OBȚINEREA SOLUȚIEI SOLIDE APARȚINÂND SISTEMULUI $Pb(Mg_{1/3}Nb_{2/3})$-$PbTiO_3$
THE ELABORATION OF $Pb(Mg_{1/3}Nb_{2/3})$-$PbTiO_3$ SOLID SOLUTIONS

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The elaboration of bulk (1-x)Pb(Mg$_{1/3}$Nb$_{2/3}$)-xPbTiO$_3$ by using the columbite method is presented. The main aim of the processing was to avoid the formation of an unwanted pyrochlore phase. Optimized sintering temperatures have been chosen in correlation with the densification evolution. Samples with the PMN/PT ratio of 1.0/0.0, 0.9/0.1 and 0.65/0.35 have been processed; X-Ray diffraction and scanning electronic microscopy investigation are presented. The results showing the formation of pyrochlore-free structure in all the investigated samples at sintering temperatures around 1,100 ^{0}C.

În lucrare se prezintă obținerea ceramicii aparținând sistemului (1-x)Pb(Mg$_{1/3}$Nb$_{2/3}$)-xPbTiO$_3$ utilizând metoda columbite. Scopul principal de utilizare a acestei metode a fost de a evita formarea fazei pyrochlor, nedorite. Temperaturile de sinterizare optimizate au fost alese în corelație cu procesul de densificare. Au fost procesate probe cu raportul PMN / PT 1.0/0.0, 0.9/0.1 şi 0.65/0.35; sunt prezentate imaginile de difracție de raze X şi imaginile de microscopie electronică. Rezultatele indică formarea structurii fără faza pyrochlor, în toate probele investigate, la temperaturi de sinterizare în jurul de 1.100 °C.

Keywords: *ceramics, PMN-PT, sintering, relaxors, X-ray methods*

1. Introduction

$Pb(Mg_{1/3}Nb_{2/3})$-$PbTiO_3$ ceramics is a multifunctional material used, due to its dielectric or piezoelectric properties, in several applications such as capacitors/multilayer capacitors and respectively as sensors and/or actuators [1]. Moreover, complex compounds based on $Pb(Mg_{1/3}Nb_{2/3})$ and $Pb(Mg_{1/3}Nb_{2/3})$-$PbTiO_3$ present giant dielectric constants at high frequencies and are used in microwave applications [2]. All this applications request ceramic materials micro or nano grained, well defined as composition, avoiding any disturbing second phase in the crystalline structure. Therefore, the elaboration process has to be established very carefully [3]. In the proccesing of perovskit solid solutions in the lead based relaxor system $Pb(Mg_{1/3}Nb_{2/3})$-$PbTiO_3$, formation of an unwanted pyrochlore phase in the sintered ceramics, even in small quantities, has been associated with inferior dielectric properties of the materials [4]. Numerous attempts have been made to develop a processing technique in which the formation of the undesirable pyrochlore phase is suppressed. Among these, the Columbite processing technique [5], in which prefabricated $MgNb2O_6$ is reacted with an appropriate proportion of PbO, has been widely used in the synthesis of pure phase perovskite $Pb(Mg_{1/3}Nb_{2/3})$. The Columbite processing technique was modified by using different sets of reactants as precursor materials. Normally, the perovskite solid solutions are sintered at temperatures between 1200^{0}C and 1300^{0}C to obtain a densified products. In the present paper a perovskite solid-solution having a composition (1-x)$Pb(Mg_{1/3}Nb_{2/3})$-x$PbTiO_3$ was sinterd at temperatures between 1000^{0}C and 1100^{0}C.

2. Experimental

(1-x)$Pb(Mg_{1/3}Nb_{2/3})O_3$–x$PbTiO_3$ ceramics with x = 0; 0.1 and 0.35 were prepared starting from high purity oxides PbO (99.5%), MgO (99.9%), Nb_2O_5 (99.9%) and $PbTiO_3$ (99.5%). A 3-steps columbite method as shown in Figure 1 has been used. $MgNb_2O_6$ powders were first synthesized at 1100^{0}C in air for 3 h from MgO and Nb_2O_5, then the (1-x)$Pb(Mg_{1/3}Nb_{2/3})O_3$–x$PbTiO_3$ powders were synthesized by the mixtures of $MgNb_2O_6$, PbO and $PbTiO_3$ calcined at 870 ^{0}C. The intermediary compounds obtained through wet milling in water, drying and calcinations became the precursor in the next step and was controlled by XRD. The PMN-PT powder, mixed corresponding to the formula, after milling in water, drying and calcinating at 870 ^{0}C, was mixed with an aqueous solution of polyvinyl alcohol and pressed into pellets. Sintering at different temperatures - 1,000 ^{0}C, 1,050 ^{0}C and 1,100 ^{0}C - was performed. Apparent density and porosity measurements for all

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the sintering temperatures have been performed. The results were presented in Figure 2. XRD measurements have been carried out by using a Bruker-AXS, D8 ADVANCE diffractometer, an incident CuK_α filtered radiation in a scattering angle range $2\theta \in (20 – 70)^0$. The diagrams obtained on PMN/PT=1/0; 0.9/0.1; 0.65/0.35 at different sintering temperatures are shown in Figure 3. SEM measurements on all these samples in order to show the densification after sintering have been performed too.

3. Results and discussions

The densification of the material in the sintering process is evident from the density and porosity measurements (Fig.2) and correlated with the SEM images which show a dense microstructure for all the samples sintered at 1,100 ^{0}C. The results are presented in Figure 4 for two compositions, PMN/PT = 0.9/0.1 and 0.65/0.35 sintered at 1,000 ^{0}C, 1,050 ^{0}C and 1,100 ^{0}C. The ceramic grain growth after sintering is evident so the formation of well defined shapes at 1,100 ^{0}C and dependent on the composition.

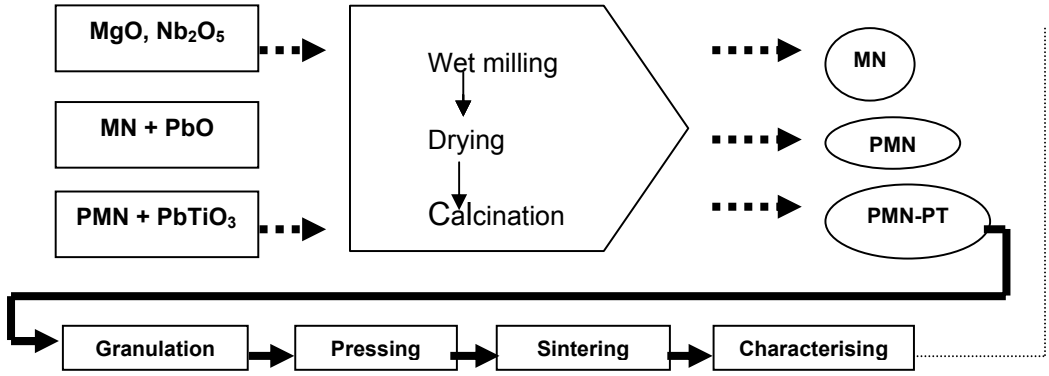
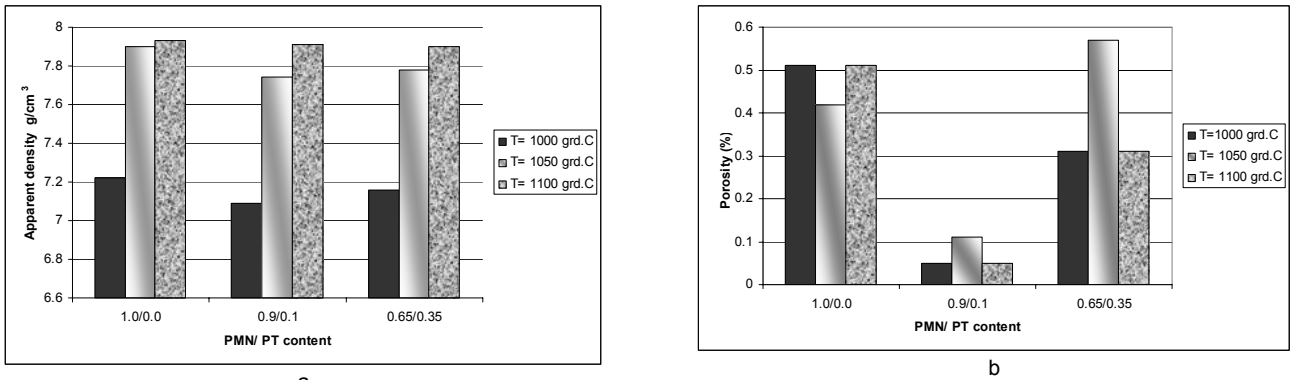
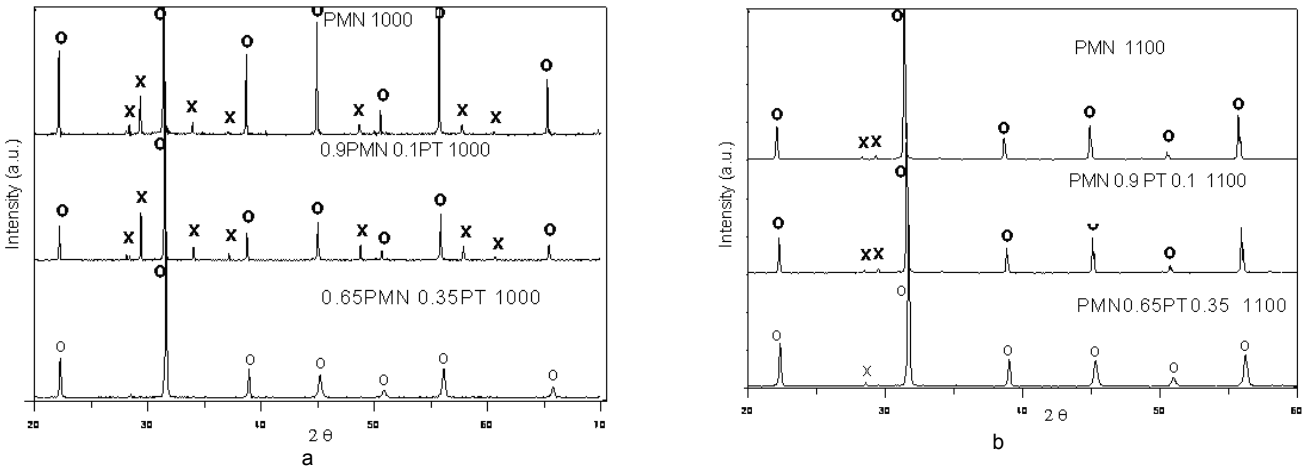


Fig.1 - The processing schema used for the PMN-PT preparation / *Schema tehnologică utilizată pentru prepararea PMN-PT.*



a b

Fig.2 - The apparent density (a) and respectively porosity (b) measurements / *Măsurători de (a) densitate aparentă şi respectiv (b) porozitate.*



a b

Fig.3 - XRD on the samples sintered at 1,000 ^{0}C (a) and respectively at 1,100 ^{0}C (b) showing the cubic (0) and pyrochlore (x) phases. *Analizele XRD pe probe sinterizate la (a) 1000 ^{0}C şi, respectiv, (b) la 1100 ^{0}C prezintă faza cubică (0) şi pyrochlore (x).*

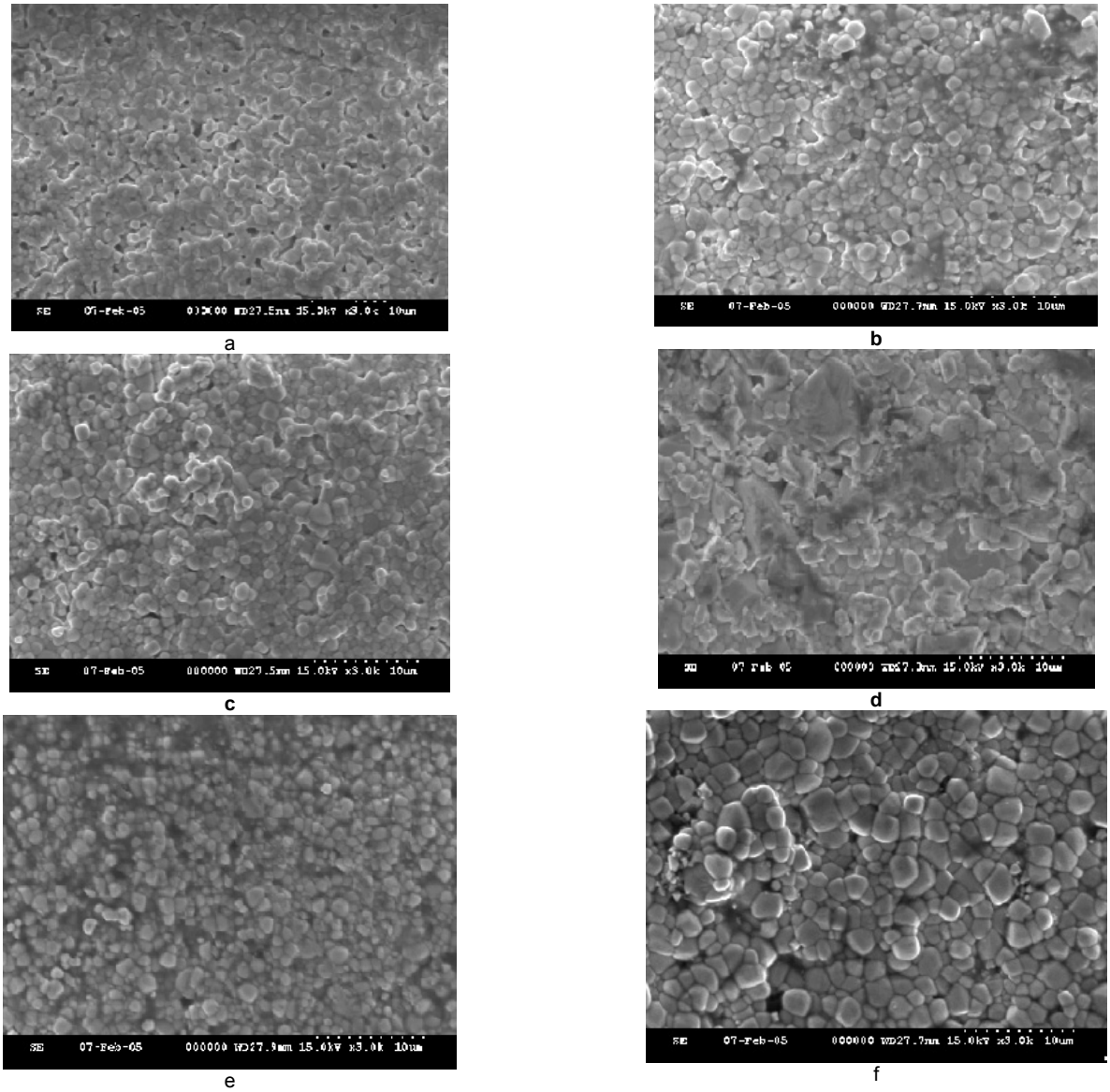


Fig.4 - SEM images showing the densification of PMN/PT= 0.65/0.35 and 0.9/0.1 at 1,000 ^{0}C , 1,050 ^{0}C and respectively 1,100 ^{0}C / *Imaginile SEM arată densificarea de PMN / PT = 0,65/0,35 şi 0,9/0,1 la 1000 ^{0}C , 1050 ^{0}C şi respectiv 1100 ^{0}C:* a) PMN-PT : 0.65/0.35 1000 ^{0}C, b) PMN-PT : 0.9/0.1 1000^{0}C, c) PMN-PT : 0.65/0.35 1050 ^{0}C, d) PMN-PT : 0.9/0.1 1050 ^{0}C, e) PMN-PT: 0.65/0.35 1100 ^{0}C, f) PMN-PT : 0.9/0.1 1100^{0}C.

The existence of the cubic symmetry is consistent with former results [4] which identified a cubic symmetry for the (1-x)PMN- xPT compositions with x < 0.4. The samples sintered at 1,100 ^{0}C, showed only the cubic phase. The samples with higher PT content (PMN/PT=0.65/0.35) present only the cubic structure independent of the sintering temperature. The (pseudo)cubic phase is present for PMN/PT = 0.35/0.65 at 1,000 ^{0}C and 1,050 ^{0}C and for all the compositions at 1,100 ^{0}C. The corresponding lattice parameters are given in Table 1and in Figure 5. The decrease of the value of the parameters with the PT content can be explained by the deformation of the symmetry of the elementary cell in the transition from cubic to tetragonal perovskite structure. This transition takes place at a concentration of PT higher than 0.35 [5].

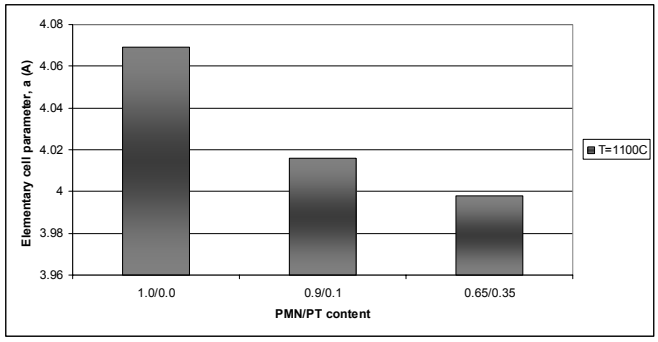


Fig.5 - The cell parameter a as calculated from XRD measurements. *Parametrul celulei calculat din măsurători XRD.*

Table 1

The cell parameter a as calculated from XRD measurements
Parametrul celulei calculat din măsurători XRD

PMN/PT	T=1,000 ^{0}C	T=1,050 ^{0}C	T=1,100 ^{0}C
1.0/0.0	Cubic+pyrochlore	Cubic+pyrochlore	Cubic $(a^2c)^{1/3}=4.06_9$ Å
0.9/0.1	Cubic+pyrochlore	Cubic+pyrochlore	Cubic $(a^2c)^{1/3}=4.01_6$ Å
0.65/0.35	Cubic $(a^2c)^{1/3}=4.00_7$ Å	Cubic $(a^2c)^{1/3}=4.00_6$ Å	Cubic $(a^2c)^{1/3}=3.99_8$ Å

4. Conclusions

The results discussed above showed the possibility to get pyrochlore-free PMN-PT ceramics by using the columbite method. The optimum sintering temperature is around 1,100 ^{0}C. In this conditions high densified ceramics with a density ρ=95% of the theoretical one has been obtained. The SEM images showed micrometric ceramic grains.

The structure is cubic, characteristic to low PT content. The elementary cell parameter decrease slightly when increasing PT content and can be explained by the deformation of the elementary cell in the vicinity of the cubic/tetragonal perovskite transition in this compositions range. This transition takes place at a concentration of PT higher than 0.35 [6].

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NOUTĂȚI / NEWS

Electroliți nanostructurați de Gd-CeO_2 pentru SOFC prin turnare apoasă în bandă

Nanostructured Gd-CeO_2 electrolyte for SOFC by aqueous tape casting

Electrolitul de oxid de ceriu dopat cu oxid de gadoliniu ($Ce_{0.9}Gd_{0.1}O_{1.95}$, GDC) a fost fabricat prin metoda turnării în bandă bazată pe ruta apoasă pentru celulele de combustie cu electrolit solid (SOFC). Pulberea ceramică preparată prin sinteza combustiei a folosit acid poliacrilic (PAA), alcool polivinilic (PVA), polietilenglicol (PEG), octanol, 2,4,7,9-tetrametil-5-decin-4,7-diol etoxilat şi apă dublu distilată ca dispersant, liant, plastifiant, antispumant, surfactant şi respectiv solvent pentru a prepara o suspensie GDC. S-au studiat şi s-au optimizat condițiile pentru prepararea suspensiilor stabile GDC prin sedimentare, potențial zeta şi măsurători de viscozitate. S-au preparat benzi netratate termic cu suprafață netedă, flexibilitate, grosime în domeniul 0,35–0,4mm şi densitate relativă a materialului netratat de 45% . Tehnici de sinterizare convențională rapidă au fost folosite şi comparate pentru densificare ceea ce demonstrează posibilitatea depăşirii sinterizării la temperaturi ridicate şi întârzierii creşterii granulelor.

Gadolinia-doped ceria (Ce0.9Gd0.1O1.95, GDC) electrolyte was fabricated by aqueous-based tape casting method for solid oxide fuel cells (SOFCs). The ceramic powder prepared by combustion synthesis was used with poly acrylic acid (PAA), polyvinyl alcohol (PVA), poly ethylene glycol (PEG), Octanol, 2,4,7,9-tetramethyl-5-decyne-4,7-diol ethoxylate and double distilled water as dispersant, binder, plasticizer, defoamer, surfactant and solvent respectively, to prepare stable GDC slurry. The conditions for preparing stable GDC slurries were studied and optimized by sedimentation, zeta potential and viscosity measurements. Green tapes with smooth surface, flexibility, thickness in the range of 0.35–0.4mm and 45% relative green density were prepared. Conventional and flash sintering techniques were used and compared for densification which demonstrated the possibility of surpassing sintering at high temperatures and retarding related grain growth.

Material prelucrat de/ *Material worked by:* Alina Melinescu

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