

Ferroelectromagnetic Smart Structures

$(1 - x)\text{Pb}(\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3 - (x)\text{BiFeO}_3$

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In this work an attempt was made to obtain three compositions of the solid solution $(1 - x)\text{Pb}(\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3 - (x)\text{BiFeO}_3$ for $x = 0.8, 0.7$ and 0.6 . The obtained specimens were subjected to microstructure and dielectric examinations and temperature dependences of the internal friction $Q^{-1}(T)$ and Young's modulus $E(T)$.

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1. Introduction

The $\text{PbFe}_{0.5}\text{Nb}_{0.5}\text{O}_3$ ceramics (PFN) belongs to a family of perovskite-like ferroelectrics with the $A(B'B'')\text{O}_3$ general formula. Materials of that group show wide isomorphism, which enables to substitute appropriate cations into positions B, and materials for different applications can be obtained in such a way [1]. PFN ceramics with ferroelectric properties has also antiferromagnetic properties at lower temperatures ($T_N \approx -130^\circ\text{C}$). In order to improve magnetic properties and to increase the Néel temperature to positive temperature, solid solutions with other materials of similar properties, but of higher T_{CE} and T_N temperatures were formed. The BiFeO_3 (BF) magnetoelectric is one of materials on which basis such solid solutions are formed [2]. The BiFeO_3 ceramics, as PFN, is a ferroelectric with the Curie temperature $T_{\text{CE}} = 820^\circ\text{C}$ and antiferromagnetic with Néel temperature $T_N = 370^\circ\text{C}$ at the same time. An interest in the BF material has increased significantly recently [3, 4], because it became a base compound together with $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ to produce ferroelectromagnetics with layer perovskite-like structure (e.g. of composition $\text{Bi}_4\text{Bi}_{m-3}\text{Ti}_3\text{Fe}_{m-3}\text{O}_{3m+3}$ ($m = 4, 5, 6, 8$)). It is also used as a base material of multicomponent solid solutions on the lead base e.g. $(x)\text{BiFeO}_3 - (1 - x)\text{PbTiO}_3$ [5], $(1 - x)\text{Pb}(\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3 - (x)\text{BiFeO}_3$ [6], and as lead free solid solutions e.g. $\text{BiFeO}_3 - \text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ [7], $\text{BiFeO}_3 - \text{BaTiO}_3$ [8], $\text{BiFeO}_3 - \text{SrBi}_2\text{Nb}_2\text{O}_9$ [9, 10] or two-layer $\text{BiFeO}_3 - \text{Bi}_{3.25}\text{Sm}_{0.75}\text{Ti}_{2.98}\text{V}_{0.02}\text{O}_{12}$ in a form of thin layers [11, 12]. To obtain pure single phase BiFeO_3 is a very difficult process with strictly determined technological conditions.

Occurrence of joint magnetic and electric influence in those materials enables to control magnetic and electric properties of the ceramics, using external influences e.g.:

magnetic, electric, elastic or thermal [13]. Those interesting properties cause that they become an interesting material for a production of multifunctional intelligent elements, namely those, which react strongly to different types of the influence. Various works concerning search for new multiferroic materials in a view of needs of highly advanced technology are undertaken all over the world.

An aim of the work was to develop conditions to produce the $(1 - x)\text{Pb}(\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3 - (x)\text{BiFeO}_3$ solid solution (PFN-BF) by selecting the optimum conditions of a synthesis and compacting and to examine their basic properties.

2. Experiment

The following solid solutions constituted the test material: $(1 - x)\text{Pb}(\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3 - (x)\text{BiFeO}_3$ with values $x = 0.8$ (PFN20-BF80), 0.7 (PFN30-BF70) and 0.6 (PFN40-BF60). The BF powders were synthesized in the conditions: $T_s = 700^\circ\text{C}/t_s = 1$ h, whereas the PFN powders were obtained by a two-stage synthesis method (a columbite method). Stage 1 took place according to reaction $\text{Fe}_2\text{O}_3 + \text{Nb}_2\text{O}_5 \rightarrow 2\text{FeNbO}_4$ ($1000^\circ\text{C}/4$ h), whereas stage 2 according to reaction $\text{FeNbO}_4 + 2\text{PbO} \rightarrow 2\text{PbFe}_{0.5}\text{Nb}_{0.5}\text{O}_3$ ($800^\circ\text{C}/3$ h). Conditions for compacting by a free sintering method for all compositions of the PFN-BF solid solution were selected in an experimental way. It has been found that the optimum sintering conditions are: 1050°C temperature and time 2 h with slow cooling.

Measurements of the dielectric parameters (ϵ and $\tan \delta$) were conducted on a capacity bridge of a Quad Tech type (for $\nu = 10$ kHz), microstructure examinations were made on a SEM scanning microscope with field emission, HITACHI S-4700, and measurements of the Q^{-1} mechanical losses and Young's modulus E were performed on an automatic acoustic frequency relaxator of a RAK-3 type.

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3. Test results and their discussion

Analyzing the obtained SEM photographs (Fig. 1), it can be stated that the more PFN component in the PFN–BF solid solution the more homogeneous non-porous with well-formed grain microstructure is.

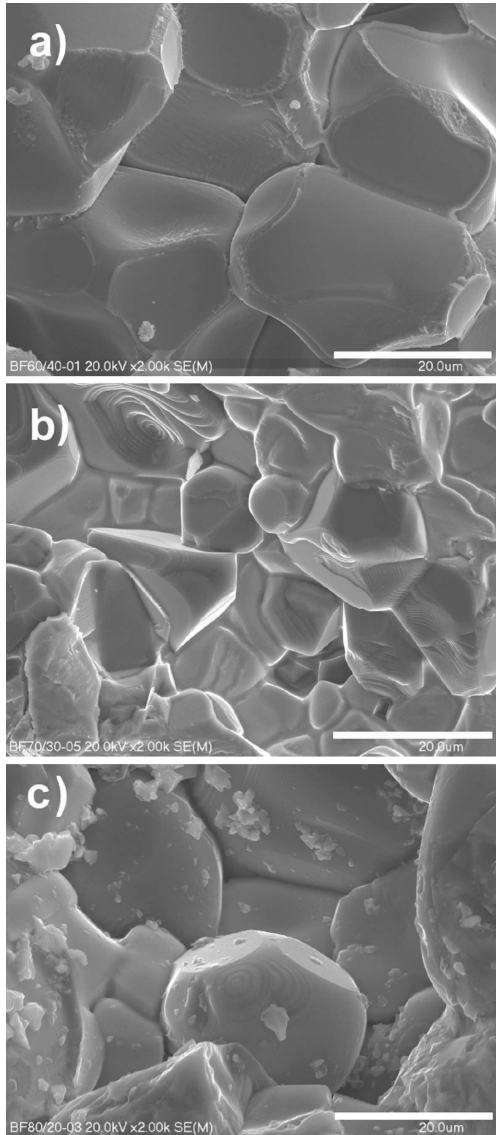


Fig. 1. SEM photographs of a fracture microstructure of PFN–BF solid solution specimens: (a) PFN40–BF60, (b) PFN30–BF70 and (c) PFN20–BF80 ($\times 2000$).

Characteristic maxima connected with presence of phase transition taking place in the material PFN–BF during heating process can be observed on the $\varepsilon(T)$ diagrams (Fig. 2). A change of the electric subsystem from the ferroelectric into paraelectric phase (FE–PE) takes place at high temperatures (T_{CE}), and a magnetic subsystem from antiferromagnetic phase to paramagnetic (AFM–PM) at lower temperatures (Table). Maxima of the internal friction called P_N , are observed in the temperature range $\approx 210^\circ\text{C}$ to $\approx 370^\circ\text{C}$ and are correlated

with the minima of Young modulus called A_N . The values of the Néel temperatures are shifting towards higher temperatures together with the increase of content of the BF. Those maxima are connected with Néel temperature which is confirmed by the conducted internal friction tests in those temperature ranges (Fig. 3).

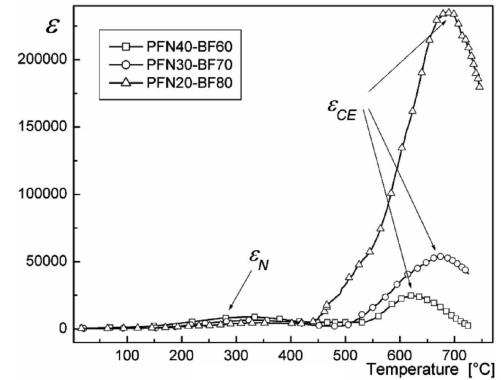


Fig. 2. Dependences of the ε electric permittivity on T temperature for the $(1-x)$ PFN– (x) BF solid solution, for $x = 0.8, 0.7$ and 0.6 ($\nu = 10$ kHz).

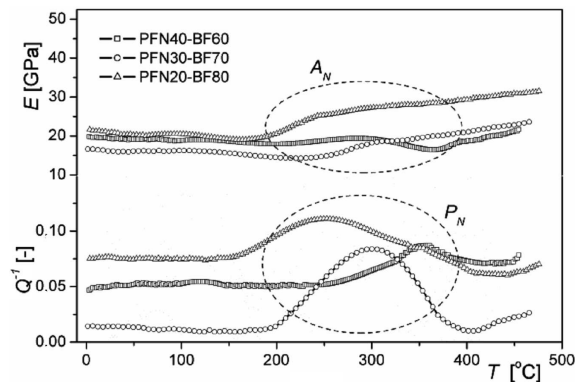


Fig. 3. Relationships of the $Q^{-1}(T)$ mechanical losses and the $E(T)$ Young modulus for the $(1-x)$ PFN– (x) BF solid solution for $x = 0.8, 0.7$ and 0.6 .

TABLE
Parameters of the solid solutions in question
 $(1-x)$ PFN– (x) BF (for $\nu = 10$ kHz).

Designation of specimens	ρ [g/cm ³]	ε_r	$\tan \delta$ in T_r	T_{CE} [°C]	ε_{CE}	$\tan \delta$ in T_{CE}
PFN40–BF60	6.21	740	0.019	624	24370	16.17
PFN30–BF70	6.02	420	0.014	673	53930	17.10
PFN20–BF80	5.25	330	0.015	690	235125	7.46

The $\varepsilon(T)$ courses show that a decrease in the BF component content in the PFN–BF solid solution decreases permittivity values and it moves phase transition of the electric and magnetic subsystem towards lower temperatures. Weak maxima of electric permittivity occurring

at the temperature range $\approx 210^\circ\text{C}$ to $\approx 370^\circ\text{C}$ are connected with a change taking place in the magnetic subsystem and it corresponds to Néel temperature.

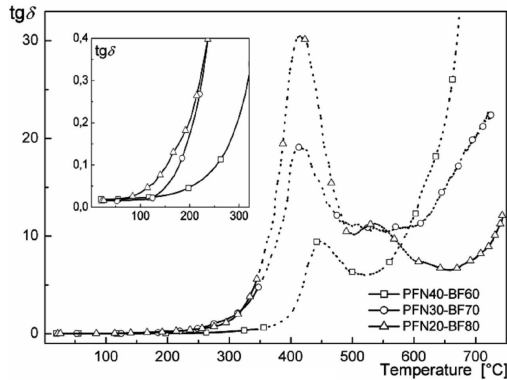


Fig. 4. Dependences of the $\tan\delta$ dielectric loss angle tangent on T temperature (in the working area — inside) for the $(1-x)\text{PFN}-(x)\text{BF}$ solid solution, for $x = 0.8, 0.7$ and 0.6 ($\nu = 10$ kHz).

At low temperatures the solid solutions in question have low dielectric losses (Fig. 4), whereas at high temperatures their values are very high (for $\nu = 10$ kHz). As in the $\varepsilon(T)$ diagrams, characteristic behaviour of those parameters in the areas of phase transition can be observed in the $\tan\delta(T)$ courses as well. At reaching T_N and T_{CE} temperatures there is a rapid increase in dielectric loss values (characteristic behaviour of losses before a phase transition), and then their rapid decrease after phase transition.

4. Conclusions

Experimentally selected technological conditions to make the $(1-x)\text{Pb}(\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3-(x)\text{BiFeO}_3$ solid solutions in question allow to obtain a ceramics of good quality by a free sintering method. Combining those two materials in the solid solution lowers high temperature of the PE-FE change of the BF component and moves the PM-AFM change of the first component (PFN) towards plus temperatures. The more the PFN component in the PFN-BF solid solution the lower temperatures, at which the change from the antiferromagnetic into paramagnetic phase takes place, are.

Temperature character of changes in permittivity shows that the magnetic subsystem has an influence on the $\varepsilon(T)$ and $\tan\delta(T)$ relationships. It confirms that there is feedback of the electric and magnetic subsystems,

occurring in the PFN-BF solid solution, which is confirmed by the performed tests of the internal friction in the characteristic temperature range.

Those characteristic properties enable to classify those types of materials into a group of biferroics, namely materials from a family of multiferroics with enhanced intelligence. High values of permittivity of the obtained PFN-BF solid solutions suggest great possibilities of applications of that type of solid solutions e.g. for low frequency transducers. However, high dielectric losses at high temperatures (T) limit possibilities of that type of applications. At the same time they imply to search for new technological solutions to improve dielectric parameters, to decrease dielectric losses in particular.

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