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Structural investigation of $PbMg_{1/3}Nb_{2/3}$-$PbTiO_3$ system

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$PbMg_{1/3}Nb_{2/3}O_3$ (PMN) and $PbTiO_3$ (PMN-PT) have been obtained by a columbite method. The sintering conditions have been determined in order to get a perovskite type structure. XRD measurements and SEM analysis have been performed to identify the structural parameters and respectively the microstructure.

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Keywords: Lead Magnesium Niobate, $PbTiO_3$, Perovskite, XRD, SEM

1. Introduction

The lead magnesium niobate – based relaxor materials have advantages for applications due to their high dielectric constant, good electrostrictive effect.

Lead magnesium niobate (PMN) belong to a family of complex Pb (B_1B_2) O_3 perovskites, where B_1 is typically a low-valence cation e.g. Mg^{+2}, Zn^{+2}, Fe^{+3},Ni^{+2} etc. and B_2 a high valence cation e.g. Ti^{+4}, Nb^{+5}, Ta^{+5} etc.[1].

It is difficult to obtain pure perovskite PMN phase without the formation pyrochlore phase by the classical route. The pyrochlore phase changes the value of the dielectric constant (decrease because of its low dielectric constant of about 130). The PMN ceramic prepared by ultrahigh purity starting powders could have a maximum dielectric constant as high as 20 000.

In order to enhance the perovskite formation, the system was prepared by a "B-site precursor method" [2,3] which is known as "columbite process."

2. Experimental procedure

(1-x) $Pb(Mg_{1/3}Nb_{2/3})O_3$ – $xPbTiO_3$ ceramics or (1-x)PMN- xPT in short with x = 0; 0.05 and 0.1 were prepared using the columbite method. In order to get a pyrochlore free material we used high purity raw materials and a processing to avoid lead volatilization. The starting materials were high purity oxides: PbO (99.5%), MgO (99.9%), Nb_2O_5 (99.9%) and $PbTiO_3$ (99.5%). In the first step MgO and Nb_2O_5 were milled in water, dried, calcined at 1000 ^oC in a covered alumina crucible and were examined by X-ray diffraction (XRD) to identify the phases. This compound became the precursor in the second step being mixed with PbO and milled again in water, dried, calcined at 850 ^oC to form the perovskite PMN. Phase identification was again carried out by XRD. The PMN powder were mixed with $PbTiO_3$ according to the formula corresponding to each system and then were milled in water, dried, calcined at 870 ^oC, mixed with aqueous solution (4 wt.%) of polyvinyl alcohol and pressed isostatically into pellets. These samples were sintered for 2h at 1180 ^oC and respectively 1230^{0}C. XRD measurements in order to identify the crystalline phases and to determine the lattice constants and X-ray density have been performed. The formation of a majoritary PMN cubic phases in connection with the modification of both the composition of the samples and the sintering temperatures has been put into evidence. The microstructure evolution on different compositions and after sintering at 1.000 ^oC, 1.050 ^oC and 1.100 ^oC has been studied by SEM.

3. Results

The XRD measurements have been carried out with an incident CuK_α filtered radiation in a scattering angle range $2\theta \in (20 - 70)^o$ by using a Bruker-AXS, D8 ADVANCE diffractometer. The diagrams obtained on samples with three different concentrations – PMN/PT=1/0; 0.9/0.1; 0.65/0.35 – every at three different sintering temperatures - 13000 ^oC, 1.050 ^oC and 1.100 ^oC - are given in Figs. 2-4.

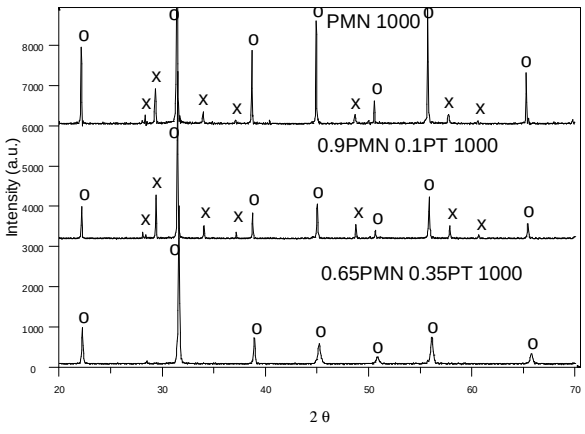

Fig. 1. X-ray diffractograms of (1-x)PMN-xPT sintered at 1000 ^oC: (o) cubic phase; (x) pyrochlore.

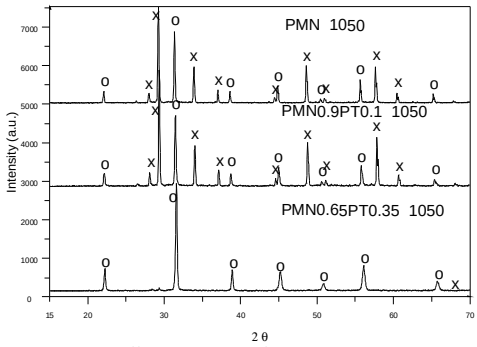

Fig. 2. X-ray diffractograms of (1-x)PMN- xPT sintered at 1050^{0}C: (o) cubic phase; (x) pyrochlore.

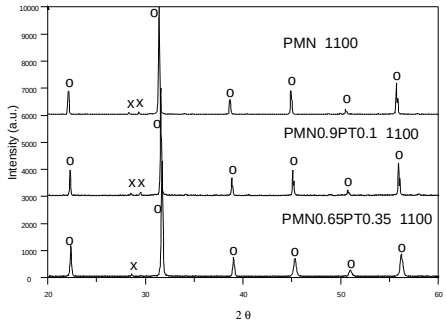

Fig. 3. X-ray diffractograms of (1-x)PMN- xPT sintered at 1100^{0}C: (o) cubic phase; (x) pyrochlore.

One can observe that in all diagrams the PMN-PT cubic phase is present. This is consistent with former former results [4] which identified a cubic symmetry for the (1-x)PMN- xPT compositions with $x < 0.4$. The second observation is the disappearing of the pyrochlore phase in some compositional and sintering temperatures ranges. For higher sintering temperature, namely at 1,100 ^{o}C, all the three samples show a majoritary cubic phase. At lower temperatures and at higher PT content the secondary phase identified as pyrochlore practically disappeared.

The (pseudo)cubic phase is present for PMN/PT = 0.35/0.65 at 1,000 ^{o}C and 1,050 ^{o}C and for all the compositions at 1,100 ^{o}C. The corresponding lattice parameters are given in table 1.

Table 1.

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

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 [4].

SEM investigation of sintered samples with different compositions (PMN/PT = 1/0; 0.9/0.1 and 0.65/0.35) and at different sintering temperatures (1,000 ^{0}C, 1,050 ^{0}C and 1,100 ^{0}C) has been performed. The evolution of these microstructures are given in Fig.4. The results were used to establish the optimum sintering temperature. Although the growth of the ceramic grains after sintering has been put into evidence. The formation of well defined shapes at 1,100 ^{0}C and dependent on the composition has been observed.

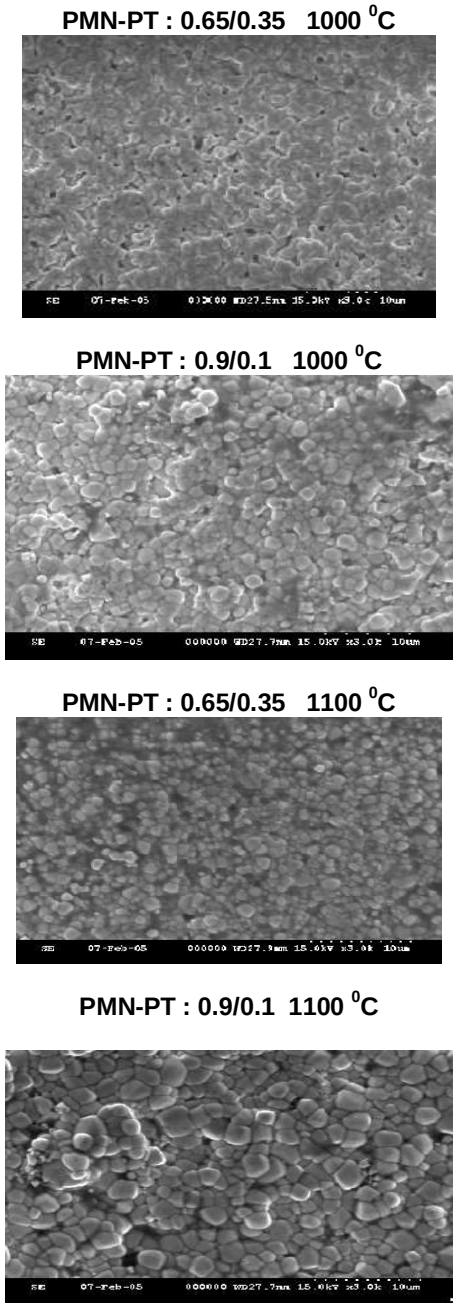

Fig. 4. Microstructures of the PMN-PT system obtained by SEM; X 3k.

4. Conclusions

The PMN-PT system with PMN/PT ratios 1/0; 0.9/0.1 and 0.65/0.35 has been obtained. The elaboration process has been the columbite method with an optimized sintering temperature of 1.100 ^oC. The sintered material presents a density >95% of theoretical one. The material sintered at 1.100 ^oC presents the (pseudo)cubic structure characteristic to the PMN-PT with a PT content under 0.4. Practically no pyrochlore phase has been identified.

The elementary cell parameter decreases slightly with the increasing of the PT content. The increase of the ceramic grains during sintering at different temperatures was put into evidence. The grain dimension at the optimum sintering temperature is around 1 μm.

References

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