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TECHNOLOGY AND PROPERTIES PMN-PT-PS-PFN:Li MATERIAL FOR MULTILAYER CAPACITOR

TECHNOLOGIA I WŁAŚCIWOŚCI MATERIAŁU PMN-PT-PS-PFN:Li NA KONDENSATORY WIELOWARSTWOWE

In this work it is designed and obtained the multicomponent material with the formula 0.6075PMN-0.2025PT-0.09PS-0.1PFN:Li (PMN-PT-PS-PFN:Li) for applications in multilayer ceramic capacitors MLCC. Obtaining of PMN-PT-PS-PFN:Li was done by two alternative methods of synthesis. In the first method a PMN-PT-PS-PFN:Li has been obtained from simple compounds (oxides, carbonates), in the second method the complex compounds ($MgNb_2O_6$ and $FeNbO_4$) and simple compounds (oxides PbO, TiO_2 and carbonate Li_2CO_3) were used.

From synthesized powder of PMN-PT-PS-PFN:Li the ceramic samples were obtained which have next undergone comprehensive investigations. The X-ray investigations, as well as ferroelectric, dielectric and elastic investigations have been made.

Keywords: ferroelectrics, multilayer capacitors, PMN-PT ceramic, relaxor

W pracy zaprojektowano i otrzymano wieloskładnikowy materiał o wzorze 0.6075PMN-0.2025PT-0.09PS-0.1PFN:Li (PMN-PT-PS-PFN:Li) dla zastosowań na podłoża do wielowarstwowych kondensatorów MLCC. Otrzymywanie materiału PMN-PT-PS-PFN:Li było prowadzone dwiema metodami syntetyzowania. W pierwszej metodzie do otrzymania PMN-PT-PS-PFN:Li zastosowano syntetyzowanie prostych związków (tlenki, węglany), w drugiej metodzie zastosowano syntetyzowanie złożonych związków ($MgNb_2O_6$ i $FeNbO_4$) oraz prostych związków (tlenków PbO, TiO_2 i węglanu Li_2CO_3).

Z syntetyzowanego proszku materiału PMN-PT-PS-PFN:Li otrzymano ceramiczne próbki które zostały poddane kompleksowym badaniom. Przeprowadzono badania rentgenowskie, mikrostrukturalne oraz ferroelektrycznych, dielektrycznych i sprężystych właściwości.

1. Introduction

Properties of many materials currently obtained can be controled by the appropriate selection of chemical composition and as a result it is possible to obtain the material with optimum parameters for specific application [1-2]. For example, two component perovskite-type solid solutions of type $(1\text{-}x)PbMg_{1/3}Nb_{2/3}O_3\text{-}xPbTiO_3$ (PMN-PT) depending on the chemical composition (i.e. x) and while maintaining appropriate conditions and technological methods, exhibit very good piezoelectric (ferroelectric) or electrostrictive (relaxor) properties [3-6]. Particularly important for practical applications in electrical engineering are compounds of groups of materials of perovskite-type structure containing in their composition the lead – Pb. It is the result of the fact that the Pb ion, although the heaviest vibrates with maximum attitude [7].

In the solid solutions $(1\text{-}x)$PMN-xPT a continuous transition from relaxor to the ferroelectric properties take place with increasing x [8-11]. The temperature at which the real part of the electric permittivity reaches reaches its maximum increases from about -3°C for $x = 0$ to about 227°C for $x = 0.5$ [12]. It can be used for control the dielectric properties of solution what is important for the obtaining of electronic elements with optimal properties in their working temperature (e.g. at room temperature).

Objective of the present work is the design and obtaining the material PMN-PT-PS-PFN:Li which can be used in future for multilayer ceramic capacitors MLCC. The application in designed multicomponent solid solution component $PbFe_{1/2}Nb_{1/2}O_3$ (PFN) should prevent, like in the previous work of the [13-14] the lower temperature of sintering what is important during obtaining MLCC [15]. Introduction of lithium (Li) to the PFN should reduce the high electrical conductivity of the undoped PFN.

2. Experimental

To obtain the ceramic powder for application in multilayer ceramic capacitors has been designed by us the material having the following chemical composition: 0.6075PMN-0.2025PT-0.09PS-0.1PFN:Li [0.9(0.9 (0.75PMN-0.25PT)-0.1PS)-0.1PFN:Li] (abbreviation PMN-PT-PS-PFN:Li). Manufacturing of PMN-PT-PS-PFN:Li was conducted by two techniques of synthesis of powders:

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the first was synthesis from simple compounds (oxides and carbonates), the second one was multi-step method obtaining of PMN-PT-PS-PFN:Li from complex compounds.

2.1. The synthesis from simple compounds

Input components for the synthesis of powder of PMN-PT-PS-PFN:Li by the method of sintering of simple compounds were following oxides: PbO, MgO, Nb_2O_5, TiO_2, Fe_2O_3, SnO_2 and the carbonate Li_2CO_3. All components have been weighed according to reaction: $0.9995PbO + 0.2025MgO + 0.2275Nb_2O_5 + 0.2025TiO_2 + 0.025Fe_2O_3 + 0.09SnO_2 + 0.0005Li_2CO_3 \rightarrow 0.6075PbMg_{1/3}Nb_{2/3}O_3\text{-}0.2025PbTiO_3\text{-}0.09PbSnO_3\text{-}0.1PbLi0.01Fe_{1/2}Nb_{1/2}O_3 + 0.0005CO_2 \uparrow$. Lead oxide PbO and magnesium oxide MgO were weighted with the excess 6.0% and 2.0% mol respectively. Weighted in a stoichiometric proportions the mixture have undergone milling in planetary mill type FRITSH Pulwerisette 6, wet in ethanol, by 8 h. The synthesis of mixture of powders have been made by sintering of pellets in solid phase, in terms: T_{synt} =850°C, t_{synt} =4 h. After synthesis, pellets were crushed into the powder, and then the powder was mixed again (as previously).

Below the ceramic samples of PMN-PT-PS-PFN:Li synthesized from simple compounds are marked as PPPP1.

2.2. The synthesis using the method of complex compounds

The synthesis of PMN-PT-PS-PFN:Li by the method of complex compounds were carried out in three stages.

In the first stage it was obtained the columbite i.e. $MgNb_2O_6$ as a result of the synthesis of oxides Nb_2O_5 and MgO according to reaction: $Nb_2O_5 + MgO \rightarrow MgNb_2O_6$. Magnesium oxide MgO was weighted with excess 2.0% mol. All components have been mixed in planetary ball mill type FRITSH Pulwerisette 6, wet in ethanol, by 8h. The synthesis of mixed oxides was done by solid phase sintering of pellets in conditions T_{1synt} =1000°C, t_{1synt} =6 h. After the process of synthesis the $MgNb_2O_6$ pellets have been crushed and powdered.

In the second stage it has been obtained the second $FeNbO_4$ as a result of synthesis of oxides Fe_2O_3 and Nb_2O_5 according to reaction: $1/2Fe_2O_3 + 1/2Nb_2O_5 \rightarrow FeNbO_4$. Like in the first stage the component oxides were mixed in the planetary ball mill by 8 h, and the synthesis was made by sintering of pellets in the solid phase in conditions T_{2synt} =1050°C, t_{2synt} =6 h. After the process of synthesis of $FeNbO_4$ it has been crushed and powdered.

In the third, the last stage of obtaining of the powder 0.6075PMN-0.2025PT-0.09PS-0.1PFN:Li, it has been mixed complex compounds ($MgNb_2O_6$ and $FeNbO_4$) and simple compounds too (oxides PbO, TiO_2 and carbonate Li_2CO_3). The components have been weighted in stoichiometric proportions according to reaction: $0.2025MgNb_2O_6 + 0.05FeNbO_4 + 0.9995PbO + 0.2025TiO_2 + 0.09SnO_2 + 0.0005Li_2CO_3 \rightarrow 0.6075PbMg_{1/3}Nb_{2/3}O_3\text{-}0.2025PbTiO_3\text{-}0.09PbSnO_3\text{-}0.1Pb_{0.995}Li_{0.01}Fe_{1/2}Nb_{1/2}O_3 + 0.0005CO_2 \uparrow$. Lead oxide PbO has been weighted with excess 6.0% mol. Similarly to the stage first and second all the components have been mixed in planetary ball mill by 8 h. The synthesis of the mixture of complex compounds has been made by sintering of pellets in the solid phase, in conditions T_{3synt} =850°C, t_{3synt} =4 h. After the process of synthesis the PMN-PT-PS-PFN:Li pellets have been crushed, powdered and mixed in planetary ball mill during 8 h.

Below the ceramic samples of PMN-PT-PS-PFN:Li synthesized by complex compounds methods are marked as PPPP2.

2.3. Sintering of PMN-PT-PS-PFN:Li samples

Using synthesized powder of PMN-PT-PS-PFN:Li ceramic disk-shaped pellets with a diameter of 10 mm were prepared using hydraulic press. The final compaction (sintering) has been done by presureless sintering in sintering conditions T_s =1050°C, t_s =3 h. After polishing and poling (to thickness 1 mm), obtained samples have been heated (in order to eliminate the internal stress arising after mechanical treatment) and then on their surfaces were covered electrodes by the method of burning silver pastes (for electrical tests).

2.4. The investigations and measurements

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 with the EDS Noran Vantage system. Dielectric measurements were performed on a capacity bridge of a BR2817 LCR meter type, with a heating rate of 0.5°/min, for a cycle of heating. 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. Electromechanical studies were conducted with the use of the sensor Philtec Inc. D63 and Matsusada Inc. HEOPS-5B6 precision high voltage amplifier.

3. The results

Fig. 1 shows the XRD patterns obtained at room temperature for synthesized powders multicomponent solid solutions of type PMN-PT-PS-PFN:Li. Material obtained by sintering of complex compounds (PPPP2) has a perovskite structure and it is monophase (without the presence of foreign phases). In the case of material obtained by sintering of simple compounds (PPPP1) there is a small diffraction maximum from the foreign phases (related with not completely reaction of components).

Ceramics obtained from simple compounds (PPPP1) shows a small grained microstructure with low regularity and homogeneity of grains (Fig. 2). It suggests that the temperature of sintering of PPPP1 ceramics should be increased what in the case of the application of this material for the construction of multilayer capacitors is not desirable. In the case of ceramics obtained by multistep columbite method (complex compounds – PPPP2) the microstructure is characterized by large grains with properly crystalized clear limits. The correct growth of the grains of PPPP2 ceramics is a result of high temperatures of synthesis of components in the various stages of obtaining of powder of material PMN-PT-PS-PFN:Li.

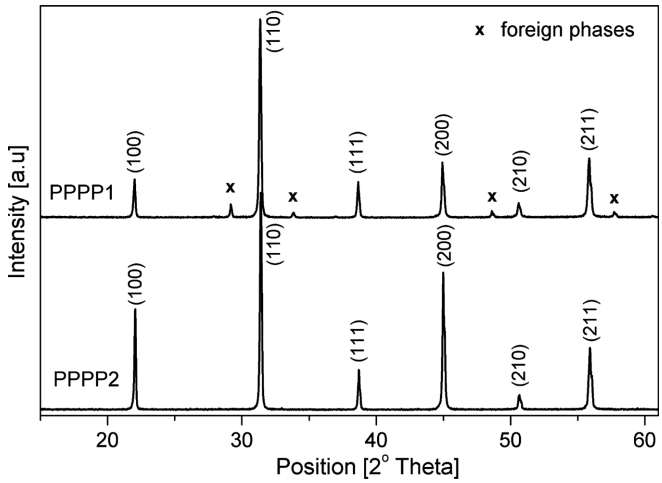

Fig. 1. XRD patterns for synthetized PMN-PT-PS-PFN:Li type powders

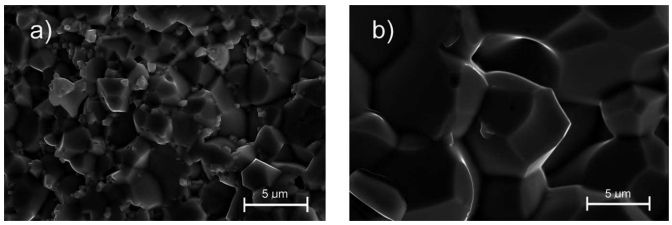

Fig. 2. SEM of fractured PMN-PT-PS-PFN:Li ceramics obtained: a) from simple compounds b) multistep method

EDS spectrum (Fig.3) confirmed the presence of the peaks from the elements constituting the composite solid solutions.

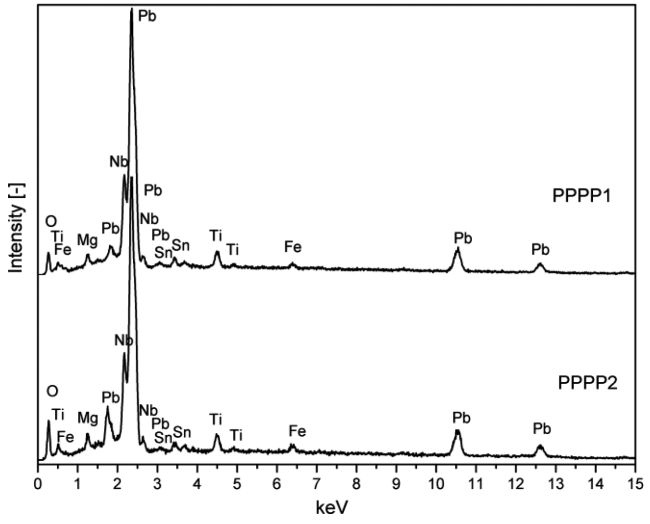

Fig. 3. EDS of PMN-PT-PS-PFN:Li type ceramics

Fig. 4 show the results of temperature investigations of dielectric permittivity and losses of ceramics PMN-PT-PS-PFN:Li synthesized from simple (PPPP1) and complex compounds (PPPP2). It is seen that applied way of synthesis does not affect much on temperature of maximum of dielectric permittivity. The values of dielectric permittivity (for 10.0 kHz) at the room temperature are about 4830 for PPPP1 and about 2020 for PPPP2 (Fig. 4a). The method of synthesis of PMN-PT-PS-PFN:Li has a large impact on the value of the maximum of dielectric permittivity at phase transition temperature and on the values of dielectric losses (Fig. 4b). The maximum values of dielectric permittivity ε_{max} at temperature of phase transition for 10 kHz are respectively about 11800 for PPPP1 and about 8200 for PPPP2.

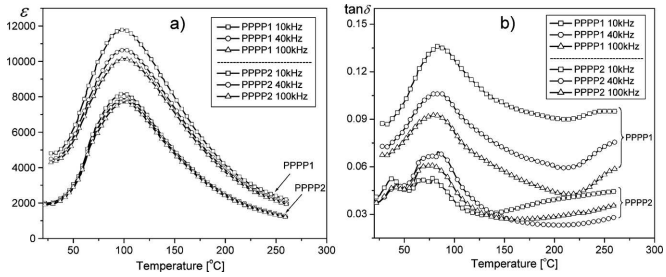

Fig. 4. Temperature dependencies of dielectric permittivity $\varepsilon(T)$ – (a) and dielectric loss tangent $\tan\delta(T)$ – (b) for ceramics PMN-PT-PS-PFN:Li obtained from powder synthesized by sintering of simple compounds, and as a result of the sintering of complex compounds (the heating cycle)

Ceramics PMN-PT-PS-PFN:Li has low dielectric losses. Comparing the two methods of synthesis it is possible to conclud that synthesis from simple compounds causes the increas of dielectric losses in all measuring range of temperatures, as compared with the material synthesized from complex oxides (Fig. 4b).

Comparison of ferroelectric hysteresis loop of ceramic samples of PMN-PT-PS-PFN:Li obtained by two methods is presented in Fig.5 (room temperature, frequency f = 1.0 Hz). Applying to the samples of type PMN-PT-PS-PFN:Li switching electric field of order ±3.0 kV/mm leads to high saturation of hysteresis loop. Both materials are ferroelectric soft, but slightly larger coercive field at room temperature has PPPP2.

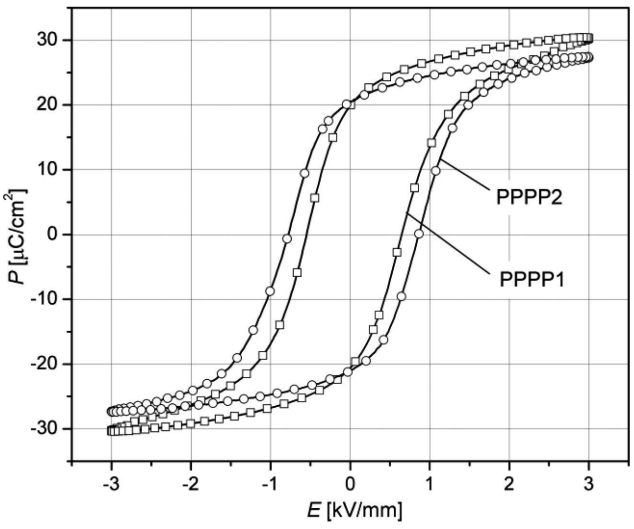

Fig. 5. $P-E$ hysteresis loops for PMN-PT-PS-PFN:Li ceramics synthesized by method of sintering of simple and complex compounds

Method of synthesis of PMN-PT-PS-PFN:Li influence in rather small step on the shape of hysteresis loop and its characteristic parameters: spontaneous polarization P_S, remnant polarization P_R, and coercive field E_C. Higher values of polarization and the coercive field exhibit ceramics obtained from powder synthesized by sintering of complex compounds (Table 1).

TABLE 1
Parameters of the PMN-PT-PS-PFN:Li type ceramics

Parameter		PPPP1	PPPP2
ρ [g/cm^3]		7.96	7.76
T_C[°C]	ν = 10 kHz	100	100
ε at T_p		4830	2020
tanδ at T_p		0.087	0.040
ε at T_C		11800	8200
tanδ at T_C		0.128	0.038
P_R [μC/cm^2]		19.90	20.40
P_S [μC/cm^2]		26.54	23.76
E_C [kV/mm]		0.61	0.81
S_{max} [%]		0.095	0.138

Charts of the strains as a function of electric field for the multicomponent ceramics of type PMN-PT-PS-PFN:Li (Fig. 6) have characteristic shapes in the form of butterfly wings. The higher values of strains and more smooth deformation loop exhibits PPPP2 ceramics (Fig. 6 and Table 1).

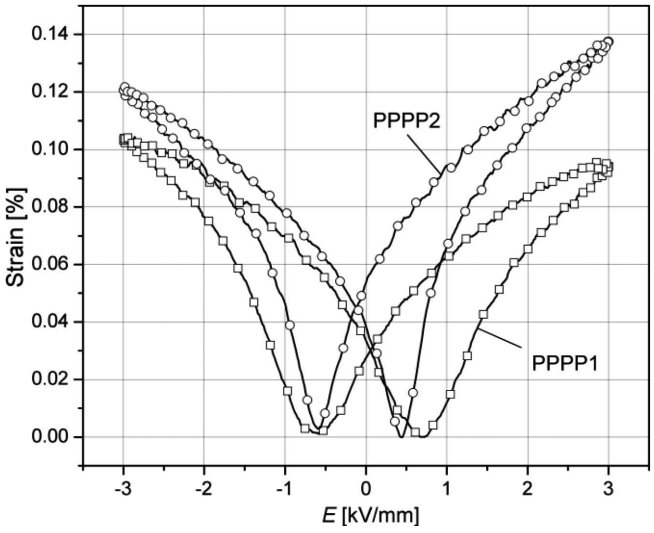

Fig. 6. Strain-electric field hysteresis loops for PMN-PT-PS-PFN:Li ceramics obtained from simple compounds and from the complex compounds

4. Summary

Comparison between two methods of obtaining of the multicomponent solid solution of type PMN-PT-PS-PFN:Li possible to use in multi-layer capacitors MLCC has been presented in this work. It is shown that the optimal growth of grains and optimal microstructure of ceramics are obtained by applying multistep technology of synthesis of PMN-PT-PS-PFN:Li from complex compounds. Despite the somewhat lower maximum of dielectric permittivity this ceramics it has a lower dielectric losses and it is monophase (without the presence of foreign phases and impurities). Optimum commercial properties and parameters of PMN-PT-PS-PFN:Li provide a suitably chosen technological conditions on different stages of synthesis. Introduction to the PMN-PT-PS the component PFN:Li allowed to decrease the temperature of all compound, so the material obtained in this technology shows the band parameters appropriate for multilayer ceramic capacitors MLCC. Single stage of synthesis of components of PMN-PT-PS-PFN:Li (the synthesis of simple oxides) does not preserve a valid microstructure of ceramics, what lead to deterioration of most of its commercial parameters.

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