

D. BOCHENEK*, F. GRABOWSKI*, P. NIEMIEC*

INFLUENCE OF COBALT ADMIXTURE ON THE MICROSTRUCTURE AND DIELECTRIC PROPERTIES OF PFN CERAMICS**WPŁYW DOMIESZKI KOBALTU NA MIKROSTRUKTURĘ I DIELEKTRYCZNE WŁAŚCIWOŚCI CERAMIKI PFN**

Within our work a ceramic of the PFN type was obtained by a single stage method and it was subjected to a cobalt modification in the amount of: 1.0, 2.0, 3.0, 4.0 and 6.0 mol%. Studies of the influence of the cobalt admixture on the crystalline structure, microstructure and ferroelectric properties of PFN ceramics were performed. It was shown that the iso-valence PFN admixing with cobalt had a positive influence on the density and ceramic microstructure. Higher cobalt admixtures (above 1.0 mol%) in PFN eliminate pyrochlore phase formation, and at the same time they reduce maximum electric permittivity values. The ferroelectric to paraelectric phase transition in the modified PFN compositions undergoes diffusion.

Keywords: multiferroics, smart materials, ferroelectromagnetics, PFN ceramics

W pracy otrzymano ceramikę typu PFN metodą jednoetapowej syntezy, modyfikowaną kobaltem w ilości: 1,0, 2,0, 3,0, 4,0 i 6,0% mol. Przeprowadzono badania wpływu domieszki kobaltu na strukturę krystaliczną, mikrostrukturę i podstawowe właściwości ceramiki typu PFN. Wykazano, że izowalencyjne domieszkowanie PFN kobaltem wpływa pozytywnie na gęstość i mikrostrukturę ceramiki. Większe ilości domieszki kobaltu (pow. 1,0%mol) w PFN eliminują powstawanie fazy pirochlorowej, a jednocześnie zmniejszają wartości maksymalnej przenikalności elektrycznej. Przemiana fazowa z ferroelektrycznej do paraelektrycznej fazy, w modyfikowanych składach PFN, ulega rozmyciu.

1. Introduction

The $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$ (PFN) is a known multiferroic material, with a perovskite-like structure, characterised by simultaneous magnetic ordering and spontaneous electric polarisation [1, 2]. The presence of both ferroelectric and anti-ferromagnetic properties in the PFN material can be used to produce diverse electronic and electro-mechanic equipment controlled by both electric field and magnetic field (piezoelectric ceramic sensors, passive and active intelligent structures, magnetoelectric transducers, pyroelectric detectors, electrostriction motor operators, micro-adjusters, memory devices (computer memories), sensors and transducers based on magnetically modulated piezoelectricity, multiferroic-based magnetic field sensors, multiferroic/semiconductor structures, such as spin filters etc.) [e.g. 3, 4].

The basic problem, occurring while obtaining the PFN ceramics is a possibility of formation the non-ferroelectric pyrochlore phase, high electric conduction and dielectric losses [5]. The application properties and parameters of the ferroelectric ceramics of the PFN

type depend on their crystalline structure and microstructure. The higher perfection of the crystalline structure and the more homogenous and nonporous microstructure, with regular sizes and well crystallised grains, the more optimal properties the ceramic has. The PFN ceramic production conditions and an accurate and precise course of the whole technological process, e.g.: the way of powder particle size reduction and the way of powder synthesis and compacting (sintering), temperature, sintering time and heating rate, etc., have a great influence on the crystal structure and microstructure [6-9].

The wide isomorphic properties of perovskites (susceptibility to deviations from stoichiometry) enable the control of their physical properties by the selection of appropriate technological conditions and method of production also by doping of the basic composition [10-13]. There are several ways for the iso-valence and hetero-valence doping of PFN, e.g. soft doping (with cations of a valence higher than those of the base cations and ionic radii close to them), hard doping (with cations of a valence lower than those of the base cations), softening-hardening doping, and moderately hard dop-

* UNIVERSITY OF SILESIA, DEPARTMENT OF MATERIALS SCIENCE, 41-200 SOSNOWIEC, 2 ŚNIEŻNA STR., POLAND

ing. The soft admixtures decrease the ferroelectric hardness of PFN, and hard admixtures result in its increase, whereas the softening-hardening admixtures perform those two functions simultaneously, that is they influence certain PFN parameters like the soft admixtures, and values of other parameters like the hard admixtures. The properties of the doped PFN ceramics depend on ionic radii, valence, electronegativity and the position of the admixture ions occupying the $\text{Pb}(\text{Fe},\text{Nb})\text{O}_3$ structure [10, 13]. The doped the PFN compounds (for example with cobalt) can contribute to decrease of the dielectric losses and to elimination of formation the pyrochlore phase during technological process.

In the presented paper PFN ceramics doped with cobalt were obtained by a single stage method and the crystalline structure examination, microstructural examination and dielectric property investigation of the PFN ceramic specimens doped with cobalt were performed.

2. Experimental

The base material $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$ was received from the following oxides: PbO , Fe_2O_3 and Nb_2O_5 (PbO was added with 2.5% allowance). The admixture of cobalt (in the form of hydrated cobalt carbonate $\text{CoCO}_3 \cdot \text{H}_2\text{O}$) was added according to formula: $(1-x)\text{PbO} + (x)\text{CoCO}_3 \cdot \text{H}_2\text{O} + 0.25\text{Fe}_2\text{O}_3 + 0.25\text{Nb}_2\text{O}_5 \rightarrow \text{Pb}_{1-x}\text{Co}_x(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3 + x\text{CO}_2 \uparrow + x\text{H}_2\text{O} \uparrow$, where $x = 0.01$ to 0.06 . The components were mixed for 8h. The powder mixtures were synthesized by a powder calcinations method at the following conditions: $T_s = 850^\circ\text{C}$ for $t_s = 3\text{h}$, and the compacting (densification of synthesis powders) was performed by a free sintering method at $T = 1125^\circ\text{C}$ for 2h.

The X-ray studies of the crystallographic structure were performed by means of a Philips X'Pert diffractometer. The microstructure and EDS tests were carried out using a scanning electron microscope HITACHI S-4700, and with the EDS Noran Vantage system (20kV, live time 100 sec, amount count 11000, magnification $\times 1.0\text{k}$). Dielectric measurements were performed on a capacity bridge of a BR2817 LCR meter type, with a heating rate of $0.5^\circ/\text{min}$, for a cycle of cooling at frequency of the measurement field of $\nu = 1\text{ kHz}$. Hysteresis ($P-E$) loops at various electric field frequencies were investigated with a Sawyer-Tower circuit and a Matsusada Inc. HEOPS-5B6 precision high voltage amplifier. Data were stored on a computer disc using an A/D, D/A transducer card. DC conductivity tests were carried out at temperatures between $20-180^\circ\text{C}$ with a Tesla BM518 multimeter. The percentage content of the P_f perovskite

phase was calculated from the following relationship:

$$P_f = \frac{I_{110} \cdot 100}{I_{110} + I_{222}} [\%] \quad (1)$$

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

3. Results and discussion

The PFN compound have a tetragonal structure at room temperature. Non-doped PFN ceramics have a low amount of the pyrochlore phase besides the perovskite phase. Doping the cobalt into PFN minimises the pyrochlore phase formation, and higher amount of cobalt (above 2.0 mol% Co) eliminates completely this disadvantageous effect and the ceramic becomes a single phase one (Fig. 1).

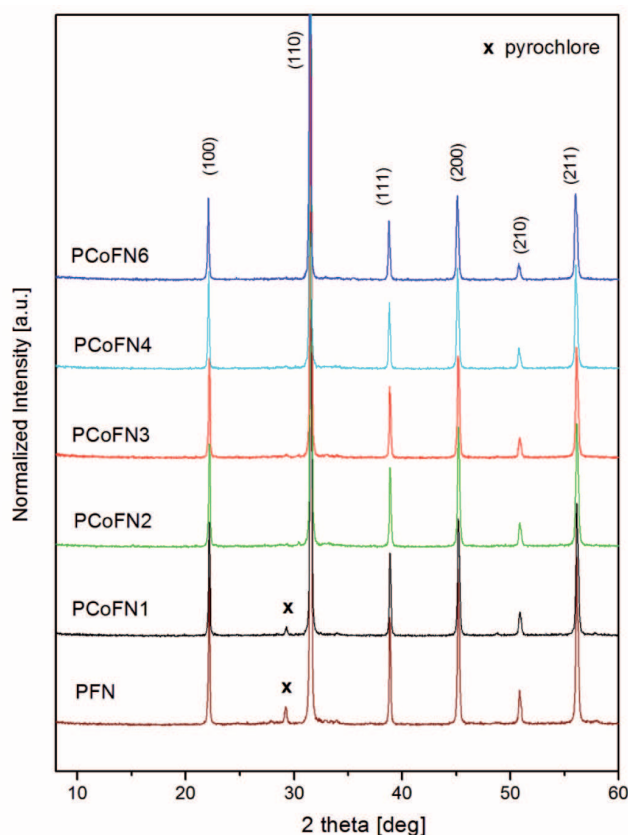


Fig. 1. X-ray diffraction patterns of PFN ceramics with various amounts of Co addition

The microstructure of the non-doped PFN ceramics shows densely packed fine grains, and fracture takes place through the grains. The average grain size increases with an increase in the cobalt admixture amount in PFN (Fig. 2). The grains of the PFN type compositions with a greater amount of cobalt admixture (above 3.0 mol% Co) have prismatic shapes.

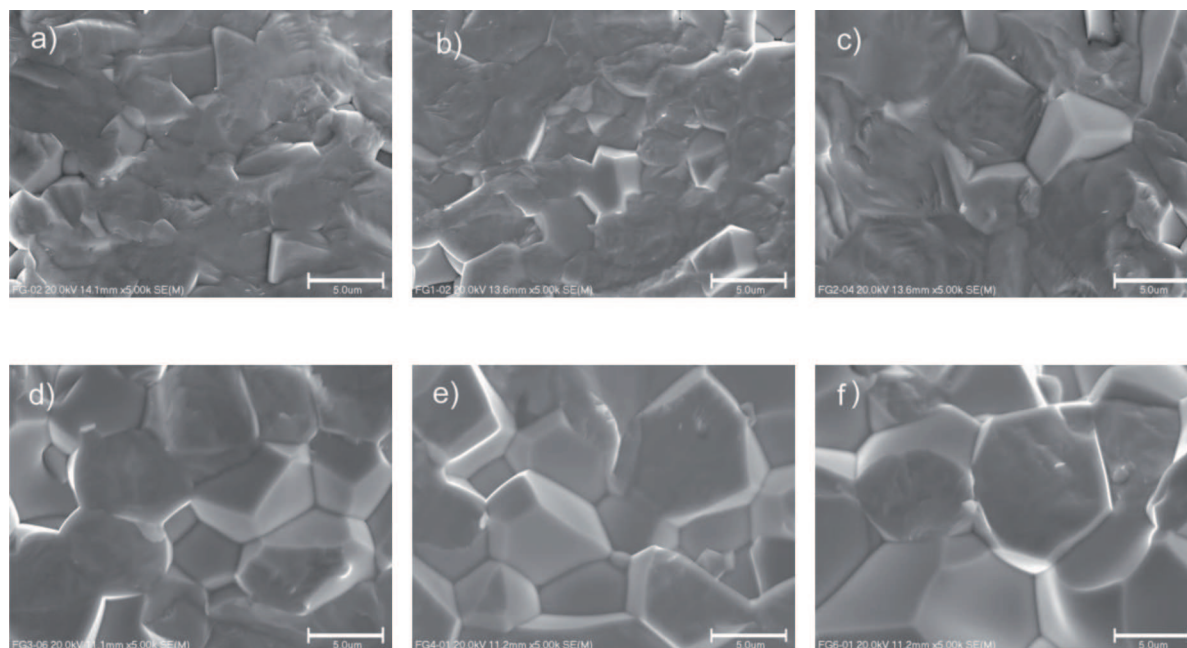


Fig. 2. The influence of Co addition into PFN ceramics on the microstructure of the samples:

a) PFN, b) PCoFN1, c) PCoFN2, d) PCoFN3, e) PCoFN4; f) PCoFN6

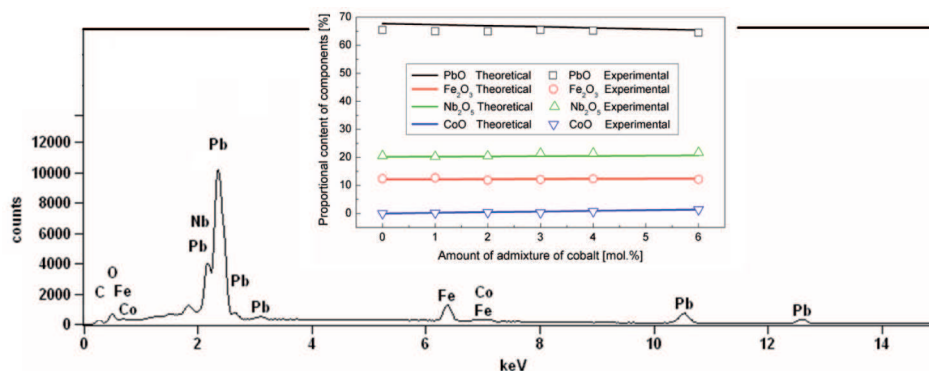


Fig. 3. EDS image of the element distribution for the PCoFN6 ceramics. The theoretical and experimental contents of the components of the PFN type ceramics (inside)

Cracking through the grain is a dominant effect in the non-doped PFN ceramics, which confirms their low strength, compared to the grain boundary strength. With the increase of the cobalt admixture amount in PFN, cracking along the grain boundary becomes a dominant effect, which confirms that the cobalt admixture changes the composition of the grain boundaries and decreasing their strength.

In Fig. 3 an example of the EDS diagram for the doped PFN (PCoFN6) composition is shown. The composition examination by the EDS point and surface method shows comparable percentage amounts of particular initial components, with their values which result from stoichiometry (Fig. 3. inside). Samples PFN, PCoFN1 and PCoFN2 exhibit deficiency lead.

The temperature investigation of σ_{DC} direct current conductivity showed that all the PFN ceramic compo-

sitions in question had similar courses (Fig. 4). In the phase transition area (from the ferroelectric phase into the paraelectric phase) there is a change of the straight line slope with activation energy. The activation energy of the PFN ceramics in the ferroelectric phase (E_{a1}) is lower than in the paraelectric phase area (E_{a2}) – Table 1.

Doping PFN with cobalt is an example of an isovalence substitution type of an equal degree of oxidation ($W_{Pb}=W_{Co}$). For the isovalence doping of PFN the following factors determine electric conduction properties: electron configuration of the valence shells, difference in ionisation energy, ratio of the doped to substituted ion radii ($R_{Co}:R_{Pb}$) and their electronegativity, EN. The electronegativity of metals means a capability of an atom to release electrons. A more electronegative element “attracts” electrons forming a bond with a less electronegative atom, which results in polarisation binding. In the

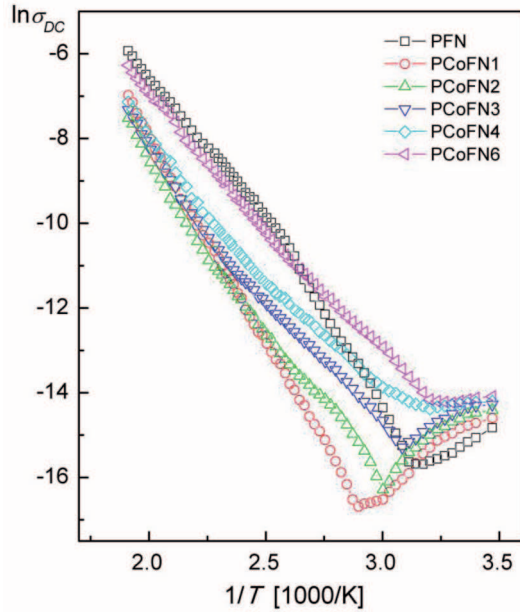


Fig. 4. The influence of Co addition into PFN ceramics on $\ln\sigma(1/T)$ dependencies

case of cobalt (a transient metal) electronegativity according to Pauling is 2.0, whereas for lead it is 1.8; it

means that cobalt will get rid of electrons bonded more weakly with the atom nucleus more harder compared to lead; this can be the reason for the decrease in electric conduction in the paraelectric phase of the PFN compositions doped with cobalt.

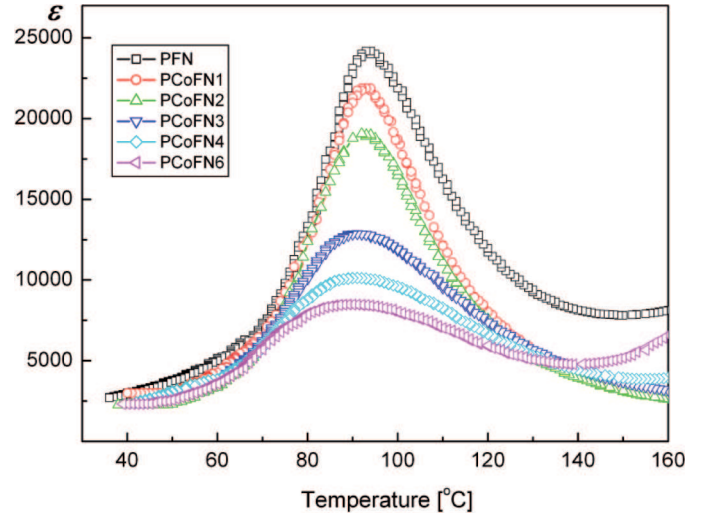


Fig. 5. Temperature dependencies dielectric permittivity $\epsilon(T)$ for various Co contents ($\nu=1.0$ kHz)

Influence of the Co-addition on the PFN ceramic parameters

TABLE 1

	PFN	PCoFN1	PCoFN2	PCoFN3	PCoFN4	PCoFN6
Co content [mol%]	0	1.0	2.0	3.0	4.0	6.0
ρ [g/cm ³]	7.93	8.02	8.06	8.11	8.14	8.21
P_{phase} [%]	97.5	98.2	100	100	100	100
T_m [°C]	94	93	92	91	91	90
ϵ_r	1,920.0	1,980.0	2,170.0	1,890.0	1,750.0	1,880.0
ϵ_m	24,150.0	21,870.0	19,000.0	12,840.0	10,080.0	8,460.0
ϵ_m/ϵ_r	12.50	11.10	8.75	6.80	5.76	4.50
$\tan\delta$ at T_r	0.09	0.03	0.06	0.05	0.07	0.08
$\tan\delta$ at T_m	0.46	0.09	0.34	0.16	0.38	0.28
α	1.54	1.67	1.77	1.84	1.95	1.99
C	$2.03 \cdot 10^{-7}$	$2.85 \cdot 10^{-7}$	$1.56 \cdot 10^{-7}$	$1.76 \cdot 10^{-7}$	$8.19 \cdot 10^{-8}$	$6.19 \cdot 10^{-8}$
E_{a1} [eV] at I range	0.25	0.38	0.35	0.25	0.05	0.03
E_{a2} [eV] at II range	0.80	0.83	0.59	0.48	0.43	0.50
P_R [μ C/cm ²]	16.24	23.28	25.40	26.53	27.24	28.06
E_C [kV/mm]	0.70	0.58	0.78	0.69	0.94	0.97

where: T_p – room temperature, $\tan\delta$ – tangent of the dielectric loss angle, ϵ_r – electric permittivity at T_r , ϵ_m – maximum dielectric permittivity at T_m , T_m – temperature of the maximum permittivity value (ϵ_m), C – constant, α – phase transition diffusion coefficient (for $\alpha=1$ the phase transition has a sharp character, when for $1 < \alpha \leq 2$ the phase transition has a diffused character), ϵ_m/ϵ_r – quotient determining the degree of phase transition diffusion (the lower its value the greater the degree of phase transition diffusion is).

An increase in the cobalt admixture in PFN decreases the maximum electric permittivity value ε_m (Fig. 5) and it moves slightly the phase transition temperature (T_m) towards lower temperatures. Phase transition in the doped compositions of the PFN type has a diffused character (with more cobalt in PFN leading to the change from ferroelectric to relaxor properties). This wide temperature range of phase transition is connected with structure ordering, i.e. with the non-uniform distribution of Fe and Nb ions (on the B side) and Pb and Co (on the A side) in the unit cell. This non-uniform distribution of the compound leads to microscopic areas formed with different Curie temperatures. The lower degree of ordering in the phase transition from the ferroelectric into paraelectric phase occurs in a wider temperature range.

Doping PFN with cobalt introduces local defect points in a form of foreign node atoms. Additionally, the ionic radius of cobalt ($R_{Co}=74$ pm) shorter than that of the PFN basic compound (lead) ($R_{Pb}=119$ pm) causes deformation of elementary cells and occurrence of local deformations of the crystal lattice in a form of its contraction.

As a measure of the diffusion of the phase transition, the ratio between the maximum dielectric permittivity (at T_m) and dielectric permittivity at room temperature ($\varepsilon_m/\varepsilon_r$) can be taken (see Table 1). The degree of diffusion can be also calculated (only for the paraelectric phase) from the formula [14]:

$$\frac{1}{\varepsilon} - \frac{1}{\varepsilon_m} = C(T - T_m)^\alpha \quad (2)$$

where: T_m – temperature of the maximum permittivity value (ε_m), ε_m – maximum permittivity value at T_m , C – temperature independent constant, α – diffuseness exponent indicating the degree of diffuseness of the ferro-paraelectric phase transition.

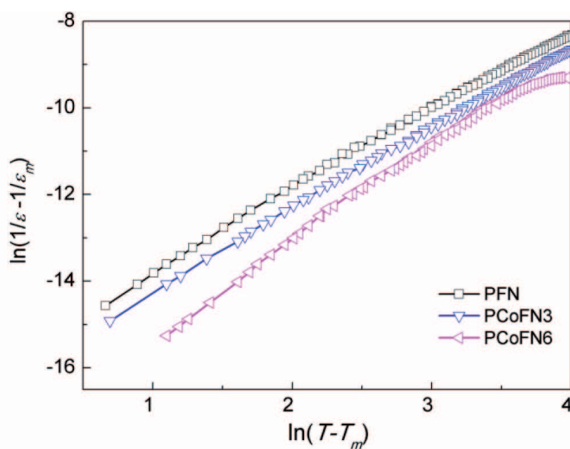


Fig. 6. Plots of $\ln(1/\varepsilon - 1/\varepsilon_m)$ vs. $\ln(T - T_m)$ for pure PFN ceramics and Co doped compositions (PCoFN3 and PCoFN6) for paraelectric phase

In Fig. 6 the $\ln(1/\varepsilon - 1/\varepsilon_m)$ diagrams of our compositions are shown in the $\ln(T - T_m)$ function, for $T > T_m$. From those diagrams on the basis of linear matching, the α parameter values were calculated and they are shown in Table 1. The diffused character of the phase transition increases with the cobalt amount increase in PFN. The lowest degree of phase transition diffusion occurs in the non-doped PFN ceramics.

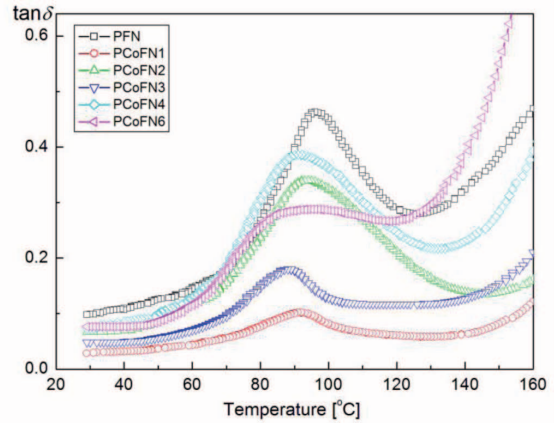


Fig. 7. Temperature dependencies dielectric losses ($\tan\delta$) for PFN for various Co contents ($\nu=1.0$ kHz)

The ceramic specimens of the PFN type are characterised by courses of dielectric losses, depending on the temperature, typical for ferroelectrics (Fig. 7). Before phase transition there is a characteristic maximum, followed by a slight decrease, and then an increase (above T_m) in dielectric losses. Doping PFN with cobalt decreases the dielectric losses in the ferroelectric phase and above the phase transition temperature (in the paraelectric phase). It proves that the PFN compositions with the cobalt admixture in the paraelectric phase have lower losses connected with electric conduction than the non-doped PFN ceramics, which is confirmed by the direct current electric conduction examination (Fig. 4).

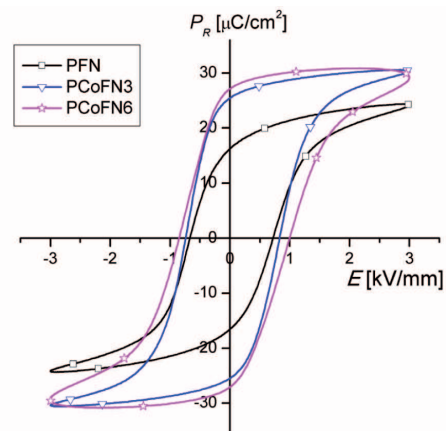


Fig. 8. Influence of the cobalt admixture on the ferroelectric hysteresis loops of the PFN ceramics

Fig. 8 presents ferroelectric hysteresis loops for the PFN ceramics. The PFN compositions doped with cobalt have narrow hysteresis loops, with high P_R polarisation values, characteristic for soft ferroelectric ceramics. With the cobalt admixture increase in PFN there is an increase in residual polarisation values P_R (Table 1).

4. Conclusions

It has been proved in the paper that doping the PFN ceramics with cobalt ($W_{Pb}=W_{Co}$) has a significant influence on their microstructure, crystal structure, electric conduction and basic dielectric properties similar to softening-hardening admixture. The cobalt doping in PFN has an advantageous influence on the ceramic crystal structure, eliminating the formation of the undesirable pyrochlore phase during the technological process. The PFN ceramics with doping of above 2.0 mol% Co are single phase materials and only have the perovskite ferroelectric phase.

With an increase in the cobalt admixture amount there is an increase in the density of the PFN ceramic specimens and the SEM microstructural images show an increase in the size of grains.

Cobalt in the PFN decreases the maximum electric permittivity value at the phase transition temperature, at slight displacement T_m , and the phase transition from the ferroelectric to paraelectric phase has a diffused character.

In the ferroelectric and paraelectric phase cobalt decreases dielectric losses. The direct current electric conduction examination showed that in the paraelectric phase the cobalt admixture decreased the electric conduction of the PFN ceramic specimens.

The PFN ceramic compositions with cobalt have narrow ferroelectric hysteresis loops, in which the increase in the cobalt admixture increases the values of their residual polarisation P_R .

Acknowledgements

Work supported by Polish Grant N R15 0005 04 and project 1S-0809-004-1-02.

REFERENCES

- [1] S.B. Majumder, S. Bhattacharyya, R.S. Katiyar, A. Manivannan, P. Dutta, M.S. Seehra, *Journal of Applied Physics* **99**, 024108 (2006).
- [2] D. Bochenek, Z. Surowiak, J. Krok-Kowalski, J. Poltiero-vejpravova, *Journal of Electroceramics* **25**, 122 (2010).
- [3] D. Khomskii, *Physics* **2**, 20 (2009).
- [4] O. Raymond, R. Font, N. Suarez, J. Portelles, J. M. Siqueiros, *Ferroelectrics* **294**, 141 (2003).
- [5] H. Brunckova, L. Medvecky, J. Mihalik, *Journal of European Ceramic Society* **28**, 123 (2008).
- [6] D. Bochenek, R. Zachariasz, *Archives of Metallurgy and Materials* **54**, 903 (2009).
- [7] D. Bochenek, Z. Surowiak, *Journal of Alloys and Compounds* **480**, 732 (2009).
- [8] K. Singh, S.A. Band, W.L. Kinge, *Ferroelectrics* **306**, 179, (2004).
- [9] M.H. Lente, J.D.S. Guerra, G.K.S. de Souza, B.M. Fraygola, C.F.V. Raigoza, D. Garcia, J.A. Eiras, *Physical Review B* **78**, 054109 (2008).
- [10] Z. Surowiak, D. Bochenek, *Materiały ceramiczne/Ceramic Materials* **4**, 124 (2004).
- [11] K. Osińska, J. Maszybrocka, J. Plewa, D. Czeka, *Archives of Metallurgy and Materials* **54**, 911 (2009).
- [12] B. Wodecka-Duś, D. Czeka, *Archives of Metallurgy and Materials* **54**, 923 (2009).
- [13] D. Bochenek, Z. Surowiak, *Physica Status Solidi A* **206**, 12, 2857 (2009).
- [14] O. Raymond, R. Font, N. Suarez, J. Portelles, J. M. Siqueiros, *Ferroelectrics* **294**, 141 (2003).