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$PbFe_{1/2}Nb_{1/2}O_3$ CERAMICS AS A BASE MATERIAL FOR ELECTROMECHANICAL TRANSDUCERS

D. BOCHENEK, P. WAWRZAŁA

University of Silesia
Faculty of Computer and Materials Science
Department of Materials Science
Śnieżna 2, 41-200 Sosnowiec, Poland
e-mail: wawrzala@ultra.cto.us.edu.pl

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$PbFe_{1/2}Nb_{1/2}O_3$ (PFN) material of perovskite structure has been rising interest because it connects both ferroelectric and antiferromagnetic properties. The paper presents tests of PFN ceramics obtained as a result of sintering simple oxides. As comparison, the base composition of the ceramics and composition with lithium admixture was synthesized. Densification was carried out using two methods: conventional sintering and hot pressing. XRD patterns, SEM micrographs of fractures surfaces, dielectric and electromechanical properties were performed.

Admixing of PFN ceramics with a little amount of lithium allowed obtaining ceramics with better set of parameters from the point of view of their practical usage. The method of densification by hot pressing additionally improves these properties.

Key words: PFN ceramics, lead iron niobate ceramics, electromechanical transducers, electromechanical properties.

1. Introduction

PFN is a member of enormous perovskite-like family of ferroelectrics with the general formula $A(B'B'')O_3$, which is characterized by wide isomorphism. It allows to substitute certain cations to B positions. Thanks to that and using appropriate technology it is possible to obtain materials suitable for many sorts of usages. In case of PFN ions of iron, niobium and lithium are substituted randomly to octahedral positions B' and B'', whereas lead locates to A position [1, 3]. Iron has a natural magnetic moment. Connecting Fe-O-Fe in the angle of 180° ensures optimum state of magnetic order occurrence [7]. Ferroelectromagnetic PFN materials are of high conductivity which can by minimized by, for example, a little amount of lithium [9].

PFN material can be used as a dielectric and magnetic medium as well as for multilayer ceramic capacitors (MLCC) and inductors, multilayer microwave resonators and

filters as tunable transducers, pyroelectric sensors, electrostrictive actuators, micropositiometers and memory devices [2, 3, 5, 8]. Technological process (selection of sintering conditions, types of pulverization and densification of powder etc.) has a great impact on ceramics density or microstructure. At the same time it influences it's final properties and stability of parameters. In the case of mass production the use of conventional ceramics powder technology is most widespread. The paper shows PFN ceramics technology as a result of simple oxides sintering and impact of a slight lithium admixture on its final properties.

2. Measurement

$(Fe_{0.5}Nb_{0.5})O_3$ ceramics was obtained using oxides: PbO ($> 99\%$), Fe_2O_3 ($> 97\%$) and Nb_2O_5 ($> 99\%$). Figure 1 show the diagram of technology together with compositions PFN and PFN with 1at.% Li admixtures determination (in diagram marked with discontinuous line). Densification was carried out conventionally (CS) and by hot pressing method (HP). Silver electrodes were fixed on the samples' surface using the method of silver paste firing. XRD tests of crystallographic structure were performed on pollycrystalic diffractometer Philips X'pert. Percentage of perovskite phase contents P_f was

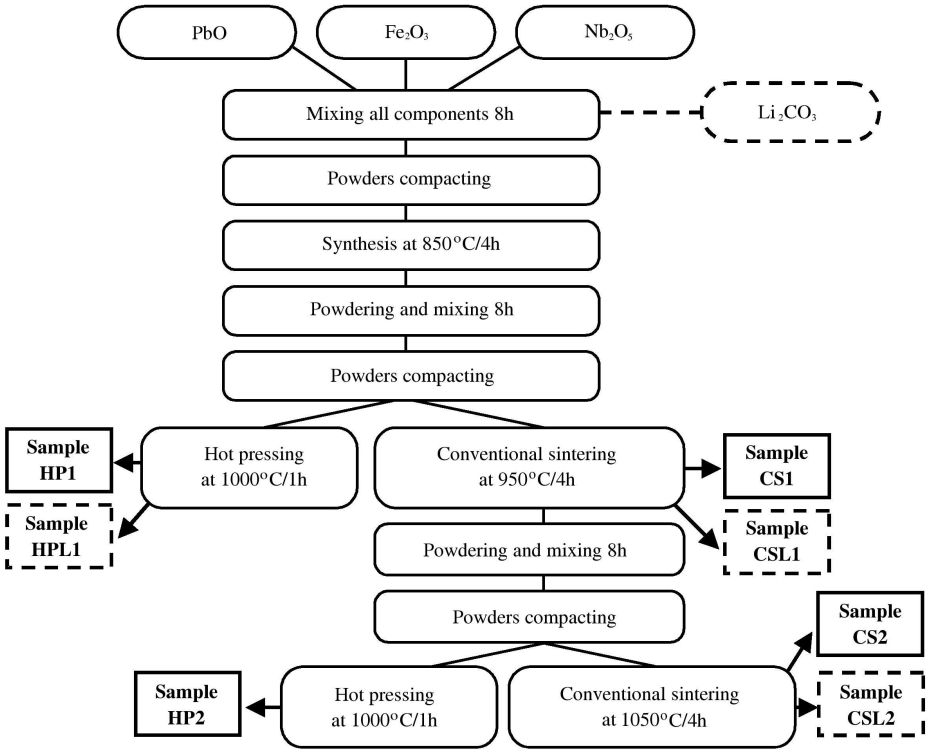

Fig. 1. Diagram of PFN ceramics technological process.

calculated from the following relation:

$$P_f = \frac{I_{110} \cdot 100}{I_{110} + I_{222}} \ [\%], \tag{1}$$

where I_{110} and I_{222} are intensities of the (110) perovskite and (222) pyrochlore diffraction lines.

Ceramics microstructure tests were carried out taking advantage of scanning microscope (SEM) HITACHI S-4700 and EDS Noran Vantage system. Temperature measurements of dielectric parameters were made using the bridge QuadTech 1920 Precision LCR Meter type, with heating speed of $0.5°$C/min, for the heating and cooling cycle. Resistivity measurements were carried out in the temperature range (20–400)°C using pA meter (Tesla BM518) and electromechanical measurements using non-contact fiberoptic displacement sensor Philtec Inc. D63 and high voltage amplifier Matsusada HEOPS-5B6 controlled by PC.

3. Results and discussion

Figure 2 shows sample XRD pattern for PFN ceramics synthesized from oxides and densified by hot pressing method (HP1). XRD data pictures co-existence of perovskite and pyrochlore phase presence. In such a case the percentage content of perovskite phase is $P_f = 93.4\%$. Despite pyrochlore phase presence PFN ceramics has good properties (Table 1).

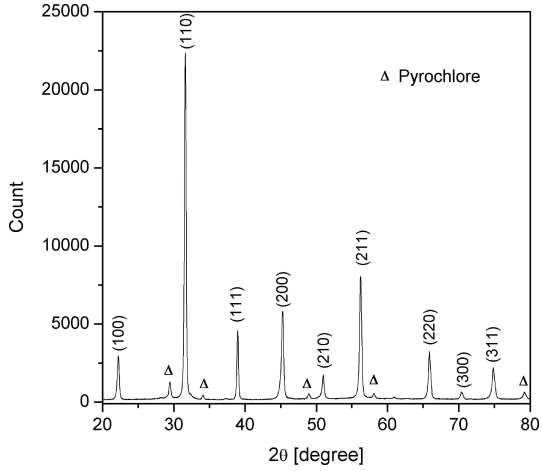

Fig. 2. XRD pattern of samples HP1, as indicated by the symbols Δ pyrochlore phase.

The technology discussed gives possibilities of obtaining ceramics with high density, which is characterized by fine grained structure ($r_{\mathrm{av}} < 2$ μm) with slight porosity and densely packed grains (Fig. 3). PFN ceramics without lithium admixture contains bigger, less formed grains comparing to samples doped with lithium. All the tested

Table 1. PFN ceramics parameters.

PFN	T_m [°C]	Density [kg/cm^3]	ρ at T_r [Ωm]	ρ at 250°C [Ωm]	ε_r	$(\tan\delta)_{Tr}$	ε_m	$(\tan\delta)\varepsilon_m$	$S_{\rm rest}$ [%]	H_S [%]	d_{33} [pC/N]
CS1	109	7.17	8.38×10^6	3.71×10^3	1450	0.0630	5725	0.5195	0.0031	6.3	145
CS2	107	7.63	5.81×10^6	4.12×10^2	2940	0.0319	8490	0.5439	0.0037	20.1	129
HP1	105	8.13	3.79×10^3	2.92×10^2	3660	0.1101	11920	1.5873	0.0060	23.6	86
HP2	102	8.18	5.37×10^3	5.84×10^2	2420	0.0601	9620	0.9651	0.0031	18.4	154
CSL1	98	8.03	1.87×10^8	9.03×10^3	3200	0.0158	9910	0.0299	0.0035	6.1	142
CSL2	95	6.94	2.09×10^6	7.83×10^3	4300	0.1489	13440	0.3546	0.0042	9.2	189
HPL1	98	8.10	1.67×10^8	4.45×10^3	3260	0.0167	10020	0.0346	0.0060	3.4	253

fractures cracked on the grains' borders. Increase of temperature and time of sintering greatly influences the samples' microstructure (average size of grains increases both with temperature increase and with prolonging of the sintering time). Additional test of PFN samples was the analysis of the contents homogeneity. Both point and surface analyses EDS confirmed qualitative contents of the samples.

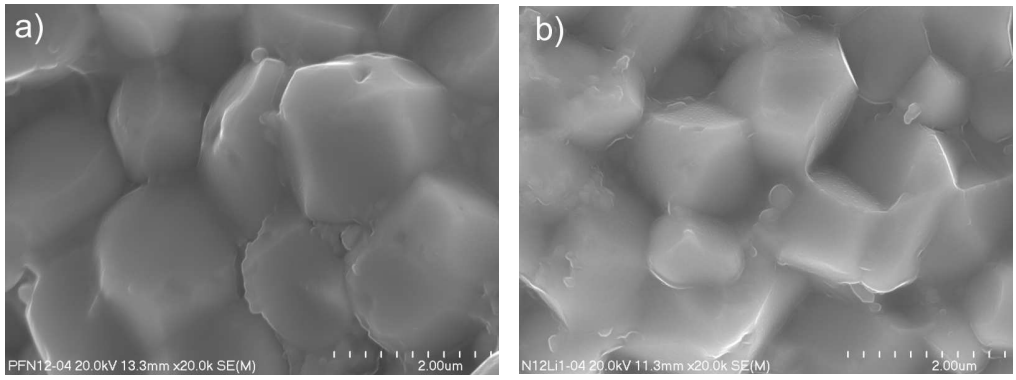

Fig. 3. Scanning electron microphotographs of samples PFN:
a) for undoped PFN and b) for PFN+1at.%Li.

In conventionally densified PFN ceramics resistivity ρ in the room temperature is $\sim 10^6$ Ωm, whereas for the samples densified by hot pressing $\sim 10^3$ Ωm. Above the temperature of phase transition ρ immediately decreases and in the temperature of 250°C is it $\sim 10^3$ Ωm and $\sim 10^2$ Ωm accordingly for CS and HP samples. In case of samples doped with lithium the values of resistivity are $\sim 10^8$ Ωm in the room temperature and $\sim 10^3$ Ωm in the temperature 250°C (Table 1).

Temperature of phase transition of PFN ceramics does not depend on frequency and conditions of sintering, it has only a slight influence on it. The value of electric permittivity increases with sintering temperature increase and multiple sintering (in case of

undoped PFN). Using densification by hot pressing (HP) also increases value of electric permittivity. In samples doped with lithium the increase of maximum electric permittivity is the greatest. Introducing lithium admixture results with decrease of phase transition temperature.

Temperature data for electric permittivity shows ferroelectric phase transition diffusion (Fig. 4a). This high temperature range of phase transition may be connected with change of material composition resulting from non-uniform positioning iron Fe^{3+} and niobium Nb^{5+} ions in octahedron which was analyzed by the authors of the paper [4]. In PFN ceramics without the lithium admixture, the phase transition occurs in wider range of temperatures comparing to ceramics doped with Li. Using densification by hot pressing only slightly influences the level of phase transition diffusion.

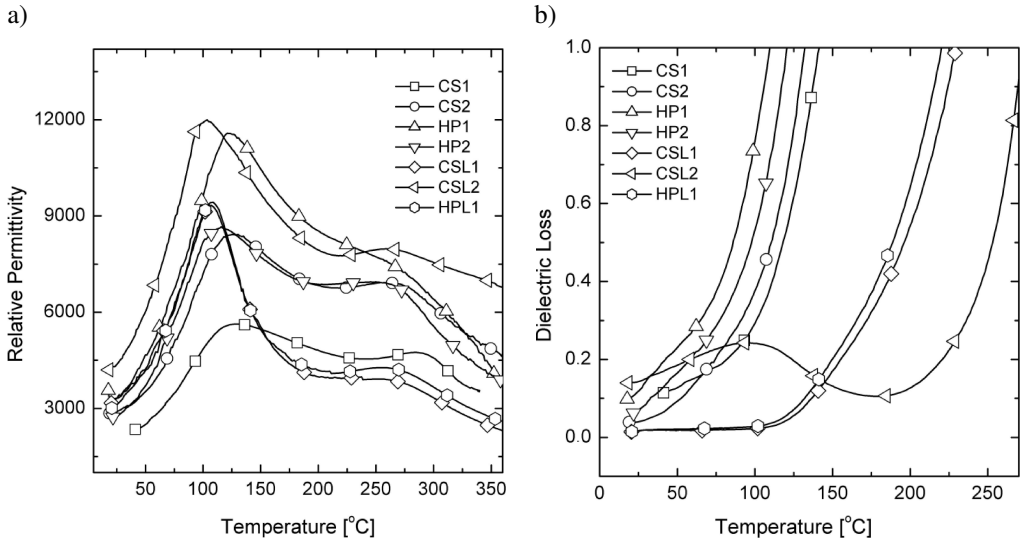

Fig. 4. Dielectric constant (a) and dielectric loss (b) as a function of temperature for the PFN (with and without Li admixture) sintered conventionally and by hot pressing method.

Undoped PFN ceramics obtained using the technology mentioned above demonstrates high values of dielectric losses (Fig. 4b). In the ferroelectric phase those losses systematically increase. Above T_m, in the paraelectric phase, a sudden increase of dielectric losses takes place, which can be connected with formation of a new thermal activation mechanism. Similar behavior was observed and analyzed in the paper [3] in which the authors attributed to partial reduction of $Fe^{3+} \leftrightarrow Fe^{2+}$ ions in octahedral positions and formation of oxygen vacancies while sintering in high temperatures. Introducing lithium admixture to basic PFN contents considerably reduces dielectric losses (Table 1).

Figure 5 shows diagrams of relative strain in the function of electric field for unpolarized PFN ceramics in the room temperature. The strain taking shape of "butterfly wings" (Fig. 5a) and practically linear relation $S(E)$ point at the piezoelectric nature of

the strain [6]. The loops demonstrate relatively low values of residual strain and hysteresis (accordingly S_{rest} and H_S in Table 1). Strain hysteresis coefficient was calculated according to the formula:

$$H_S = (H_{\mathrm{half}}/S_{\max}) \cdot 100\%, \tag{2}$$

where H_{half} – strain hysteresis for $1/2$ maximum electric field [%], $S_{\max}$ – strain for the maximum applied electric field [%].

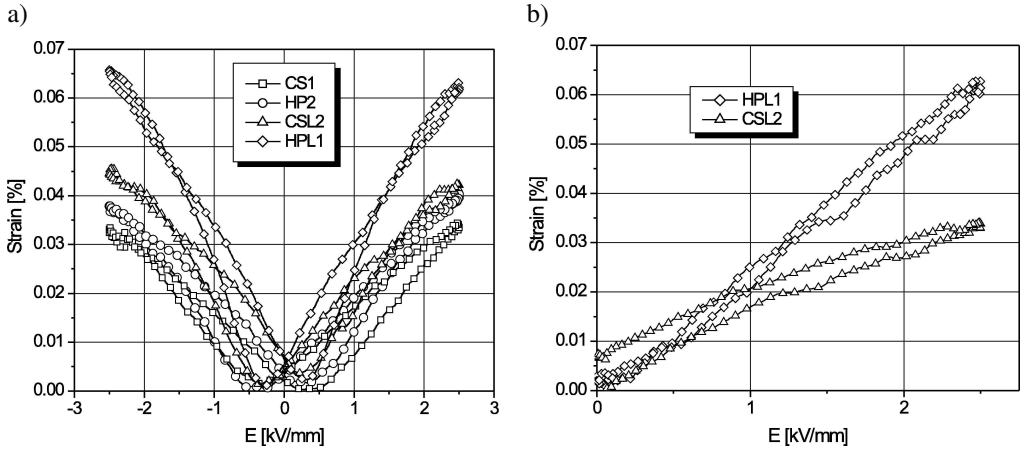

Fig. 5. Strain loops as a function of electric field (1 Hz); a) bipolar, b) unipolar for selected samples of unpolarized PFN ceramics.

Such a behavior is caused by ferroelectric softness – low values of coercive field E_C. Test of polarization in the electric field function $P(E)$ showed that samples PFN possess very narrow, ellipsoidal electrical hysteresis loops. Figure 5b shows behaviors of HPL1 and CSL2 samples under the influence of unipolar electric field. It may be observed that hot pressed ceramics demonstrates clear dominance over conventionally sintered ceramics both according to the strain value, and at the same time linearity module d_{33} and hysteresis H_S coefficient (Table 1).

4. Conclusion

XRD analysis of ceramics samples $PbFe_{1-x}Nb_xO_3$ confirmed attachment of their crystalline structure to the materials of perovskite type group. Microstructure tests showed that introducing small amount of lithium to the basic contents of PFN reduces the average size of grains (< 2 μm) and increases their homogeneity in the whole volume of the sample. Lithium substantially reduces high dielectric losses which is also manifested in increase of samples' resistivity both in low and in high temperatures. In case of necessity of PFN ceramics obtention as a result of simple oxides sintering, it is indispensable to introduce a slight amount of lithium (1%at.) before the process of synthesis.

Ferroelectric hysteresis loop tests showed very low values of coercive field (close to zero). It facilitates PFN polarizability (good electromechanical properties), however high conductivity constitutes a barrier for using high electric fields. Interesting properties of PFN ceramics encourage further testing, improving and optimizing technology in order to obtain a product able to find application in manufacturing electromechanical transducers.

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