ARCHIVES OF ACOUSTICS
32, 4 (Supplement), 111–116 (2007)

ELECTRIC AND MECHANICAL PROPERTIES OF $\mathbf{Pb(Fe_{0.5}Nb_{0.5})O_3}$ FERROELECTRIC CERAMICS

Radosław ZACHARIASZ, Jan ILCZUK

University of Silesia
Faculty of Computer Science and Material Science
Department of Material Science
Żeromskiego 3, 41-200 Sosnowiec, Poland
e-mail: rzachari@us.edu.pl

(*received July 15, 2007; accepted October 5, 2007*)

In this work we report the synthesis of the $Pb(Fe_{0.5}Nb_{0.5})O_3$ (PFN) powders and sintered ceramics. The ceramics were prepared from oxides: Fe_2O_3, Nb_2O_5 and PbO by two-stage columbite method by calcination. PFN powders were dried and formed in samples in shape of discs (10×1) mm^3 and rectangular bars $(26 \times 10 \times 1)$ mm^3. The samples were sintered by conventional ceramic sintering (CCS) method at temperature of 1323 K for 2 h in air. The density of the ceramic samples was determined to be $\rho = 8200$ kg/m^3. The obtained results of investigations of electric and mechanical properties such as: Young's modulus E, electric permittivity ε and tangent of dielectric loss of angle $\tan\delta$ of the $Pb(Fe_{0.5}Nb_{0.5})O_3$ ceramics obtained are presented.

Keywords: PFN ceramics, Curie temperature, Néel temperature.

1. Introduction

Compounds with perovskite type structure can be treated as model materials because of the richness in physical properties and relatively simple structure. These materials have found many technical applications viz., computer memories, pyroelectric sensors, piezoelectric transducers and multilayered capacitors. For the first time SMOLENSKII *et al*. [1] have synthesized lead iron niobiate hence after abbreviated as PFN. It is a disorder captive type ferroelectric material with magnetic ordering having rhombohedral symmetry ($a = 4.017$ Å and $\alpha = 89.57$ Å) which exhibits broad phase transition around 383 K [2–4]. Lead iron niobiate, $Pb(Fe_{0.5}Nb_{0.5})O_3$ (PFN) belonging to the complex perovskite family of structures, exhibits frequency dependent on dielectric properties. The very low reactivity with silver [5], low sintering temperatures easy synthesizability and high permittivity of PFN make it a very interesting component in the commercial electro ceramic materials. The presence of Fe leads to high conductivity and hence dissipation factor, $\tan\delta$, is very high. The coexistence of ferroelectricity and the magnetism in the PFN materials may have advantage for electro-magnetic device applications, because most of the electronic devices work with not only the electric field, but also magnetic field or both simultaneously [6].

In this work, the obtained results of investigations of electric and mechanical properties such as: Young's modulus E, electric permittivity ε and tangent of dielectric loss of angle $\tan\delta$ of the $\mathrm{Pb(Fe_{0.5}Nb_{0.5})O_3}$ ceramics obtained are presented.

2. Experiment

PFN perovskite ceramics were prepared by following conventional method. Initial ingredients PbO, $\mathrm{Fe_2O_3}$ and $\mathrm{Nb_2O_5}$ were dried for 4 hrs. Firstly, $\mathrm{FeNbO_4}$ was prepared by taking $\mathrm{Fe_2O_3}$ and $\mathrm{Nb_2O_5}$ in $1:1$ molar ratio. The above ingredients were calcined at 1273 K for 4 hrs. During calcination $\mathrm{FeNbO_4}$ forms according to following solid state reaction:

$$\mathrm{Fe_2O_3} + \mathrm{Nb_2O_5} = 2\mathrm{FeNbO_4}\,. \tag{1}$$

Later it was crushed and pulverized with PbO by reacting:

$$\mathrm{FeNbO_4} + 2\mathrm{PbO} = 2\mathrm{Pb(Fe_{1/2}Nb_{1/2})O_3} \tag{2}$$

at the temperature of 1123 K for 4 hrs.

Finally, the slurry of powders was dried and formed in samples in shape of discs (10×1) mm^3 and rectangular bars $(26 \times 10 \times 1)$ mm^3. The samples where sintered by conventional ceramic sintering (CCS) method at temperature of 1323 K for 2 h in air. The density of the ceramic samples was determined to be $\rho = 8200$ kg/m^3.

The temperature dependences of the electric parameters $\varepsilon(T)$ and $\tan\delta(T)$ were determined for the samples in the shape of discs during the heating processes at the rate of 3 K/min. In order to do it the capacity bridge type QuadTech 1920 Precision LCR Meter was used. The measurements of the temperature dependences of internal friction $Q^{-1}(T)$ and temperature dependences of Young's modulus $E(T)$ were performed by automatic resonance mechanical spectrometer of the RAK-3 type controlled by computer. The measurements were conducted for the samples in the shape of rectangular bars during the heating process at the rate of 3 K/min.

3. Results and discussion

Figure 1 demonstrates the temperature dependences of the Young's modulus $E(T)$ and the internal friction $Q^{-1}(T)$ for the tested ceramic samples for two different resonance frequencies, which the values at the room temperature are respectively: $f_r = 799$ Hz and $f_r = 852$ Hz. It is visible clearly, that together with increasing the values of the frequencies, the values of the Young's modulus are increase. It is compatible with dependence used in calculations:

$$E = 94.68 \times \left(\frac{l_r}{h}\right)^3 \times \frac{m_d}{b} \times f_r^2, \tag{3}$$

where l_r, h, b and m_d – respectively: length, thickness, width and mass of vibratile part of the sample.

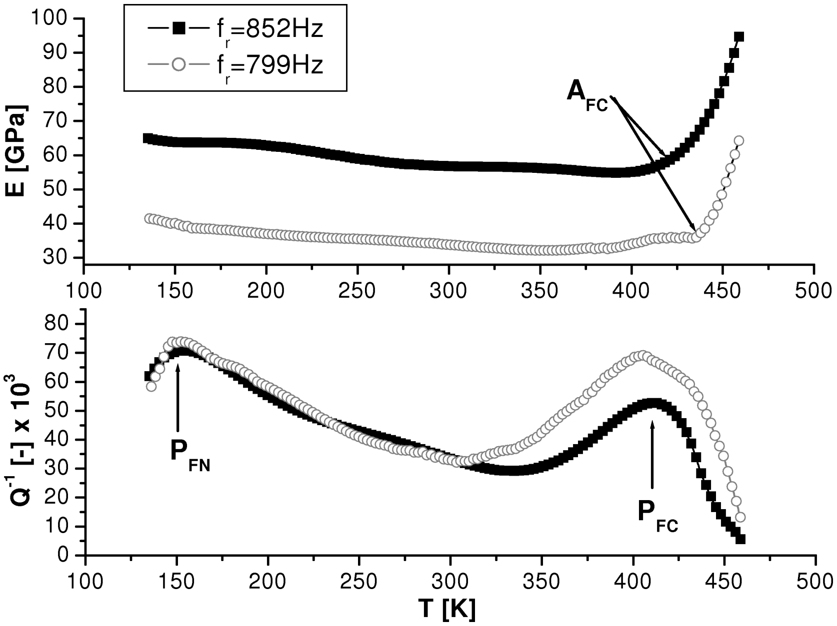

Fig. 1. The dependences of $E(T)$ and $Q^{-1}(T)$ for the tested PFN ceramics.

In the temperature range from ∼390 K to ∼465 K distinct changes of the values E correlated with maximum P_{FC} on the $Q^{-1}(T)$ dependences are observed. The maximum P_{FC} does not change its temperature position even though there are changes in frequency. However, an increase in height of the P_{FC} together with decrease in the frequency is observed. Such behavior of the P_{FC} related with $E(T)$ changes shows that it is responsible for ferroelectric ↔ paraelectric phase transition. Another maximum of the internal friction called P_{FN} is observed in the temperature range from ∼160 K to ∼120 K. On the basis of investigations of other scientists [7, 8] we believe that it is responsible for paramagnetic ↔ antiferromagnetic phase at the Néel temperature. The value of the Néel temperature is about 140 K [9]. However, so far the nature and behavior of this P_{FN} maximum have not been established yet and investigations will be conducted further in this scope.

Figure 2 shows the temperature dependences of electric permittivity $\varepsilon(T)$ and tangent of dielectric loss of angle $\tan\delta(T)$ obtained for the PFN ceramic samples. A broad peak of ε in the temperature range from ∼325 K to ∼450 K with maximum value at

$T_C = 390$ K originated from phase transition is observed on the $\varepsilon(T)$ dependences. The peak confirms the phase transition observed before on the $Q^{-1}(T)$ dependences. The character of the $\tan\delta(T)$ dependences is connected with a process of domain reorientation and associated with loss in electric conductivity (increase in the temperature range above phase transition).

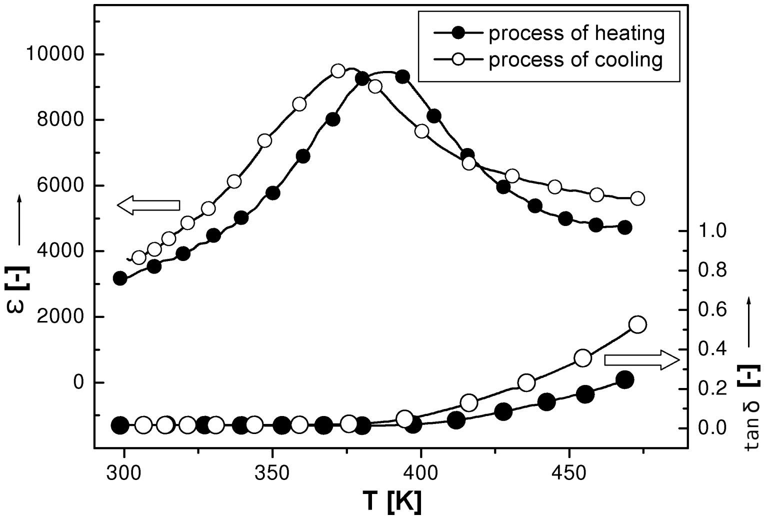

Fig. 2. The dependences of $\varepsilon(T)$ and $\tan\delta(T)$ for the tested PFN ceramics.

The temperature dependences of $\varepsilon(T)$ show diffuse character and can be well described by the linear and quadratic Curie–Weiss law (Fig. 3). For the paraelectric phase, above $T_1 = 398$ K to 442 K temperatures, this law can be used in the form:

$$\varepsilon = \frac{C_{CW}^{+}}{T - T_m}\,, \tag{4}$$

where C_{CW}^{+} is the paraelectric Curie–Weiss constant being 1.78×10^5 K. For the ferroelectric phase in the temperature range from $T_2 = 364$ K to 309 K the area applicability of linear Curie–Weiss law can be used as follows:

$$\varepsilon = \frac{C_{CW}^{-}}{T_m - T}\,, \tag{5}$$

where C_{CW}^{-} is the ferroelectric Curie–Weiss constant being 1.64×10^5 K.

The temperature range from T_1 to T_2 corresponds to the diffuse phase transition. Within the temperature range from T_m to T_1 the experimental $\varepsilon(T)$ curve follows to the quadratic Curie–Weiss law as:

$$\frac{1}{\varepsilon^*} = \frac{1}{\varepsilon} - \frac{1}{\varepsilon_m} = K(T - T_m)^2, \tag{6}$$

where ε_m is the value of electric permittivity at $T_m = T_C = 390$ K temperature and K is constant equal to 7.52×10^6 K^2.

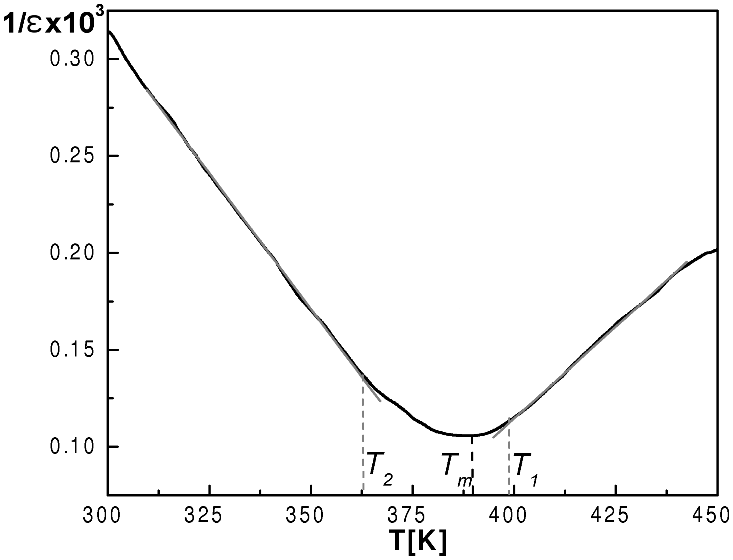

Fig. 3. The dependences of $1/\varepsilon(T)$ for the tested PFN ceramics.

4. Conclusions

The experimental results obtained in this work show that the features of low-frequency internal friction and Young's modulus in the ferroelectric and paraelectric phases as well as in the vicinity of the Curie temperature T_C of Pb($Fe_{0.5}Nb_{0.5}$)O_3 ceramics are considerably due to the dynamics of crystal lattice defects and domain walls. It was found that the changes in the temperature dependences of the Young's modulus $E(T)$ and internal friction $Q^{-1}(T)$ correspond to the temperature range of the diffuse ferroelectric phase transition determined from electric measurements of the $\varepsilon(T)$ and $\tan\delta(T)$ dependences. In the work it was shown that PFN ceramics had an additional maximum at the Néel temperature $\sim$140 K, related to the antiferromagnetic phase transition.

References

[1] Smolenskii G. A., Bokov V. A., Isupov V. A., Krainik N. N., Pasynkov R. E., Sokolov A. I., *Ferroelectrics and Related Materials*, Gordon and Breach Sci. Publishers, New York 1984.

[2] Bokov V. A., Mylinikova I.E., Smolenskii G.A., J. Exp. Theor. Phys. USSR, Phys. Ser., **42**, 643 (1962).

[3] Isupov V. A., Agranovskaya A. L., Khuchua N. P., Bull. Acad Sci. USSR, Phys. Ser., **24**, 1268 (1960).

[4] Smolenskii G. A., J. Phys. Soc. Jpn., **28**, 26 (1970).

[5] LU C. H., LIN J. Y., Ceram. Int., **23**, 223 (1977).

[6] SINGH K., BAND S. A., Ferroelectrics, **175**, 193 (1996).

[7] MARYANOWSKA A., PIETRZAK J., Ferroelectrics, **162**, 81 (1994).

[8] TAWFIK A., ABD EL-ATI M. I., ABOU-SEKKINA M. M., J. Phys. Soc. Japan, **54**, 2730 (1985).

[9] IVANOV O. N., SKRIPTCHENKO E. A., PRYAKHINA M. E., Ferroelectrics, **298**, 145 (2004).