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INTERNAL FRICTION IN THE PFN CERAMICS WITH CHROMIUM DOPAND

TARCIE WEWNĘTRZNE W CERAMICE PFN DOMIESZKOWANEJ CHROMEM

An aim of this work was to determine an influence of an admixture, the chromium (for x from 0.01 to 0.06), on the mechanical properties of the PFN ceramics. The ceramics with chemical composition $Pb(Fe_{0.5-x}Cr_xNb_{0.5})O_3$ was synthesized in two steps from simple oxides PbO, Fe_2O_3, Nb_2O_5, Cr_2O_3. The first stage was based on obtaining the $FeNbO_4$ from the Fe_2O_3 and Nb_2O_5 simple oxides. At this stage an admixture in a form the Cr_2O_3 chromium oxide was added to the solution. In the second stage the PbO lead oxide and the doped $FeNbO_4$ (obtained earlier) were synthetized. The sintering of ceramic samples PFCN type was carried out by free sintering method. Temperature measurements of the internal friction were conducted on a computer-controlled automatic resonant mechanical spectrometer (heating cycle with 3 deg/min).

Keywords: PFN ceramics, mechanical properties, ferroelectromagnetics, perovskites.

W pracy przedstawiono wpływ domieszki chromu (dla x = 0,01 – 0,06) na właściwości mechaniczne ceramiki PFN. Ceramika o składzie chemicznym $Pb(Fe_{0.5-x}Cr_xNb_{0.5})O_3$ została syntezowana z prostych tlenków PbO, Fe_2O_3, Nb_2O_5, Cr_2O_3 w dwóch etapach. Pierwszy etap polegał na otrzymaniu $FeNbO_4$ w wyniku reakcji prostych tlenków Fe_2O_3 i Nb_2O_5. W tym etapie została również wprowadzona domieszka tlenku chromu Cr2O3. W drugim etapie zsyntezowano tlenek ołowiu z otrzymanym wcześniej domieszkowanym $FeNbO_4$. Spiekanie ceramicznych próbek PFCN typu przeprowadzono metodą spiekania swobodnego. W celu określenia parametrów mechanicznych wykorzystano metodę tarcia wewnętrznego. Temperaturowe pomiary tarcia wewnętrznego zostały wykonane za pomocą sterowanego komputerowo automatycznego relaksatora częstotliwości akustycznych (cykl grzania z szybkością 3°/min).

1. Introduction

The perovskite structure materials have been used widely in a lot of fields of the modern technology. They are used as high density capacitors, actuators, pyroelectric detectors and piezoelectric transducers [1]. The PFN – $Pb(Fe_{0.5}Nb_{0.5})O_3$ ceramics also belongs to the group of perovskite type materials, in which ions Fe^{3+} and Nb^{5+} are arranged in the octahedral positions at random [2]. This ferroelectromagnetic material is characterized by magnetic ordering and spontaneous electric polarization taking place simultaneously [3]. At the temperature of about 358-383 K during heating cycle, there is a phase transition from the rhombohedral ferroelectric phase to the cubic paraelectric phase [4]. The magnetic Neel temperature is reported to be 149 K [5]. In this material the electric order is caused by shift of Pb on A side and Nb on B side in one direction and the shift of O at the corner of the octahedral in the opposite direction. Fe has a natural magnetic moment. Fe-O-Fe connecting line forms a 180° angle, with provides an optimum condition to the existence of magnetic ordering [6].

In the recent years there has been an increase in the interest in this material and its specific ferroelectromagnetic properties. A detailed insight into relationships between the chemical composition, the crystalline structure, the electro-physical properties and the domain structure enables to obtain the ceramics with better and better properties, which are necessary to be used in the modern technology. It is necessary to conduct intensive investigations dealing with factors influencing properties of this material. A change of the base chemical composition of the PFN ceramics by incorporating admixtures is one of those factors. A lot of admixtures both soft and hard ones can be added into the PFN ceramics [7-8].

In the non-admixed PFN ceramics there are deficiencies of oxygen formed during processing (PbO evaporation, during sintering at high temperatures) which generate the oxygen vacancies [9]. In a case of admixing the PFN ceramics with chromium, the Cr^{3+} ion will replace the Nb^{5+} niobium ion in sublattice B ($W_{DB} < W_B$) or replace the Fe^{3+} iron ion as a result of isovalence admixing ($W_{DB} = W_B$). In the first case the admixing Cr^{3+} chromium ion in PFN constitutes acceptors. Such admixing will generate the *p*-type conduction, what

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decreases electric conductivity of ceramics [8]. There is also a possibility here for the excess of the chromium admixture to be placed in the interstitial positions, what results in formation of donor centers generating additional electrons. It is possible because the chromium on the valence orbit has a single weakly bound electron. These additional electric charges will be placed in the interstitial areas causing a decrease in effective resistance of the grain boundaries. In this case conductivity of the PFN type ceramics may increase [8].

An internal friction method is often used in the mechanical properties testing. This method enables to obtain information about the material behavior at an atom level by observing macroscopic vibrations of a specimen. This method is applied widely in the ceramic materials testing due to its high sensitivity to changes in the point defect concentration, an interaction between the defects and changes in the real structure [10-12].

An aim of this work was to determine an influence of an admixture, the chromium, on the PFN ceramics mechanical properties.

2. Material tested and experiment

The properties of PFN-type ceramics depend on a structure formed during a synthesis. While synthesizing a pyrochlore phase is formed besides the perovskite and its presence decreases the PFN ceramics properties. A two-stage columbite method was selected as a production method to limit the pyrochlore phase formation [13]. The $Pb(Fe_{0.5-x}Cr_xNb_{0.5})O_3$ ceramics (PFCN) was obtained from simple oxides PbO, Fe_2O_3, Nb_2O_5, Cr_2O_3. The first stage of the production was based on obtaining the $FeNbO_4$ from the Fe_2O_3 and Nb_2O_5 oxides [14]. At this stage an admixture in a form the Cr_2O_3 chromium oxide (x from 0.01 to 0.06) was added to the solution. The oxides were milled for 10 hours, and the powder obtained was synthesized at 1173 K for 2 hours. The second stage was based on adding the PbO lead oxide into the doped $FeNbO_4$ (5.0 % allowance of PbO was taken into account to level the lead evaporation). The powders were milled (10 h) and next synthesized at 1073 K / 2 h. The ceramic samples were made by the free sintering (FS) in the following conditions: temperature sintering T_s = 1398 K and time sintering t_s = 2 h. On the surface of the samples was applied silver electrode by burning method.

The internal friction $Q^{-1}(T)$ and resonance frequency f longitudinal vibration of the sample were measured with a resonance mechanical spectrometer of the RAK-3 type controlled by a computer. The values of the Young's modulus E were calculated on the ground of the measurements of resonance frequency f vibration of the sample, conducted simultaneously with the internal friction measurements, using with dependence (1):

$$E = 94,68 \left(\frac{l_r}{h} \right)^3 \cdot \frac{m_d}{b} \cdot f^2 \qquad (1)$$

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

The testing set of the RAK-3 type mechanical spectrometer is built with two chambers: the testing chamber and the cooling chamber. The testing chamber is put into the cooling one. The ceramic specimen tested is mounted in the holder, which is put into the testing chamber. Before starting the measurements air is removed from the chamber by a rotary vacuum pump (the vacuum obtained is about 10 Pa). The specimen in question placed in the holder is between two electrodes: exciting (E_w) and registering (E_r). Voltages U_1 and U_2 of the value from $0 - 2$ kV are constantly applied to the electrodes from a high voltage power unit. Additionally, a.c. voltage, which results in mechanical vibrations of the specimen, is applied to the exciting electrode from a generator. Work of a resonance mechanical spectrometer is controlled by an appropriate computer program. This program by co-operating with a set of appropriate DAC transducers analyzes signals coming from the testing chamber. Then, it changes those calculating values of the internal friction at the given temperature [15].

In the case of the Q^{-1} values the error is assumed to be at a level of 2.0 %, whereas in the case of the f values, the error is 1.0 %. The temperature is determined with accuracy of about 0.5 K.

3. Results and discussion

Measurement results of the internal friction $Q^{-1}(T)$ and the dynamic Young's modulus $E(T)$ are presented in Fig.1. The measurements were performed at frequency f = 760 Hz (heating rate of 3.0 K/min) for the non-admixed PFN ceramics.

There is one maximum on the Q^{-1} = f(T) relationship at the temperature range 360–385 K (P_F). This maximum is related to phase transition from the rhombohedral ferroelectric phase to the cubic paraelectric phase [16]. In the temperature range of the maximum presence on the $Q^{-1}(T)$ curve, anomalies from normal are also observed on the E = f(T) relationship - gradual increase in the value observed from the A_{fl} point minimum. The phase transition taking place in the given temperature range is also confirmed by the performed measurements of the temperature relationship of electric permittivity. For the undoped PFN ceramics a clear wide peak was observed on the $\varepsilon(T)$ relationship in the temperature range of 350 - 450 K [16].
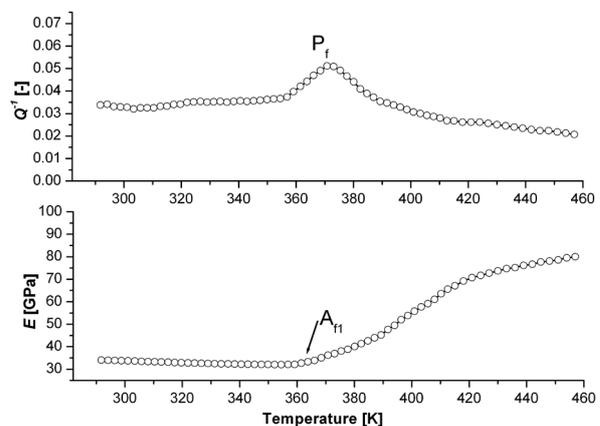
Fig.1. Temperature relationships of the Q-1(T) internal friction and the E(T) dynamic Young's modulus for the non-admixed PFN ceramics (f = 760 Hz)

Temperature relationships of the internal friction obtained for the PFCN type ceramics admixed with the chromium are presented in Fig.2. The $Q^{-1}(T)$ relationships obtained for the ceramics with $x = 0.01$, 0.03 and 0.05 are presented for the comparison. Values of the internal friction at a room temperature Q_R^{-1}, a temperature T_{OF} of the P_F friction peak at its highest point, as well as values Q_{max}^{-1} for the PFCN type ceramics are shown in Table 1.
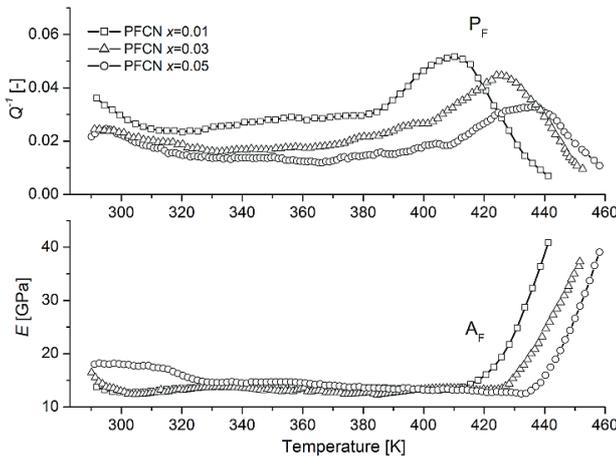
Fig.2. Temperature relationships of the Q-1(T) internal friction and the E(T) dynamic Young's modulus of the admixed PFCN ceramics for x = 0.01, 0.03 and 0.05 (f = 753 Hz).

Analyzing the data presented in Table 1 and in Fig.2 it can be stated that an increase in the chromium content in the PCFN ceramics results in the internal friction background decrease. The observed relationship between the chromium admixture concentration increase and the internal friction value is identical as relationships observed for other ceramics doped with hard admixtures. The admixture concentration increase leads to lowering of the maximum P_F height. A displacement of the P_F peak maximum towards higher temperatures is also observed with the chromium concentration increase and the temperature range increase from the ferroelectric to the paraelectric phase transition. The chromium concentration increase is also responsible for the phenomenon observed. An increasing number of the admixture atoms can cause an increase in a number of new phase nuclei. Analyzing the $Q^{-1}(T)$ values obtained for PFCN with $x = 0.06$ we can see the further decrease in the internal friction value at a room temperature (Q_R^{-1}), lowering of the P_F peak height ($Q_{F max}^{-1}$) and a slight displacement towards higher temperatures (T_{OF}). On the $E(T)$ relationships minima corresponding to them are observed. The ferroelectric to paraelectric phase transition is responsible for the P_F maximum formation as for other compositions in question, including the non-admixed PFN ceramics (Fig.1). Referring to the earlier works authors proved that such of the maximum $Q^{-1}(T)$ in the areas of phase transitions was mainly connected with phenomena described by the Delorme and Gobin model [17]. The relative changes of the volume undergoing to phase transition are shown in this model. These changes are the function of the heating and cooling processes. Thus the following formula was derived:

$$Q^{-1} = \frac{KG}{\omega} \cdot \frac{\partial m}{\partial T} \cdot \frac{\partial T}{\partial t} \qquad (2)$$

where: K – material constant, G – shear modulus, ω - frequency of the sample vibrations, $\omega = 2\pi f_r$ (f_r – resonance frequency), $\frac{\partial m}{\partial T}$ - the volume of substance undergoing the phase transition in unit temperature change, $\frac{\partial T}{\partial t}$ - the rate of the temperature changes (during heating or cooling processes).

Height of the internal friction peaks connected with the phase transition is directly proportional to rate of the temperature changes and inversely proportional to resonance frequency changes, what was introduced in the formula 2.

TABLE 1

Specification of characteristic mechanical parameters and a temperature of the internal friction maximum presence for the PFCN type samples.

x	Q_R^{-1} [-]	$Q_{F max}^{-1}$ [-]	T_{OF} [K]
0	0.0350 ± 0.0007	0.0241 ± 0.0005	370 ± 0.5
0.01	0.0362 ± 0.0007	0.0227 ± 0.0004	412 ± 0.5
0.02	0.0286 ± 0.0006	0.0193 ± 0.0004	419 ± 0.5
0.03	0.0242 ± 0.0005	0.0177 ± 0.0004	423 ± 0.5
0.04	0.0240 ± 0.0005	0.0165 ± 0.0003	425 ± 0.5
0.05	0.0238 ± 0.0005	0.0146 ± 0.0003	433 ± 0.5
0.06	0.0237 ± 0.0005	0.0129 ± 0.0002	440 ± 0.5

4. Conclusions

Specimens of multiferroic ceramics $Pb(Fe_{0.5}Nb_{0.5})O_3$ and of the admixed with the chromium $Pb(Fe_{0.5-x}Cr_xNb_{0.5})O_3$ ceramics, were prepared for the test needs. Analyzing the data presented in the work it can be stated that an increase in the chromium content in the PCFN ceramics results in the internal friction background decrease. It is identical as relationships observed for other ceramics doped with hard admixtures. A displacement of the P_F peak maximum towards higher temperatures is also observed with the chromium concentration increase and the temperature range increase of the transition from the ferroelectric to the paraelectric phase.

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