MINISTERUL EDUCAȚIEI
ROMÂNIA
UNIVERSITATEA DE MEDICINĂ, FARMACIE, ȘTIINȚE ȘI TEHNOLOGIE „GEORGE EMIL PALADE" DIN TÂRGU MUREȘ

Acta Marisiensis. SeriaTechnologica
Vol. 19 (XXXVI) no. 1, 2022
ISSN 2668-4217, ISSN-L 2668-4217

sciendo

10.2478/amset-2022-0003

OBTAINING AND CHARACTERIZING THE $PB(MG_{1/3}NB_{2/3})O_3$–$LN(MG_{1/2}TI_{1/2})O_3$ DOPED SYSTEM

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Abstract

The $Pb(Mg_{1/3}Nb_{2/3})O_3$-based ceramic system was obtained by using a modified variant of the conventional ceramic method in order to get pyrochlore-free compositions. Solid solutions obtained from $Pb(Mg_{1/3}Nb_{2/3})O_3$ and $Ln(Mg_{1/2}Ti_{1/2})O_3$ with Ln = Y^{3+}, La^{3+}, Pr^{3+}, Nd^{3+} and Sm^{3+}, were synthesized using a 3-step columbite precursor method and appropriate milling and sintering conditions. The structural phases of all sintered compositions were investigated in detail. The X-ray diffraction results demonstrate that all the samples possess a perovskite structure. The influence of dopant on the incorporation degree in the solid solutions was studied. The dielectric constants at three frequencies were measured and the influence of the dopant on these values was discussed.

Key words: piezoceramics, ferroelectric relaxors, mixed oxide, perovskit structure

1. Introduction

The lead manganite niobate, $Pb(Mg_{1/3}Nb_{2/3})O_3$, and further solid solutions such as $Pb(Mg_{1/3}Nb_{2/3})O_3$ - $PbTiO_3$ are known as ferroelectric relaxors and present dielectric, piezoelectric or electrostrictive properties depending on their composition [1-5]. Due to these properties, the niobate ferroelectric relaxors are suitable for many applications such as capacitors tunable transducers, actuators and memory devices. These materials are also used as micropositioners or actuators in dot-matrix printer heads and videotape heads, because of their large electrostrictive strains. Several compounds are used as piezoelectric transducers, because of their large piezoelectric coefficient (d_{33}) [6-8]. Their dielectric permittivity presents high values even at high frequencies (ε~10.000 at 1 kHz and over 100 at 3 to 5 GHz) and therefore they are used in microwave components [9]. Compounds described by the general formula $Ln(Mg_{1/2}Ti_{1/2})O_3$ with Ln = lanthanide element were characterized as dielectric materials with low losses [10-11].

In the present research paper some results will be presented on the investigation performed to get lower lead content ferroelectric relaxors in the frame of the European decissions to eliminate lead from applications.

So, starting from the well-known $Pb(Mg_{1/3}Nb_{2/3})O_3$ - $PbTiO_3$ solid solution [12], it has been developed further solid solutions in which the lead concentration is diminished, such as in $Pb(Mg_{1/3}Nb_{2/3})O_3$ - $Ln(Mg_{1/2}Ti_{1/2})O_3$ by maintaining the above mentioned properties.

2. Materials and methods

Pure perovskite lead-based ferroelectric relaxors without the pyrochlore phase are difficult to be prepared by the conventional mixed oxide method. The presence of pyrochlore causes a big decrease of the dielectric constant. Therefore special techniques have to be taken into account [13,14] in order to avoid the formation of the pyrochlore phase.

Starting from the Columbite route [15,16] and B-Oxide route we prepare pyrochlore free samples, a combined columbite with B-oxide route. The new materials described by the formula:

$0.9Pb(Mg_{1/3}Nb_{2/3})O_3 - 0.1Ln(Mg_{1/2}Ti_{1/2})O_3$ with Ln = {Y, La, Pr, Nd, Sm} were prepared by a solid state reaction method with two steps: method columbit it was combined with B-oxide route. In the columbite method the first step is the synthesis of MgO and Nb_2O_5 powders to form columbite, $MgNb_2O_6$, prior to reaction with PbO. In the B-oxide method the oxides corresponding to the elements in B positions are introduced first, all at once or in steps, prior to the reaction with PbO. B' and B" are the elements in a perovskite formula A(B'B")O_3.

The all raw materials had high purity {>99%}. Powders were synthesized by the mixtures of MN obtained in our laboratory, PbO, Ln_2O_3 and TiO_2. In this technology the advance time milling was used. The calcined temperature was 870°C for 4 hours. X-ray diffraction (XRD) was used for phase identification. The compounds obtained at each step, controlled from structural point of view, became raw materials for the next step. The optimum sintering temperatures were established by controlling the formation of the perovskite structure in an extended range between 1100°C and 1250°C. The synthesized powders were pressed into 18 mm in diameter compacts under 2.5 tf and then sintered 3 hours in a close alumina crucible in air at the corresponding temperature. The bulk density was calculated by dimensional method for all the sintered compositions. The X-ray diffractometer (BRUKER AXS D8 Advance) was used in order to determine the crystalline structure of the sintered compositions. The dielectric properties have been measured after lapping and applying the silver electrodes. Electrical measurements were performed at frequencies 1, 10 and 100 kHz at room temperature using a LCR meter. Dielectric permittivity was determined for all sintering compositions.

3. Results and Discussion

Structural analysis

The XRD patterns of $0.9Pb(Mg_{1/3}Nb_{2/3})O_3 - 0.1Ln(Mg_{1/2}Ti_{1/2})O_3$ compositions abbreviated 0.9PMN-0.1LnMT and calcined for 4 hours at 870°C are shown in Figure 1. In Figures 2-4 shows the XRD patterns of sintered compositions 0.9PMN-0.1LnMT for 3 hours at 1100°C, 1200°C and 1250°C.

The pyrochlore phase is present in the calcined powders. XRD measurements indicate that for all sintered compositions the pyrochlore phase disappears and at 1250°C a single perovskite phase is formed, indicating the formation of the solid solution.

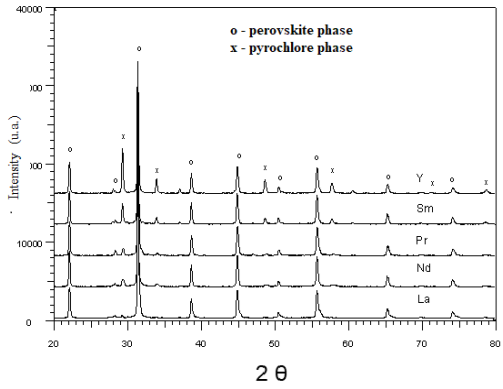

Fig.1: XRD patterns of $0.9Pb(Mg_{1/3}Nb_{2/3})O_3 - 0.1Ln(Mg_{1/2}Ti_{1/2})O_3$ calcinated 4h at 870°C

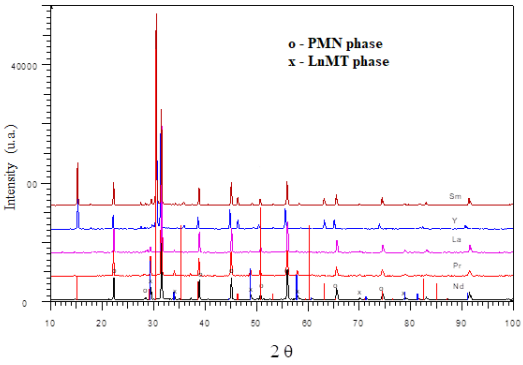

Fig.2: XRD patterns of $0.9Pb(Mg_{1/3}Nb_{2/3})O_3 - 0.1Ln(Mg_{1/2}Ti_{1/2})O_3$ sintered 3h at 1100°C

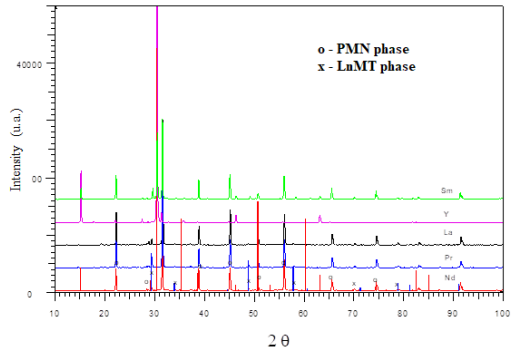

Fig.3: XRD patterns of $0.9Pb(Mg_{1/3}Nb_{2/3})O_3 - 0.1Ln(Mg_{1/2}Ti_{1/2})O_3$ sintered 3h at 1200°C

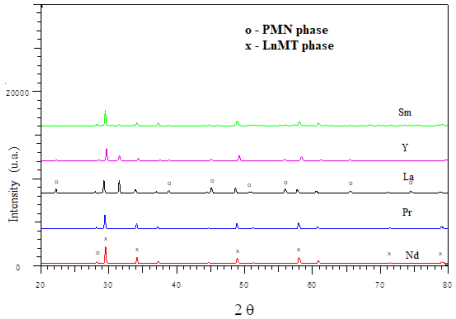

Fig.4: XRD patterns of $0.9Pb(Mg_{1/3}Nb_{2/3})O_3 - 0.1Ln(Mg_{1/2}Ti_{1/2})O_3$ sintered 3h at 1250°C

For all sintered compositions the crystallinity of the structure depends on the nature of the dopant (lanthanide) and the sintering temperature. The cation

contributes to the deviation of the perovskite structure from its ideal configuration.

Study of the sinterability

Figure 5 shows the densities of the all sintered compositions measured using the Archimedes method. The densities of the samples sintered at 1250°C are in the range of 6.70 and 7.11 g/cm^3 and dependent of the nature of dopant. The high density values can be considered as a good indication that all samples can be submitted to electrical characterization.

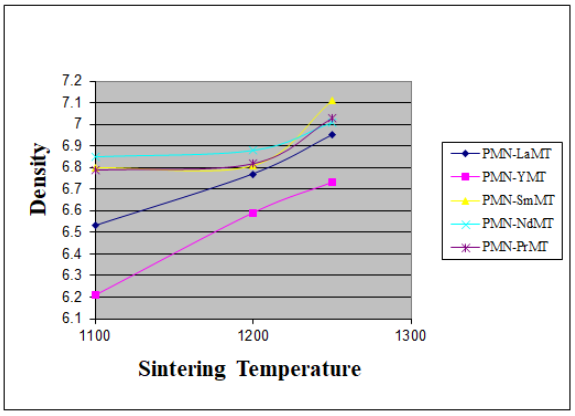

Fig.5: Variation of apparent density with sintering temperature of the 0.9Pb($Mg_{1/3}Nb_{2/3}$)O_3 – 0.1Ln($Mg_{1/2}Ti_{1/2}$)O_3 compositions

Dielectric properties

Electrical measurements at low frequencies were performed. The dielectric permittivity, ε_r at 1, 10 and 100 kHz frequencies for all sintering compositions were measured. The values obtained for the dielectric permittivity for PMN-LnMT compositions are given in Tables 1-5. The values obtained for the dielectric permittivity depend on the nature of the dopant. One can observe that the highest values for the dielectric permittivity were obtained for 0.9PMN – 0.1LnMT substituted with Y.

Table1: The dielectric permittivity, ε_r, at 1, 10 and 100 kHz for PMN-YMT as a function of sintering temperature

	Sintering Temperature [°C]	Frequency [kHz]		
PMN-YMT		1	10	100
	1100	1665	1835	1763
	1200	2380	2741	2584
	1250	2992	3775	3417

Table2: The dielectric permittivity, ε_r, at 1, 10 and 100 kHz for PMN-NdMT as a function of sintering temperature

	Sintering Temperature [°C]	Frequency [kHz]		
PMN-NdMT		1	10	100
	1100	581	582	581
	1200	546	546	547
	1250	199	201	200

Table3: The dielectric permittivity, ε_r, at 1, 10 and 100 kHz for PMN-SmMT as a function of sintering temperature

	Sintering Temperature	Frequency [kHz]		
PMN-SmMT	[°C]	1	10	100
	1100	380	654	618
	1200	746	754	749
	1250	594	598	597

Table4: The dielectric permittivity, ε_r, at 1, 10 and 100 kHz for PMN-PrMT as a function of sintering temperature

	Sintering Temperature [°C]	Frequency [kHz]		
PMN-PrMT		1	10	100
	1100	428	430	429
	1200	306	308	307
	1250	268	271	269

Table5: The dielectric permittivity, ε_r, at 1, 10 and 100 kHz for PMN-LaMT as a function of sintering temperature

	Sintering Temperature [°C]	Frequency [kHz]		
PMN-LaMT		1	10	100
	1100	248	256	250
	1200	137	143	139
	1250	-	-	-

Figures 6 and 7 show the variation of the dielectric permittivity with the composition at the sintering temperature of 1250°C (Figure 6) and at the frequency of 1kH (Figure 7).

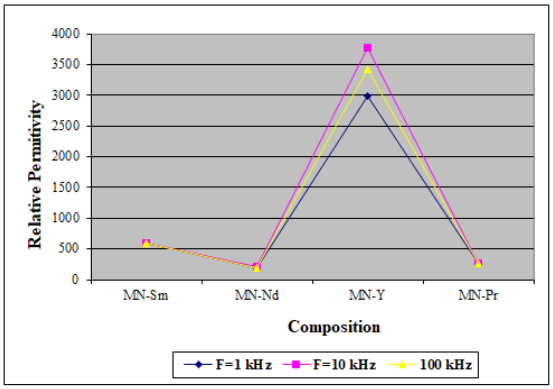

Fig.6: Variation of dielectric permittivity with composition at 1250°C

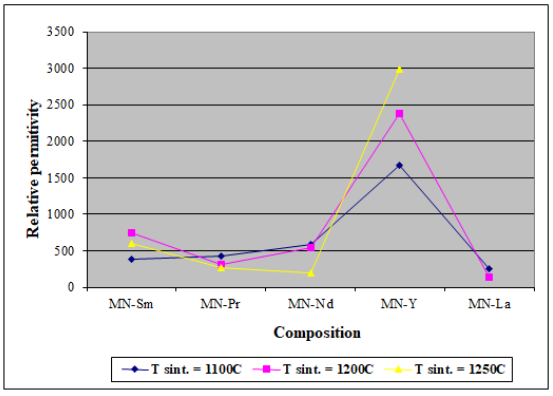

Fig.7: Variation of dielectric permittivity with composition at 1 kHz

The incorporation of Ln($Mg_{1/2}Ti_{1/2}$)O_3 in the Pb($Mg_{1/3}Nb_{2/3}$)O_3 structure is the determining factor

regarding the values obtained for the dielectric properties. Usually in the B-site regions of (Mg,Nb) cations coexist with the regions of (Mg,Ti) cations [17]. According to the permittivity measurements, the optimum sintering temperatures are different and depend on the nature of the dopant (lanthanide). Thus for Y the optimum sintering temperature is 1250°C, for Sm it is 1200°C and for the other dopants it is around 1100°C.

4. Conclusions

The $Pb(Mg_{1/3}Nb_{2/3})O_3$ - $Ln(Mg_{1/2}Ti_{1/2})O_3$ compositions, modified with lanthanides Y, La, Pr, Nd, Sm as dopants, have been synthesized by a solid-state reaction method with two steps: the columbit method combined with B-oxide route. The results obtained indicate an influence of the dopant nature on the structure and dielectric properties. The pyrochlore phase was revealed in the calcined powders. XRD analysis revealed that for all sintered compositions the pyrochlore phase disappear and at 1250°C a single perovskite phase was developed, demonstrating the development of the solid solution. Electrical characterization was carried out at low frequencies. The results obtained for the dielectric permittivity was influenced by the nature of the dopant: the highest values for the dielectric permittivity were obtained for 0.9PMN – 0.1LnMT substituted with Y. Integration of $Ln(Mg_{1/2}Ti_{1/2})O_3$ in the $Pb(Mg_{1/3}Nb_{2/3})O_3$ structure results to be the responsible feature concerning the dielectric properties. In line with the permittivity measurements, the optimum sintering temperatures were different and were influenced by the nature of the dopant (lanthanide). Thus for Y the optimum sintering temperature is 1250°C, for Sm it is 1200°C and for the other dopants it is around 1100°C.

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