EFECTUL DOPANȚILOR ASUPRA PROPRIETĂȚILOR PIEZO-ELECTRICE ALE CERAMICII TITANAT DE PLUMB MODIFICAT
EFFECT OF DOPANTS ON PIEZO - ELECTRICAL PROPERTIES OF MODIFIED LEAD TITANATE CERAMICS

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The influence of dopants, such as Y^{3+}, Sm^{3+} and Bi^{3+} and poling conditions on the piezo - electrical properties of $(Pb_{0.91}Me_{0.06})(Ti_{0.98}Mn_{0.02})O_3$ compositions have been investigated. The compositions have been obtained at high sintering temperature (1190°C and 1240°C) by solid state reaction methode. In the present research paper the effect of sintering temperature on some properties, in particular on the physical characteristics, on the structural and microstructural features and on the dielectric and piezo-electric properties of the bulk materials have been considered and investigated.

From the studies carried out, it comes out that the type of dopant has an effect on the structure and microstructure, as well as on the dielectric and piezoelectric properties. The structure has been identification by X-ray measurements and the crystallite size has been monitored by SEM analyses. At room temperature, all the sintered samples show a tetragonal perovskite structure. Piezoelectric parameters (k_p) determinations have been performed using resonance - antiresonance methods. The obtained results indicate that the sintered compositions (doped PT) can be used in obtaining active elements as well as targets for deposition.

The obtained results indicate that the sintered compositions (doped PT) can be used in obtaining active elements as well as targets for deposition.

A fost studiată influența dopanților, Y^{3+}, Sm^{3+} și Bi^{3+} precum și condițiile de polarizare asupra proprietăților piezoelectrice ale compozițiilor $(Pb_{0.91}Me_{0.06})(Ti_{0.98}Mn_{0.02})O_3$. Compoziţiile au fost obţinute prin metoda reacţiilor în stare solidă, la temperatură ridicată de sinterizare (1190°C și 1240°C). În lucrarea de față a fost luat în considerare și investigat efectul temperaturii de sinterizare asupra unor proprietăți, în special asupra caracteristicilor fizice, asupra caracteristicilor structurale și microstructurale și asupra proprietăților dielectrice și piezo-electrice ale materialelor.

Din studiile efectuate, reiese că tipul de dopant are efect asupra structurii și microstructurii cât și asupra proprietăților dielectrice și piezoelectrice. Structura a fost identificată prin măsurători cu raze X, iar dimensiunea cristalitelor a fost determinată prin analize SEM. La temperatura camerei, toate probele sinterizate prezintă o structură perovskit tetragonală.

Determinările parametrilor piezoelectrici (k_p) au fost efectuate folosind metoda de rezonanță - antirezonanță. Rezultatele obținute indică faptul că compozițiile sinterizate (PT dopat) pot fi utilizate în obținerea de elemente active cât și ținte pentru depunere.

Keywords: *doped PZT, dielectric and piezoelectric properties, ferroelectric properties*

1.Introduction

Lead titanate (PT ↔ $PbTiO_3$) is an important material with perovskite type structure (described by the general formula ABO_3) and high anisotropy (c/a = 1,064) which presents dielectric and piezoelectric properties to be employed in transducer applications [1,2]. Un-doped PT materials have a high Curie temperature (490°C) and a low dielectric constant (200), which make them interesting for in high-temperature transducers and high-frequency transducers applications [1,2]. Additionally, the resistivity of the pure/ un-doped PT material is very low (10^7 to 10^8 Ωcm).This low value of resistivity is due to the vacancies that arise during the sintering process involving lead evaporation [3]. Because of its high anisotropy and its low resistivity, it is difficult to be obtained, buy sintering and to be poled pure/ un-doped PT material [1].

The main difficulties in the obtaining process of pure/un-doped PT material occur when the temperature decreases. Internal stresses generated during the transition from the cubic phase to the tetragonal phase, determining higher fragility. Using the dopants in A and/or B positions the properties can be modified. By substitution of the Pb^{2+} positions with isovalent dopants like Ca^{2+}, Ba^{2+}, Sr^{2+}, or off-valent dopants such as Sm^{3+}, La^{3+}, Y^{3+} the anisotropy is reduced [3-7] and the produced materials become denser. Some researchers have reported in some studied [4] that it is possible obtaining higher values of the k_t/k_p ratio by doping with Ca or Sm in PT materials compared to PZT materials [4,7–9]. La^{3+} is one of the most used

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dopants for such applications. Doping with La^{3+} modifies the dielectric properties of PT materials [10-12]. Substitution, in position B of Ti^{4+}, by Mn^{4+} improves the resistivity by compensating the charges that appear through the replacements outside the valence for the position Pb^{2+}. Thus, the doped $PbTiO_3$ compositions can be polarized [13]. Some applications of these materials include bulk ultrasonic transducers, gas sensors [14] and substrates for SAW devices [15].

In the present paper, structural, dielectric and piezoelectric properties of modified lead titanate materials, prepared by solid-state reaction at high sintering temperature, doped with Y^{3+}, Sm^{3+} and Bi^{3+} have been investigated and interpreted.

2. Experimental

The compositions with the general formula $(Pb_{0.91}Me_{0.06})(Ti_{0.98}Mn_{0.02})O_3$ where Me = Y^{3+}, Sm^{3+} and Bi^{3+} have been prepared at high sintering temperature during solid-state methode. Materials labelled PT-Y , PT-Sm and PT-Bi have been obtained starting from high purity oxides (>99.0% purity). Raw materials PbO, TiO_2, MnO_2, Y_2O_3, Sm_2O_3 and Bi_2O_3 have been weighed and then mixed for 8h using ethyl alcohol. The obtaining powders have been dried, calcined at 870°C for 4 hours and milled again for 10h in ethyl alcohol. Further, for bulk measurements the powders were dried, granulated with 7 wt% of a 5% polyvinyl alcohol (PVA) solution and uniaxial pressed in the form of discs of 12 mm diameter and 1.5-2.0 mm thickness, using a pressure of 70 MPa. At the end the samples have been sintered at 1190°C and 1240°C with a holding time of 2h at the maximum temperature. In the sintering process the binder has been removed at 600°C. During sintering process, to avoid the evaporation of PbO a special atmosphere, rich in $PbTiO_3$ powder, has been used [16]. On the sintered samples the apparent density has been determined by Archimedes' method. The crystallite structure has been analyzed using X-rays diffraction (BRUKER AXS D8 Advance Diffractometer) and the microstructure has been investigated using scanning electron microscopy (SEM, Model Workstation Auriga). In order to measure the electrical properties, the lapping samples has been coated on both sides of the samples with silver paste and has been treated at 600°C/30 minute to form electrodes. In order to measure the electrical properties, the lapping samples has been coated on both sides of the samples with silver paste and has been treated at 600°C/30 minute to form electrodes. The dielectric properties, measured at 1 kHz, have been determined using LCR meter (HAMEG) and the piezoelectric properties have been evaluated after poling 30 minute at 160°C in a silicone oil bath under 6 kV/mm using an impedance analyzer (Agilent 4294A). Standard resonance measurement method has been considered for the piezoelectric properties calculation [17]. The value of the Curie temperature (T_C) was determined by measuring the variation of the relative permittivity with the temperature using an impedance analyzer (Agilent 4294A) being corresponding to maximum of the permittivity. Hysteresis curves have been obtained using the TF analyzer 2000 ferroelectric characterization system.

3. Results and discussion

Table 1 reports the values obtained for porosity and apparent density of the sintered samples as a function of dopant. As reported, the as the sintering temperature increases density slightly increases. The obtained density/porosity results to be dependent on the nature of the dopant employed.

Table 1

The porosity and the apparent density of the samples obtained as a function of the sintering temperature/*Porozitatea și densitatea aparentă a probelor obținute în funcție de temperature de sinterizare*

Samples	Temperature [°C]	Porosity [%]	Apparent Density [g/cm³]
PT-Y	1190	2.92	7.04
	1240	2.87	7.16
PT-Sm	1190	0.58	7.60
	1240	0.39	7.62
PT-Bi	1190	0.16	7.69
	1240	0.10	7.74

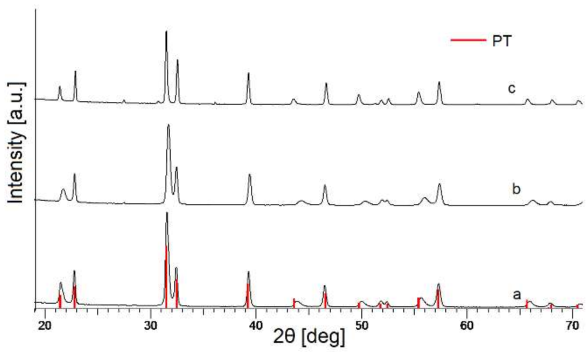

Fig.1 - XRD pattern of samples sintered at 1190°C for 2h, (a) PT-Bi, (b) PT-Sm and (c) PT-Y/ *Difractogramele probelor sinterizate la 1190ºC pentru 2 ore, (a) PT-Bi, (b) PT-Sm și (c) PT-Y*

The X-ray analyses indicated that all PT-doped compositions show clear peaks, which can be correlated to a good crystallization, while the presence of the main peaks at [101] indicates for all of them that they are belonging to the tetragonal phase. Fig.1 show the X-ray diffraction patterns for the samples sintered for 2h at 1190°C.

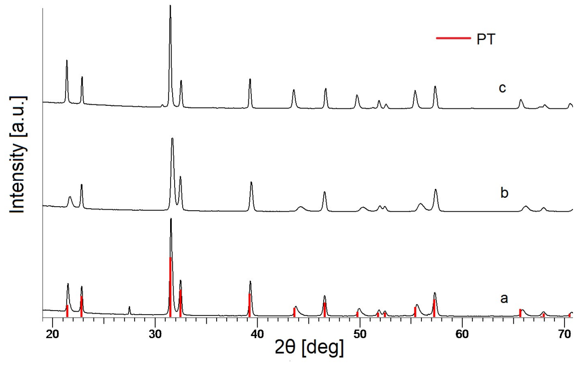

Fig. 2 - XRD pattern of samples sintered at 1240°C for 2h, (a) PT-Bi, (b) PT-Sm and (c) PT-Y/ *Difractogramele probelor sinterizate la* 1240°C *pentru 2 ore (a) PT-Bi, (b) PT-Sm și (c) PT-Y*

The differences of X-ray diffraction patterns between the doped PT compositions can be observed at the peaks [002] and [200] (around 2θ = 45◦) which have been moved toward each other as a in function of dopant (Fig. 1.). Fig. 2 shows the X-ray diffraction patterns for the sintered samples at 1240°C and it is observed at the peaks [002] and [200] (around 2θ = 45◦) that have moved toward each other in function of dopant.

By the temperature increasing from 1190°C to 1240°C, an increase of the grade of crystallinity is observed.

The SEM micrographs of the sintered $PbTiO_3$ doped compositions have been presented in Figs. 3-5. All composition shows a dense and homogeneous behavior. The morphology of all sintered samples is almost similar for all compositions.

For the PT-Bi composition (Fig.3), the micrographs obtained reveals the formation of tetragonal particles with rounded corners, with grain sizes arrive up to 1.3 µm (for a temperature of 1190°C), dimensions that increase to 2.8 µm for a temperature of 1240°C. Additionally, the domain structure characteristic of modified lead titanate compositions is highlighted.

The shape of the granules for the PT-Sm composition is similar to the character of the PT-Bi particle. There are some differences concerning the size of the grains. For the PT-Sm composition (Fig. 4) two types of polyhedral grains can be identified (small 700-800 nm and large 1.54-2.09 µm). The average grain size increases with increasing the temperature from 1.5 µm (at 1190°C) to 1.8 µm (at 1240°C).

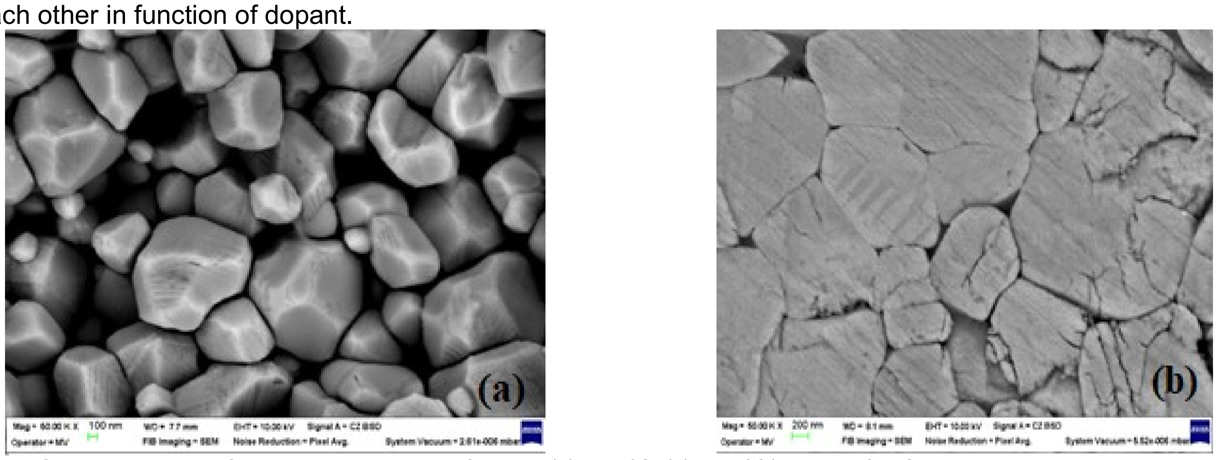

Fig.3 - SEM micrographs of PT-Bi samples sintered for 2h at (a) 1190°C, (b) 1240°C/ *Micrografiile SEM a probelor PT-Bi sinterizate pentru doua ore la (a) 1190°C și (b) 1240°C*

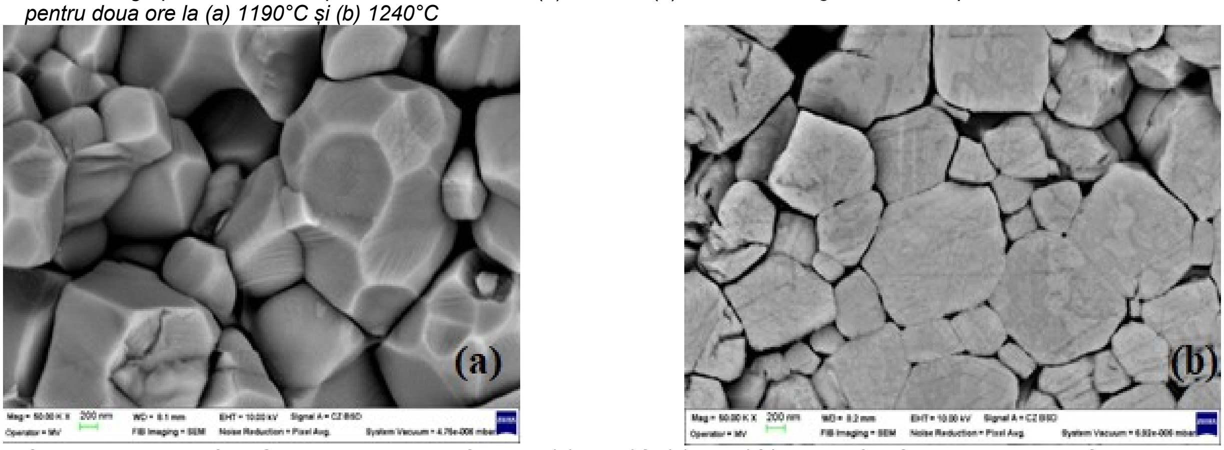

Fig.4 - SEM micrographs of PT-Sm samples sintered for 2h at (a) 1190°C, (b) 1240°C/*Micrografiile SEM a probelor PT-Sm sinterizate pentru doua ore la (a) 1190°C și (b) 1240°C*

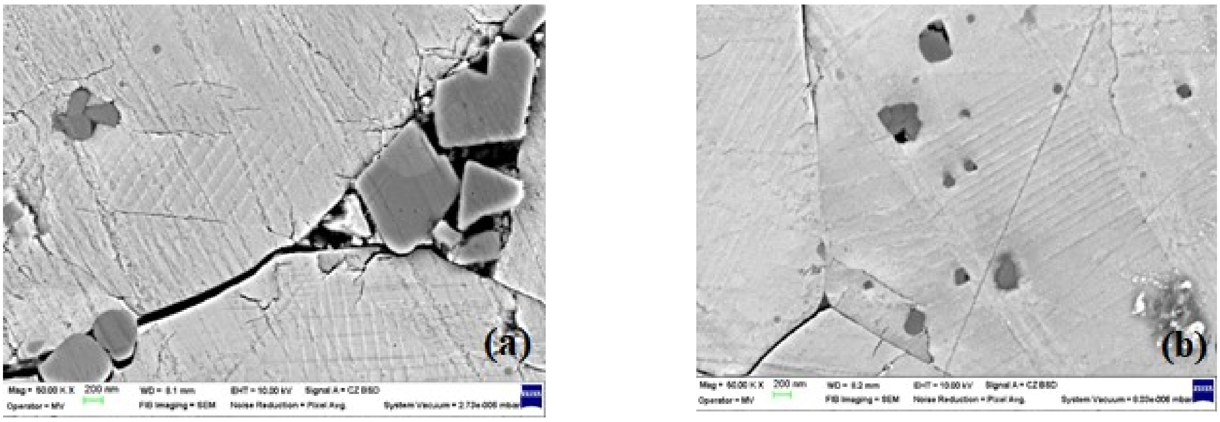

Fig.5 - SEM micrographs of PT-Y samples sintered for 2h at (a) 1190°C, (b) 1240°C/ *Micrografiile SEM a probelor* PT-Y *sinterizate pentru doua ore la (a) 1190°C și (b) 1240°C*

Table 2

Values of the tg δ, ε_r and T_C of the samples sintered at 1190°C and 1240°C
Valorile tg δ, ε_r și T_C a probelor sinterizate la 1190°C ți 1240°C

Samples	T [^{0}C]	tg δ	ε_r	T_C [^{0}C]
PT-Bi	1190	0.014	74.55	520
	1240	0.016	89.43	
PT-Y	1190	0.172	56.05	440
	1240	0.017	66.91	
PT-Sm	1190	0.016	115.89	425
	1240	0.016	129.26	

To identify the domain structure for the PT-Y composition, the samples have been polished and then chemically etched. Thus the fine white stripes represent 90° domains and the irregular lines that cross the 90° domains are 180° domain limits [18]. It is observed that the texture that defines the structure of the domain is very fine contoured. The formation of the domain structure for the piezoceramic materials depends on the size of the granules which is directly affected by the nature of the additives (Bi, Sm, Y) and by the conditions during processing, as grinding, pressing, sintering concerns. For all compositions the porosity decreases with increasing sintering temperature.

The values obtained for the dielectric permittivity (ε_r) and the dielectric losses (tan*δ)* at the frequency of 1kHz are presented in Table 2.

The Curie temperature (T_C) is determined from the curve representing the variation of the electrical capacity with temperature. It is found that the Curie temperature (T_C) can be increased and decreased depending on the type of additives for the compositions in the titanate lead (PT) system. From some literature data, [19] it comes out that in the case of the addition of Bi in some components/ compositions, this temperature can reach higher values than 600^{o}C and even higher than 800^{o}C. Therefore, in the case of the addition of Bi, the Curie temperatureT_C rises well above the Curie temperature (T_C) of lead titanate (PT) which is 490^{o}C. In the case of the addition of Y^{3+}, the Curie temperature is found to be lower than the Curie temperature of un-doped lead titanate (PT). In the case of doping with Sm^{3+}, the Curie temperature decreases even more, being a little over 400^{o}C. This is mainly due to the fact that both Sm^{3+} and Y^{3+} enter position A, replacing lead ions and leading to easier polarization of the system.

The increase of the dielectric permittivity (ε_r) value is observed as a result of the increase of the level of the crystallite and the size of the granules and also due to extension of the ordered areas inside the disordered matrix [20]. The increase in sintered PT-Bi dielectric losses (tan*δ*) observed at 1240°C can be attributed either to spatial loads at the boundary of the granules, to defects, or to the development of nano-regions because of the composition change.

The P-E hysteresis loops gives information about the dynamic polarizability. The curves related to the PT-Bi, PT-Y and PT-Sm un-poled samples sintered at 1190°C and 1240°C has been reported in Figs. 6-8. The PT doped compositions shows similar dependence of P-E curves like “soft” or “hard” PZT ceramics [21].

The shape of hysteresis loops obtained for all compositions are characteristic of ferroelectric compositions. Also, they are influenced by the phases in the structure of the material and the amount of tetragonal phase. There is a small displacement of the P-E curves along the field axis in the absence of application of the electric field which corresponds to the modified ferroelectric compositions with lower valence. This displacement of the P-E curve along the field axis occurs due to the internal dipole field [22].

The results obtained for the remanent polarisation (P_r) and for the coercitive field (E_c) for the sintered samples are in relation of the nature of dopant and have been presented in Table 3.

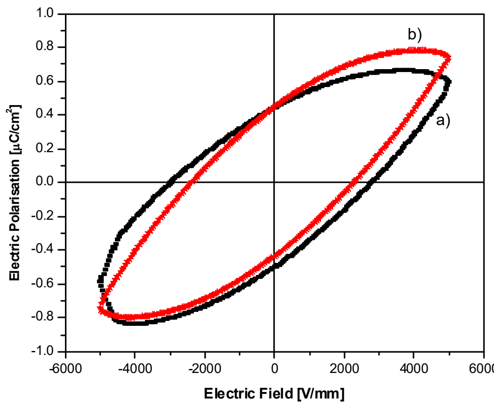

Fig. 6 - Hysteresis curves for the samples PT-Bi sintered at (a) 1190°C, (b) 1240°C/*Curbele de histerezis pentru probele* PT-Bi *sinterizate la (a) 1190°C, (b) 1240°C*

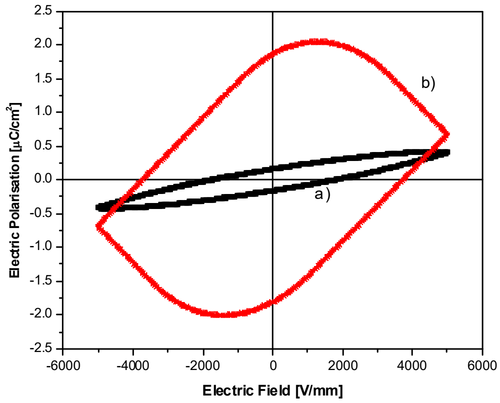

Fig.7 - Hysteresis curves for the samples PT-Y sintered at (a) 1190°C, (b) 1240°C/ *Curbele de histerezis pentru probele PT-Y sinterizate la (a) 1190°C, (b) 1240°C*

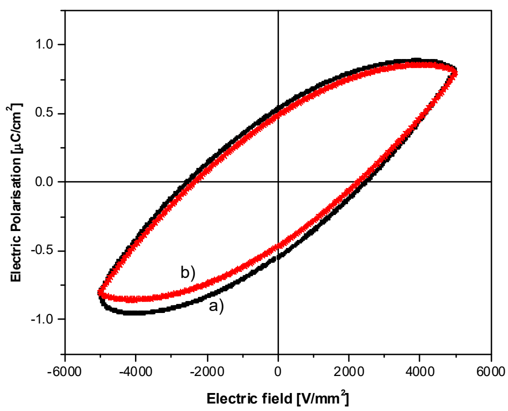

Fig.8 - Hysteresis curves for the samples PT-Sm sintered at (a) 1190°C, (b) 1240°C/ *Curbele de histerezis pentru probele PT-Y sinterizate la (a) 1190°C, (b) 1240°C*

The results obtained for the remanent polarisation (P_r) and for the coercitive field (E_c) for the sintered samples are in relation of the nature of dopant and have been presented in Table 3.

For the sintered samples at 1240°C the planar coupling factor k_p has been measured using resonance - antiresonance methods.The resonance frequency (f_r) and anti-resonance frequency (f_a) has been measured using an impedance analyzer (Agilent 4294A). The planar coupling factor (k_p) has been determined from the following equation $k_p^2 = 2.51(f_r - f_a)/f_r$. The values obtained for f_r, f_a and k_p have been reported in Table 4. In all cases low values for k_p have been obtained. These values can be explained by the high values used for the polarization conditions [23].

Takeuchi and Hiroshi [24], noted that the coupling factor k_p decreases gradually with an increases in the poling field for Ln-Sm. This property improves the electromechanical coupling anisotropy for $PbTiO_3$ type compositions.

Table 3

Values of the P_r and E_c of the samples sintered at temperature 1190°C and 1240°C

Valorile P_r și E_c pentru probele sinterizate la 1190°C și 1240°C

Samples	T [^{0}C]	P_r, (µC/cm^2)	E_c, (V/mm)
PT-Bi	1190	0.448	2820
	1240	0.448	2320
PT-Y	1190	0.165	1820
	1240	1.800	3620
PT-Sm	1190	0.529	2459
	1240	0.486	2223

Table 4

Values of f_a, f_r and k_p for the samples sintered at temperature 1240°C/ *Valorile f_a, f_r și k_p pentru probele sinterizate la temperature de sinterizare de 1240°C*

Samples	f_r, [kHz]	f_a, [kHz]	k_p
PT-Bi	229	233	0.21
PT-Y	237	241	0.21
PT-Sm	231	239	0.29

4.Conclusions

In this paper, the influence of some dopants and poling conditions on the piezo - electrical properties of $(Pb_{0.91}Me_{0.06})(Ti_{0.98}Mn_{0.02})O_3$ compositions obtained by solid state reaction method were studied. Investigation on the relationship between the sintering temperature and some properties of the bulk materials were performed. The introduction of the dopants Bi^{3+}, Sm^{3+} and Y^{3+} in the lattice of the $Pb(Ti_{0.98}Mn_{0.02})O_3$ determined the improvemend of the dielectric properties of the material. All composition reveals a dense and homogeneous behavior and the morphology of all sintered samples is almost similar for all compositions. The compositions sintered at lower temperature shows a structural inhomogeneity and this defect does not allow the polarization of the samples.The values of dielectric permittivity (εr) increased with the increasing of the sintering temperature. Thereby, the increase of the sintering temperature determines the improvement of the dielectric properties of the samples. On the basis of the investigations carried out one can conclude that the materials can be proposed for targets for ceramic coatings.

Acknowledgements: *The authors would like to acknowledge for the financial support the Ministry of Research and Innovation, through PN 19310103/ 2019 and Subsidiary contract type D, no.133-D1 ICPE. Furthermore, the authors would like to thank to their colleagues Marinescu Virgil and Sbarcea Gabriela-Beatrice for their help for SEM and XRD measurements.*

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