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# Thermodynamic Properties and Phase Transitions of Multiferroics (1 - x)BiFeO<sub>3-x</sub>PbFe<sub>0.5</sub>Nb<sub>0.5</sub>O<sub>3</sub>

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Received January 11, 2022

Revised January 11, 2022

Accepted January 13, 2022

Studies of the heat capacity and dielectric properties of (1 - x)BiFeO<sub>3-x</sub>PbFe<sub>0.5</sub>Nb<sub>0.5</sub>O<sub>3</sub> ceramic multiferroics in the temperature range of 300–800 K were carried out. Based on studies of the temperature and concentration dependences of the heat capacity and dielectric constant, the phase transition temperatures of the (1 - x)BiFeO<sub>3</sub> system were determined. (1 - x)PbFe<sub>0.5</sub>Nb<sub>0.5</sub>O<sub>3</sub> with various x concentrations. It is shown that with an increase in the PbFe<sub>0.5</sub>Nb<sub>0.5</sub>O<sub>3</sub> component, the temperatures of the ferroelectric and antiferromagnetic transitions in BiFeO<sub>3</sub> shift to low temperatures. Taking into account structural studies, a „temperature-concentration“ phase diagram has been constructed.

**Keywords:** heat capacity, dielectric properties, ferromagnet, antiferromagnet, multiferroics.

DOI: 10.21883/PSS.2022.05.53521.271

## 1. Introduction

Multiferroics that implement ferroelectric and magnetic ordering simultaneously in a wide temperature range are currently of great interest on both practical and theoretical grounds. The reason for this is their potential engineering application thanks to association between the ferroelectric and magnetic domains. Bismuth ferrite BiFeO<sub>3</sub> and plumbum ferroniobate Pb(Fe<sub>0.5</sub>Nb<sub>0.5</sub>)O<sub>3</sub> are the two best studied multiferroics in which ferroelectric and antiferromagnetic orders can coexist. Plumbum ferroniobate PbFe<sub>0.5</sub>Nb<sub>0.5</sub>O<sub>3</sub> (PFN) is a well-known representative of multiferroics with a perovskite-like structure and general chemical formula A(B'<sub>0.5</sub>B''<sub>0.5</sub>)O<sub>3</sub> (was first synthesized and studied in 1958 by a team under the supervision of G.A. Smolensky). In PFN, a smeared phase transition from paraelectric (PE) to ferroelectric (FE) phase takes place at the Curie temperature T<sub>C</sub> = 370 K [1,2]. Despite the fact that FE and antiferromagnetic (AFM) orderings in PFN coexist only below the Neel point T<sub>N</sub> = 120–150 K [1,2], a low magnetoelectric and magnetodielectric effects may occur in it also at temperature above room temperature [3,4]. Bismuth ferrite BiFeO<sub>3</sub> (BFO) is a multiferroic, where high-temperature FE- (ferropolarization achieves 100 μC/cm<sup>2</sup>) and AFM- (G-type antiferromagnetism with incommensurate cycloidal magnetic ordering in [1–10] direction) phase transitions, respectively, at T<sub>C</sub> = 1103 K and T<sub>N</sub> = 643 K [1,5]. However, high leakage currents due to the presence of oxygen vacancies and impurity phases in BFO impose restrictions on the use of BFO for the manufacture of multifunctional devices. These issues

may be solved, for example, through the development of multicomponent materials based on bismuth ferrite with improved magnetoelectric properties. In particular, the authors of [6] observed the stabilization of magnetic and electric properties in a binary solid solution (SS) of (1 - x)BiFeO<sub>3-x</sub>PbFe<sub>0.5</sub>Nb<sub>0.5</sub>O<sub>3</sub> system with x = 0.2, and the increase in magnetoelectric effect in SS with x = 0.3 and x = 0.4 [7]. Phase transition diagram for this SS system was first made in 1965 [8] and updated for room temperature in [9]. Concentration ranges were identified for existence of single-phase and morphotropic regions and coexistence regions of different phase states. However, all known research findings show that (1 - x)BFO-xPFN solid solution system has not been well studied up to date and the data is often contradictory which is caused by the difficulty in achievement of high quality experimental samples. Phase transition process in such heterogeneous multicomponent systems is complex and is not clear enough until now. All these factors give incentives to further detailed investigations of their structural features and various physical properties. In particular, calorimetric testing in a wide temperature range make it possible to record abnormal heat capacity of any origin and to acquire important information regarding the nature of physical phenomena in the materials of interest. To the best of our knowledge, no any investigations of heat capacity of (1 - x)BFO-xPFN solid solutions have been carried out.

The findings of the heat capacity and dielectric property investigations in a set of (1 - x)BFO-xPFN ceramic compounds in a wide temperature range are discussed herein.

## 2. Research targets and experiment

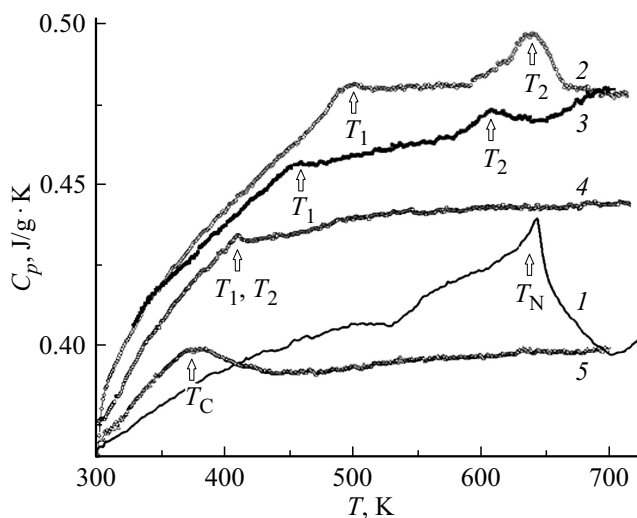
Stoichiometric  $(1-x)\text{BiFeO}_3-x\text{PbFe}_{0.5}\text{Nb}_{0.5}\text{O}_3$  SS, where  $x = 0.0, 0.4, 0.5, 0.6, 1.0$ , are the target of the research. Material synthesis regulations are given in [9], compatibility of the SS elemental composition with the specified stoichiometry was determined by the X-ray fluorescence analysis method [10]. High-temperature X-ray testing was carried out by X-ray powder diffraction using ADP diffractometer (Bragg–Brentano focusing) with CoK-emission. Temperature control accuracy was  $\pm 1$  K, temperature increase rate was random and isothermal time was 10 min. X-ray testing has shown that impurity-free 0.5BFO–0.5PFN ceramics were formed [11]. At room temperature, SSs with concentrations  $0.40 \leq x \leq 0.85$  have a structure similar to a cubic structure, no diffraction peak splitting takes place, all peaks are expanded a little [9,12]. This may be indicative of very small local deviations from the cubic symmetry, but they are not identified because of the cooperative effect of X-ray radiation.

Heat capacity was measured by NETZSCH DSC 204 F1 Phoenix differential scanning calorimeter. The heat capacity test sample was a plate with a diameter of 4 mm and thickness of 1 mm. The rate of temperature change was 5 K/min. Heat capacity measurement accuracy did not exceed 3%.

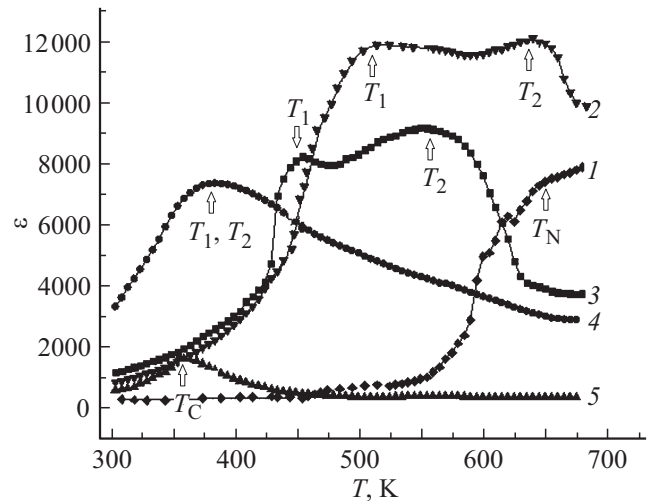
For permittivity measurement, LCR-78110G meter was used. The samples were made in a form of flat capacitors with silver paste electrodes.

## 3. Research results

Fig. 1 shows temperature dependences of heat capacity at constant pressure  $C_p$  of  $(1-x)\text{BFO}-x\text{PFN}$  system, where  $x = 0, 0.4, 0.5, 0.6, 1.0$ . As shown in the



**Figure 1.** Temperature dependence of heat capacity  $C_p$  of  $(1-x)\text{BFO}-x\text{PFN}$  multiferroics:  $x = 0$  (curve 1), 0.4 (2), 0.5 (3), 0.6 (4), 1.0 (5).

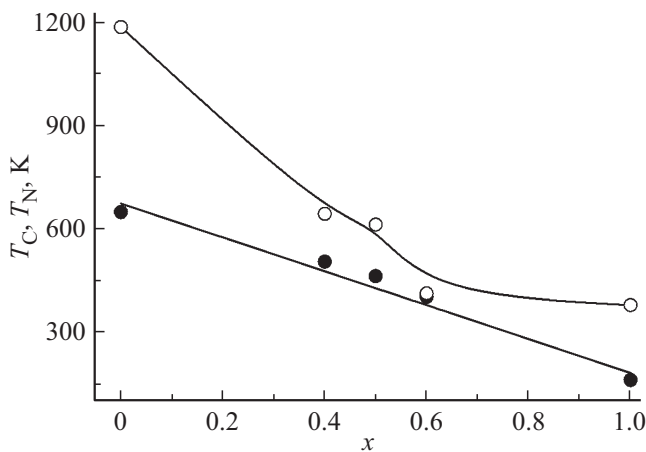


**Figure 2.** Temperature dependence of permittivity of  $(1-x)\text{BFO}-x\text{PFN}$  (at 10 kHz):  $x = 0$  (curve 1), 0.4 (2), 0.5 (3), 0.6 (4), 1.0 (5).

Figure, abnormal heat capacity  $C_p$  are observed for phase transitions in  $(1-x)\text{BFO}-x\text{PFN}$  binary system at temperatures (defined by the maximum on curve  $C_p(T)$ )  $T_1 = 502$  K and  $T_2 = 640$  K for compound with  $x = 0.4$ ,  $T_1 = 460$  K and  $T_2 = 609$  K with  $x = 0.5$ ,  $T_1 = 410$  K with  $x = 0.6$ . The specified phase transitions are smeared. Fig. 2 shows temperature dependences of permittivity  $\varepsilon$  of  $(1-x)\text{BFO}-x\text{PFN}$  system, where  $x = 0, 0.4, 0.5, 0.6, 1.0$ .

In Fig. 2, temperatures abnormalities at  $T_1 \approx 500$  K and  $T_2 \approx 640$  K are observed for compound with  $x = 0.4$ ,  $T_1 \approx 450$  K and  $T_2 \approx 600$  K with  $x = 0.5$ ,  $T_1 \approx 400$  K with  $x = 0.6$ . All observed phase transitions are smeared by temperature and, therefore, phase transition temperatures defined by  $\varepsilon(T)$  may differ a little from the data obtained from heat capacity measurements. For BFO multiferroics, AFM phase transition and PFN FE transition temperatures defined from curves  $C_p(T)$  and  $\varepsilon(T)$  almost coincide and are equal to, respectively,  $T_N = 645$  K and  $T_C = 370$  K.

Curves  $C_p(T)$  and  $\varepsilon(T)$  are distinguished by the presence two maxima at  $T_1$  and  $T_2$  whose temperature relationship depends on  $x$  to a great extent. In [12] using Mössbauer spectroscopy, magnetic phase transition temperatures  $T_N$  were measured in the same  $(1-x)\text{BFO}-x\text{PFN}$  system compounds with  $x = 0.4, 0.5, 0.6$ , which coincide herein with temperatures  $T_1$  of abnormal heat capacity and permittivity behavior as shown in Fig. 1 and 2. X-ray diffraction and electric tests in [11–13] show that temperatures  $T_2$  are FE phase transition temperatures. Thus, the above results and structural study data demonstrate that the test sample is simultaneously a ferroelectric and antiferromagnetic at  $T < T_1$ . Fig. 3 shows a „temperature–concentration“ phase diagram,  $T_N(x)$  and  $T_C(x)$ , which has been plotted on the basis of analysis of  $C_p(T)$  and  $\varepsilon(T)$ .



**Figure 3.** „Temperature–concentration“ phase diagram.

According to [12], for  $0.8 \geq x \geq 0.40$  compounds, pseudo-cubic phase and relaxing behavior are implemented for  $(1-x)\text{BFO}-x\text{PFN}$  ceramics. In our case, expansion of peaks on the curves of temperature dependence of heat capacity and permittivity are indicative of the relaxing behavior (see Fig. 1 and 2).

Fig. 1 and 2 show that with the growth of PFN concentration,  $T_1$  and  $T_2$  shift to the low temperature range and become closer to each other, and the height of maxima is decreased with the increase in  $x$  and temperature, and they almost coincide with each other for  $x = 0.6$  compound. It should be noted that the structural changes due to  $x$  lead to high permittivity and heat capacity in a wide temperature range. High values for relaxing ceramics occur as a result of Maxwell–Wagner polarization [14], and the increased heat capacity is attributed to the appearance of a nanopolar structure in ferroelectrics with smeared phase transitions as shown in [15].

## 4. Conclusion

Thus, based on the study of temperature and concentration dependences of heat capacity and permittivity, ferroelectric and antiferromagnetic phase transition temperatures have been defined for  $(1-x)\text{BiFeO}_3-x\text{PbFe}_{0.5}\text{Nb}_{0.5}\text{O}_3$  system with different concentrations  $x$ , and taking into account the structural study, the „temperature–concentration“ phase diagram has been plotted. The findings shown herein are suitable for the use in the development of functional multiferroic materials based on  $(1-x)\text{BiFeO}_3-x\text{PbFe}_{0.5}\text{Nb}_{0.5}\text{O}_3$  solid solutions.

## Conflict of interest

The authors declare that they have no conflict of interest.

## References

- [1] Yu.N. Venevtsev, V.V. Gagulin, V.N. Lyubimov. Segnetomagnitiki. Nauka, M. (1982). 224 p. (in Russian).
- [2] A.V. Pavlenko, A.T. Kozakov, S.P. Kubrin, A.A. Pavelko, K.A. Guglev, L.A. Shilkina, I.A. Verbenko, D.A. Sarichev, L.A. Reznichenko. *Ceram. Int.* **38**, 8, 6157 (2012).
- [3] A.V. Turik, A.V. Pavlenko, K.P. Andryushin, S.I. Shevtsova, L.A. Reznichenko, A.I. Cherobabov. *FTT* **54**, 5, 891 (2012) (in Russian).
- [4] O. Raymond, R. Font, J. Portelles, J.M. Siqueiros. *J. Appl. Phys.* **109**, 9, 094106 (2011).
- [5] A.M. Kadomtseva, Yu.F. Popov, A.P. Pyatakov, G.P. Vorob'ev, A.K. Zvezdin, D. Viehland. *Phase Trans.* **79**, 12, 1019 (2006).
- [6] J.P. Patel, A. Singh, D. Pandey. *J. Appl. Phys.* **107**, 10, 104115 (2010).
- [7] D. Bochenek, P. Niemiec, P. Guzdek, M. Wzorek. *Mater. Chem. Phys.* **195**, C, 199 (2017).
- [8] N.N. Krainik, N.P. Khuchua, A.A. Berezhnoy, A.G. Tutov. *FTT* **7**, 1, 132 (1965) (in Russian).
- [9] L.A. Shilkina, A.V. Pavlenko, L.A. Reznichenko, I.A. Verbenko. *Kristallografiya* **61**, 2, 262 (2016) (in Russian).
- [10] A.S. Golofastova, N.M. Novikovskiy, V.M. Raznozov, A.V. Pavlenko, I.A. Verbenko, D.A. Sarychev, L.A. Reznichenko, A.V. Makhboroda. *UPF* **4**, 1, 24 (2016) (in Russian).
- [11] A.V. Pavlenko, K.M. Zhidel, L.A. Shilkina. *FTT* **62**, 10, 1677 (2020) (in Russian).
- [12] A.V. Pavlenko. Avtoref. dis. d.f.-m.n., NII fiziki Yuzhnogo federal'nogo universiteta, Rostov n/D. (2019) (in Russian).
- [13] A.V. Pavlenko, K.M. Zhidel, S.P. Kubrin, T.A. Kolesnikova. *Ceram. Int.* **47**, 15, 21167 (2021).
- [14] A.V. Pavlenko, A.V. Turik, L.A. Reznichenko, L.A. Shilkina, G.M. Konstantinov. *FTT* **53**, 9, 1773 (2011) (in Russian).
- [15] S.N. Kallaev, Z.M. Omarov, R.G. Mitarov, A.R. Bilalov, K. Bormanis, S.A. Sadykov. *ZhETF* **138**, 3, 475 (2010) (in Russian).