properties of relaxors are observed at T_d . Figure 3 shows the graph of the inverse dielectric permittivity depending on temperature for a specimen with $x = 0.2$, which was approximated according to the Curie–Weiss law with a straight line. The Burns temperature was then determined using this graph. The values of the Burns temperature were determined in this manner for all samples.

Curie–Weiss temperature T_0 is obtained by extrapolating the linear part of dependence $1/\epsilon'(T)$ up to its intersection with the abscissa axis. For the studied compositions, the Curie–Weiss law is valid starting from a temperature much higher than T_m corresponding to the dielectric permittivity maximum [6].

To describe the dielectric properties of systems with fully smeared phase transitions, Bokov [7] proposed using an empirical law with variable exponent

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

where ϵ_m is the maximum value of dielectric permittivity, T is temperature, σ describes the Curie–Weiss law when $\gamma = 1$ and the smeared phase transition (SPT) at

$\gamma = 2$. Parameter σ has the dimension of temperature only at $\gamma = 2$ and characterizes the temperature range of SPT, i.e., the width of the Curie region.

In analyzing the experimental data obtained in this work, updated Curie–Weiss law (1) was used to describe the temperature dependence of ϵ . To determine γ , we plotted curves $\ln((\epsilon/\epsilon_m) - 1)$ vs. $\ln(T - T_m)$ in the region of the ϵ peak, with γ being the tangent of

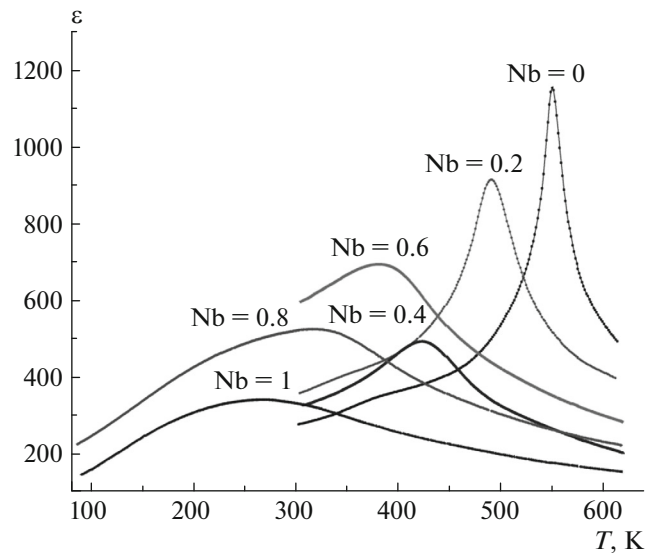


Fig. 2. Temperature dependence of real part ϵ' of dielectric permittivity for $\text{Sr}_{2+x}\text{Bi}_{4-x}\text{Ti}_{5-x}\text{Nb}_x\text{O}_{18}$ when $x = 0, 0.2, 0.4, 0.6, 0.8, \text{ and } 1$ (measuring field frequency, 100 kHz).

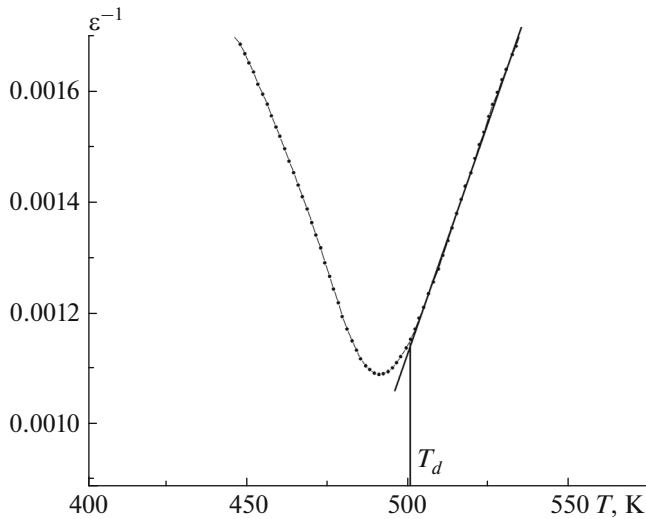


Fig. 3. Dielectric permittivity, depending on temperature in coordinates $1/\epsilon(T)$ in layered perovskite $\text{Sr}_{2+x}\text{Bi}_{4-x}\text{Ti}_{5-x}\text{Nb}_x\text{O}_{18}$; $x = 0.2$.

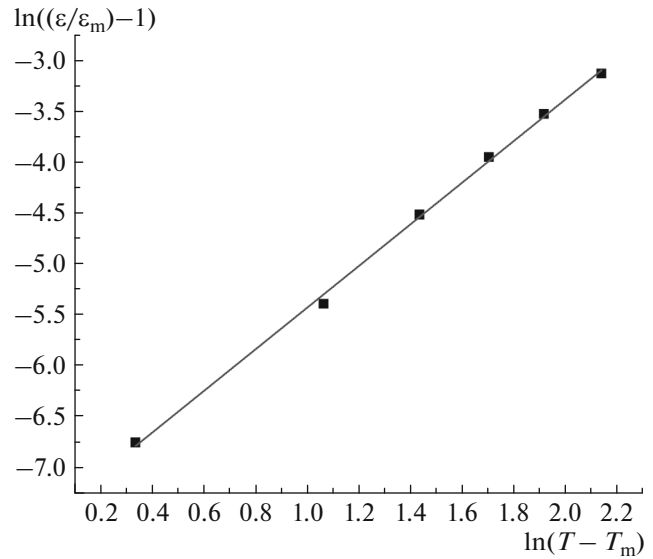


Fig. 4. Function $\ln((\epsilon/\epsilon_m) - 1)$ vs. $\ln(T - T_m)$ in layered perovskite $\text{Sr}_{2+x}\text{Bi}_{4-x}\text{Ti}_{5-x}\text{Nb}_x\text{O}_{18}$; $x = 0.2$.

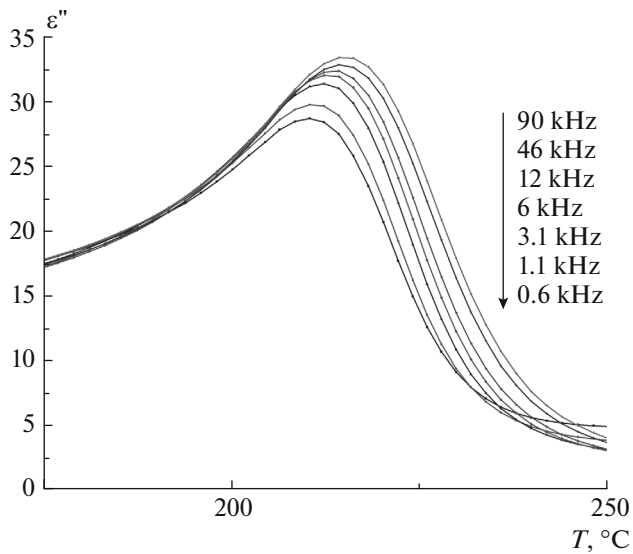


Fig. 5. Temperature dependence of ϵ'' at measuring field frequencies in the interval of 0.6–90 kHz for a specimen with $x = 0.2$.

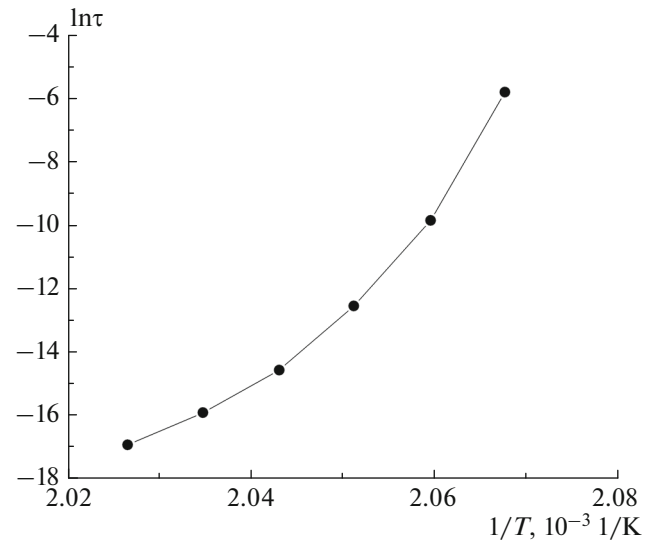


Fig. 6. Function $\ln\tau$, depending on the inverse temperature for a specimen with $x = 0.2$.

the linear fitting curve's inclination. For all of examined compositions with a smeared peak of ϵ' , the magnitude of γ is ~ 2 (Fig. 4). Using the calculated values of γ , we determined the phase transition's degree of blurring σ .

For compositions where the Nb content has a smeared peak of ϵ' (Fig. 5), the dispersion of ϵ'' was found to be caused by the dielectric response relaxation. In addition, the temperature dependence of relaxation time τ does not obey the Arrhenius law $\tau = \tau_0 \exp[U/kT]$, (Fig. 6), where $1/\tau_0$ is the frequency of

hopping of the potential barrier; U is the activation energy of the relaxation process; and k is the Boltzmann constant.

Non-Debye relaxation thus occurs, the characteristic time of which varies with temperature according to the Vogel–Fulcher law [8, 9] (Fig. 7)

$$\tau = \tau_0 \exp[U/k(T - T_0)], \quad (2)$$

where the temperature dependence of activation energy U is accounted for by introducing Vogel–Fulcher–Tamman temperature T_0 . This testifies to the

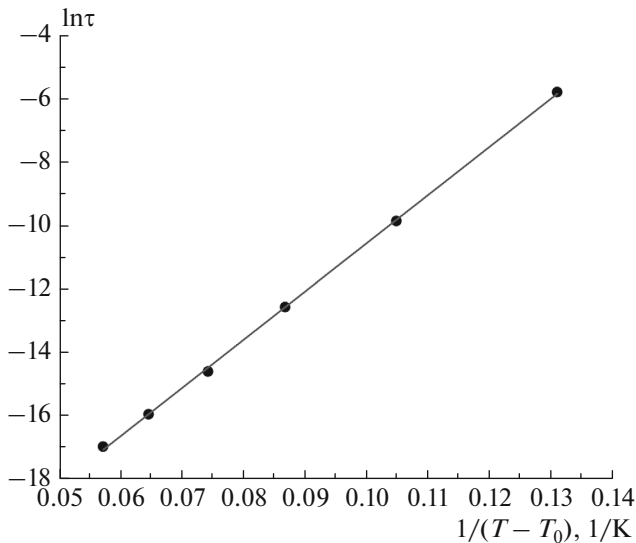


Fig. 7. Function $\ln\tau$ vs $1/(T - T_0)$ for a specimen with $x = 0.2$.

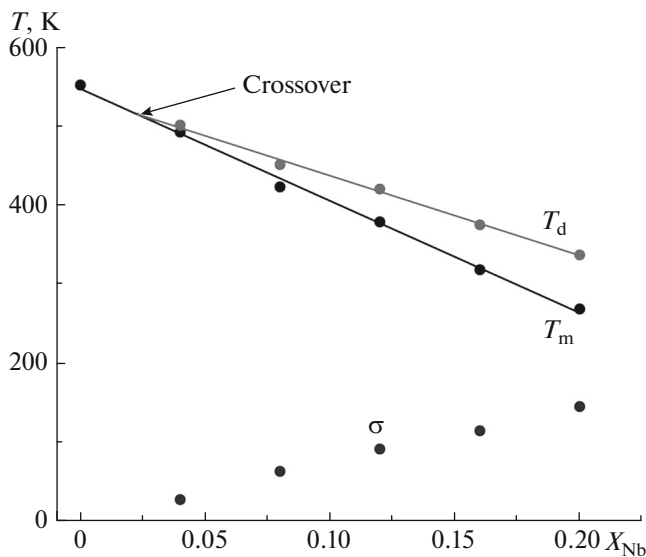


Fig. 8. Concentration dependences of Burns temperature T_d , blurring parameter σ of the phase transition, and temperature T_m of the dielectric permittivity maximum in our $\text{Sr}_{2+x}\text{Bi}_{4-x}\text{Ti}_{5-x}\text{Nb}_x\text{O}_{18}$ specimen.

glasslike behavior of materials; i.e., the resulting materials are relaxors.

Based on these results, we plotted the temperature of the dielectric permittivity maximum, the Burns temperature, and blurring parameter of the phase

transition, depending on the concentration. As we can see from Fig. 8, temperature T_m of the dielectric permittivity peak, and Burns temperature T_d , are shifted downward on the scale of temperature as the concentration of niobium in the composition of layered perovskite rises. If we approximate the concentration dependences of T_m and T_d with straight lines, they intersect when the niobium content in the sample is 2.2%. In other words, we find that $T_m = T_d$. This means the smeared phase transition at niobium concentrations of $\text{Nb} > 2.2\%$ becomes a classical phase transition when $\text{Nb} = 2.2\%$.

CONCLUSIONS

Analysis of our data shows that in the specimen $\text{Sr}_{2+x}\text{Bi}_{4-x}\text{Ti}_{5-x}\text{Nb}_x\text{O}_{18}$ of layered perovskite, we observe a crossover from conventional phase transition to relaxor transition at a niobium content of $\text{Nb} = 2.2\%$. We can also see that the blurring parameter grows linearly along with the concentration of niobium in the sample.

ACKNOWLEDGMENTS

This work was supported by the RF Ministry of Science and Education, project no. 391, task no. 2014/21.

REFERENCES

1. Smolenskii, G.A., *Fizika segnetoelektricheskikh yavlenii* (Physics of Ferroelectrical Phenomena), Leningrad: Nauka, 1985.
2. Aurivillius, B., *Ark. Kemi*, 1949, vol. 1, no. 58, p. 499.
3. Yan, H.X., Zhang, H.T., Zhang, Z., Ubie, R., and Reece, M.J., *J. Eur. Ceram. Soc.*, 2006, vol. 26, p. 2785.
4. Duran-Martin, P., Jimenez, B., Millan, P., and Castro, A., *J. Phys. Chem. Solids*, 2000, vol. 61, p. 1423.
5. Rentsehler, T., Karus, M., Wellm, A., and Reller, A., *Solid State Ionics*, 1996, vol. 90, p. 49.
6. Smolenskii, G.A., Isupov, V.A., Agranovskaya, A.I., and Popov, S.N., *Fiz. Tverd. Tela*, 1960, vol. 2, no. 11, p. 2906.
7. Bokov, A.A., Bing, Y.-H., Chen, W., et al., *Phys. Rev. B*, 2003, vol. 68, p. 052102.
8. Cross, L.E., *Ferroelectrics*, 1994, vol. 151, no. 35, p. 305.
9. Gridnev, S.A., Efimov, E.S., and Tsotsorin, A.N., *Izv. Akad. Nauk, Ser. Fiz.*, 2001, vol. 65, no. 8, p. 1122.

Translated by G. Dedkov