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Phase analysis of seeded and doped $PbMg_{1/3}Nb_{2/3}O_3$ prepared by organic solution of citrates

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$PbMg_{1/3}Nb_{2/3}O_3$ (PMN) prepared by organic solution of citrates was analyzed by the Rietveld method to determine the influence of seeds and dopants on the perovskite and pyrochlore phase formation. It was observed that pyrochlore phase formation increases with an increase in calcination time when no additives are included during the preparation. It was also observed that a greater amount of perovskite phase appeared in doped or seeded samples. The fraction of perovskite phase increased from 88 mol% in pure sample to ~95 mol% in doped and seeded samples calcined at 800 °C for 1 h. It is clear that the addition of dopants or seeds during PMN preparation can enhance the formation of perovskite phase.

I. INTRODUCTION

$PbMg_{1/3}Nb_{2/3}O_3$ (PMN) has been studied since 1950.[1] It has perovskite (Pe) type structure ABO_3[2] at room temperature and characteristics that make it useful as dielectric in multilayer ceramic capacitors.[2–5] These characteristics are low sintering temperature (<1000 °C), high dielectric constant (8000–15,000), and a high electrostriction coefficient[6] (0.1%). These properties depend on the precursors' purity, the processing method, as well as the reaction time and temperature. Any change in these parameters can induce the formation of pyrochlore phase (Py). This phase has a low dielectric constant (130–200)[7] that causes the overall dielectric constant of PMN to decrease. The PMN was first prepared by mechanical mixture of oxide precursors[3,5] that promote the formation of pyrochlore phase. Aiming to get PMN free of pyrochlore phase, several PMN preparation methods have been performed.

Swartz and Shrout[5] prepared perovskite PMN at 800 °C by using columbite precursor which was then prepared at 1000 °C; even so, 2% of pyrochlore phase was present. Ravindranathan *et al.*[2] prepared PMN by the sol-gel method where Pe phase could be formed at 775 °C. In this work, they were able to prepare pure perovskite type PMN by seeding the material with 1 wt.% of Pe PMN, also taking advantage of lowering the crystallization temperature by 75 °C. Liou and Wu[8] could enhance the dielectric properties of PMN by adding $PbTiO_3$ and excess of MgO and PbO. Among all the methods described in the literature, chemical routes have shown better performance to decrease the amount of pyrochlore phase.

In this work PMN has been prepared by organic solution of citrates[9] using the concept of controlled nucleation[10] through the introduction of $BaTiO_3$ seed particles or barium/titanium doping solution.

II. EXPERIMENTAL

Precursor reagents used were niobium ammoniac oxalate $NH_4H_2[NbO(C_2O_4)]$ 20.5% in niobium (CBMM–Companhia Brasileria de Mineração e Metalurgia), basic magnesium carbonate $(MgCO_3)_4Mg(OH)_2 \cdot 5H_2O$ (Cinética Química), lead acetate $(CH_3COO)_2Pb \cdot 3H_2O$ (Merck), citric acid $C_6H_8O_7 \cdot H_2O$ (Merck), ethylene glycol $HOCH_2CH_2OH$ (Synth), barium acetate $C_4H_6BaO_4$ (Vetec), and titanium isopropoxide $Ti(OC_3H_7)_4$ (Rulsag).

Standard solutions of precursor citrates were prepared (magnesium, niobium, barium, and titanium) and gravimetric analyses were used to standardize these solutions. Lead acetate aqueous solution was also prepared and standardized by complexometry with ethylenediamine tetra-acetic acid (EDTA). Magnesium carbonate was also standardized by EDTA.

TABLE I. Preparation conditions for lead magnesium niobate doped with 1 wt.% of barium/titanium Pechini solution or seeded with 1 wt.% of $BaTiO_3$, and the codes used for them in the text.

Temperature (°C)	Calcination time (h)	Additive type	Code
700	1.5	Seed	15S7
700	1.5	Dopant	15D7
700	1.5	None	15N7
700	3.0	Seed	30S7
700	3.0	Dopant	30D7
700	3.0	None	30N7
800	1.0	Seed	10S8
800	1.0	Dopant	10D8
800	1.0	None	10N8

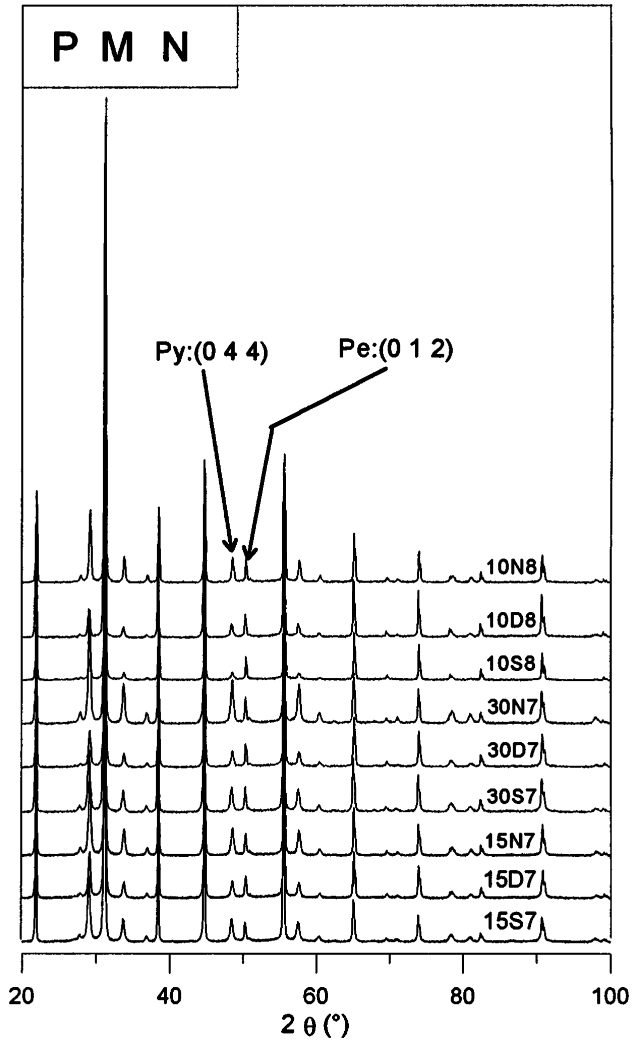

FIG. 1. X-ray diffractograms of all samples.

Stoichiometric mixtures of respective cation solutions were stirred at 90 °C until complete chelation. At this point seeds or dopants were introduced into the solution, as described in the next paragraph, and then the temperature was increased to 140 °C until the complete polymerization that results from sterification among metallic citrates and ethylene glycol in acid environment. The so-formed resin was characterized by differential thermal analysis and infrared spectroscopy.[11,12] The polymer was calcined at 350−400 °C in order to eliminate the organic matter, and the resultant material was pulverized in an agate mortar. This powder was calcined at different temperatures and times, and characterized by x-ray diffraction and infrared spectroscopy.

Barium and titanium citrate solubilized in ethylene glycol with stoichiometry 1 : 1 were prepared to be used as dopant. Gravimetric analysis was used to standardize this solution. Weighted amount of this solution was included to the PMN resin at 90 °C under stirring, in order to represent 1 wt. % of the entire ferroelectric mass, after calcination and elimination of the polymer. The remaining solution was polymerized at 140 °C and heated at 400 °C, pulverized, and calcined at 800 °C for 1 h. The resulting powder was characterized by XRD and IR, and then ground in a ball mill (with ethylene glycol as medium) for 72 h. The resulting suspension was then classified by centrifugation, and particles smaller than 0.1 μm were selected as seeds. An amount of this suspension representing 1 wt. % of seed particles in relation to the entire ferroelectric mass, after calcination and elimination of the polymer, was introduced into the PMN resin at 90 °C while stirring. In both cases the PMN-based polymers were calcined and characterized by x-ray diffraction and infrared spectroscopy.

$BaTiO_3$ composition was chosen as dopant and seed because it is a ferroelectric material and has a perovskite type structure, with lattice dimension very close to that of PMN.

X-ray diffraction data was obtained in a Siemens D-5000 model equipment with monochromatized copper radiation obtained by 40 kV and 30 mA filament current. The Rietveld method[13] program used was the DBWS9006-PC release 12.8.91[14] and the pseudo-Voigt function[15] was applied to the refinements. The crys-

TABLE II. Lattice dimensions, molar phase percentage, and agreement factor indexes. Enclosures are the standard deviations obtained in the computations.

	Perovskite		Pyrochlore		Refinement indexes	
Samples	a (Å)	mol %	a (Å)	mol %	R_{wp}	S
15N7	4.0487(2)	85.35(2)	10.6056(7)	14.65(2)	10.66	1.55
15D7	4.0474(3)	91.77(3)	10.6051(8)	8.23(2)	11.12	1.59
15S7	4.0485(2)	86.61(2)	10.6157(6)	13.39(2)	11.16	1.52
30N7	4.0475(2)	80.84(2)	10.6015(7)	19.16(3)	9.37	1.51
30D7	4.0455(3)	93.18(3)	10.599(1)	6.82(2)	11.61	1.84
30S7	4.0477(3)	89.30(3)	10.6073(9)	10.70(3)	10.32	1.60
10N8	4.0467(2)	88.04(2)	10.5962(6)	11.96(2)	10.02	1.71
10D8	4.0452(2)	94.55(3)	10.599(1)	5.45(2)	12.67	1.77
10S8	4.0459(2)	95.01(2)	10.605(1)	4.99(2)	10.83	1.75

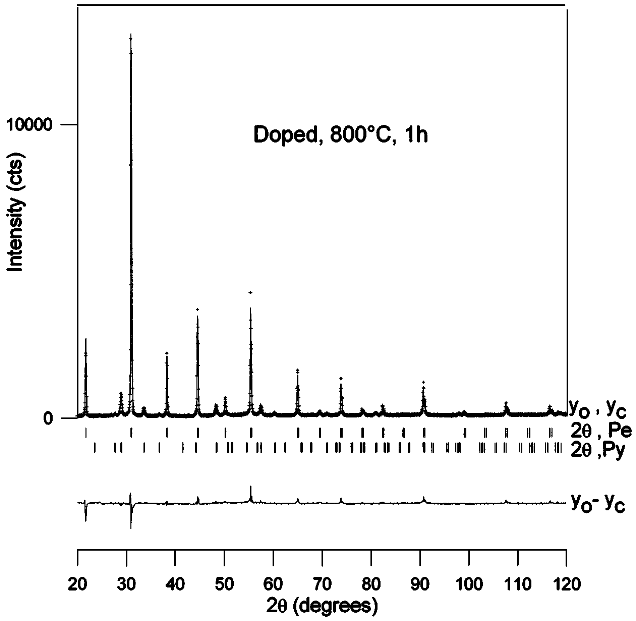

FIG. 2. Final Rietveld plot of PMN doped with 1 wt.% of barium/titanium in Pechini solution, calcined at 800 °C for 1 h: (+) observed, y_0; (—) calculated, y_c; (—) residual, $y_0 - y_c$; (|) Bragg positions.

tal structure parameters used for perovskite (Pe) phase were[16] space group $Pm3m$, $\mathbf{a} = 4.0441$ Å, with the atomic positions Pb (0.027, 0.027, 0.0697), Mg/Nb (0.523, 1/2, 1/2), and O (0.540, 1/2, 0). The crystal structure parameters used for pyrochlore (Py) phase were[17] space group $Fd3m$, $\mathbf{a} = 10.6029$ Å, with the atomic positions Pb (1/2, 1/2, 1/2), Mg/Nb (0, 0, 0), O (0.3175, 1/8, 1/8), and O′ (3/8, 3/8, 3/8). Chemical composition of the pyrochlore phase, determined by Wakiya *et al.*,[17] is $Pb_{1.86}Mg_{0.24}Nb_{1.76}O_{6.5}$.

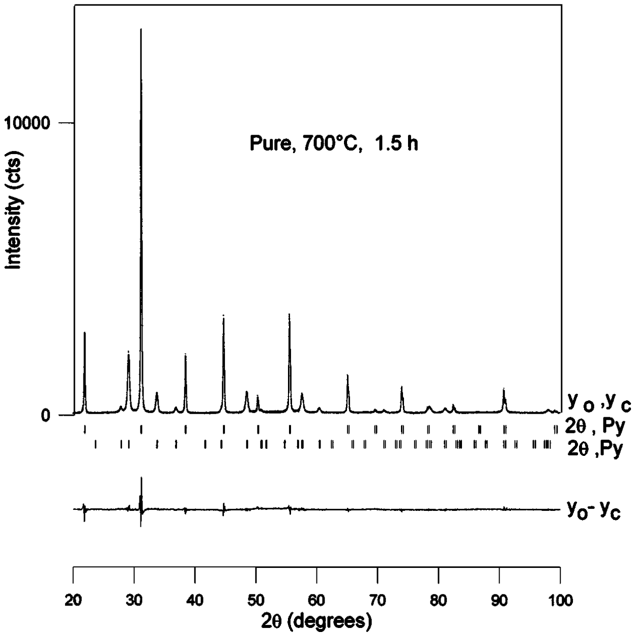

FIG. 3. Final Rietveld plot of pure PMN, calcined at 700 °C for 1.5 h: (+) observed, y_0; (—) calculated, y_c; (—) residual, $y_0 - y_c$; (|) Bragg positions.

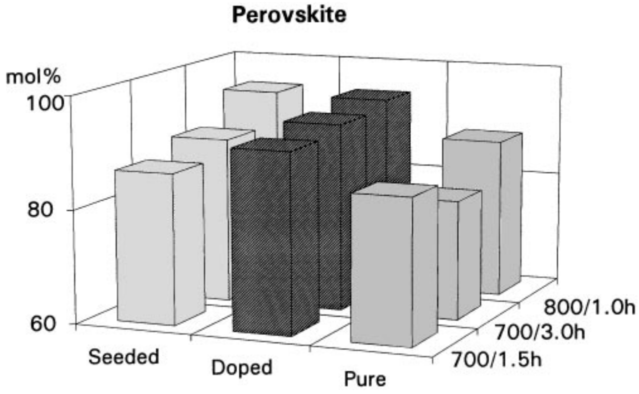

FIG. 4. Perovskite molar percentage obtained by Rietveld method of all PMN samples.

Infrared spectrums were obtained in Perkin-Elmer-567 and Nicolet FTIR spectrometers. All conditions considered to prepare powders used in this work are listed in Table I.

III. RESULTS AND DISCUSSIONS

All samples considered in Table I were analyzed using x-ray diffraction. Figure 1 shows that the relative intensity of (012) perovskite peak to the (044) pyrochlore peak (around $2\theta = 50°$ indicated in the figure) changes accordingly to the kind of heat treatment applied to the sample. In pure samples (15N7, 3ON7, and 10N8) the relative peak intensity of pyrochlore phase is greater than that of other samples. This is an indication that the proportion of pyrochlore phase is greater in pure samples.

A precise quantitative phase analysis was done by using the Hill and Howard[18] method. This method is based on the fact that the scale factor obtained in Rietveld method is proportional to the pattern intensity. Also, the relative intensity of peaks for the phases in the pattern is proportional to their relative amount in the sample, so the relative mass fraction is also proportional to the relation of scale factor for each phase, given by Eq. (1).

$$W_i = (\mathrm{SVZM})_i \Big/ \sum_j (\mathrm{SVZM})_j \, , \qquad (1)$$

where S is the scale factor, V is the unit cell volume, and ZM is the weight of the unit cell in atomic units (number of formula units, Z, per cell times the atomic weight, M, of the formula unit).[18,19]

Listed in Table II are the cell parameters, molar percentage of each phase, and the agreement factors as defined by Scott[20] (R_{wp}, S). Figures 2 and 3 show the results of refinement of two different samples (respectively 15N7 and 10S8). The calculated (y_c), the observed (y_0), and the residual ($y_0 - y_c$) diffractograms indicate that the refinement was very satisfactory. These diffractograms show that there is no other phase beside the perovskite and pyrochlore. In fact, the diffractograms for all samples considered in this study show (Fig. 1) that only these two phases are present.

Figure 4 and Table II show the evolution of perovskite phase with calcination conditions. For a pure sample treated at 700 °C, the amount of Pe phase decreases with the calcination time, from 85.35(2) mol % when treated for 1.5 h to 80.84(2) when treated for 3 h. However, for the PMN powder calcined at 800 °C for 1 h, the amount of Pe phase increases from 88.04(2) mol % for pure sample to 94.55(3) and 95.01(2) mol % for doped or seeded samples, respectively. These are significant increases, considering the estimated standard deviation obtained in the Rietveld refinements, and justify the use of seeds or dopants. Figure 4 also shows that the effect of seeds on the formation of perovskite phase is more significant for higher calcination temperature (800 °C).

Figure 5 shows the variation in 2θ of full width at half maximum (FWHM) to the phases of all samples studied. This figure indicates that perovskite phase has sharper peaks than pyrochlore phase for all samples considered, indicating greater crystalline size for perovskite phase. It is also observed that the crystalline size for perovskite phase increases from 700 °C to 800 °C.

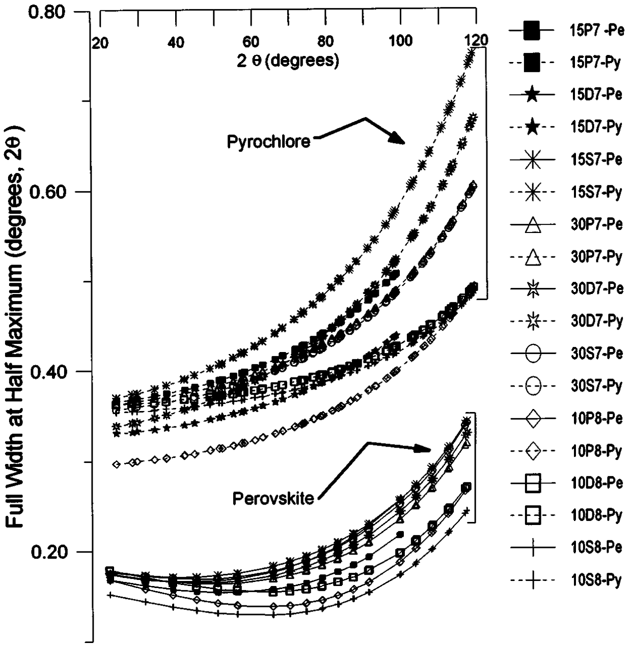

FIG. 5. Full width at half maximum (degrees) of perovskite and pyrochlore phases.

The FWHM[21] for perchlorate phase presents a striking variation with 2θ at 700 °C. This can indicate the presence of inhomogeneity or defect in its lattice. The compositional fluctuation, if present, can be explained by the presence of carbonates at temperatures lower than 800 °C, as indicated in Fig. 6. This figure shows the infrared spectroscopy of pure sample calcined at 750 °C for 3 h. The observed band in this figure at 1400 cm^{-1} is characteristic of carbonate stretching. For samples calcined at 800 °C for 1 h, the infrared spectrum showed no characteristic band at 1400 cm^{-1}, indicating that the carbonates have vanished after calcination at this temperature (Fig. 7).

The formation of carbonates during calcination of powders prepared by using the decomposition of polyester has been observed by several authors.[10,22–25] During the polymer decomposition, intermediates lead titanium and lead zirconium carbonates are formed

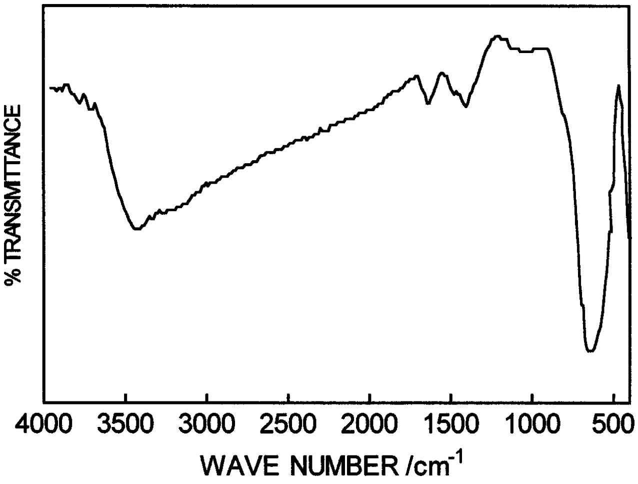

FIG. 6. Infrared spectrum of pure PMN calcined at 750 °C for 3 h.

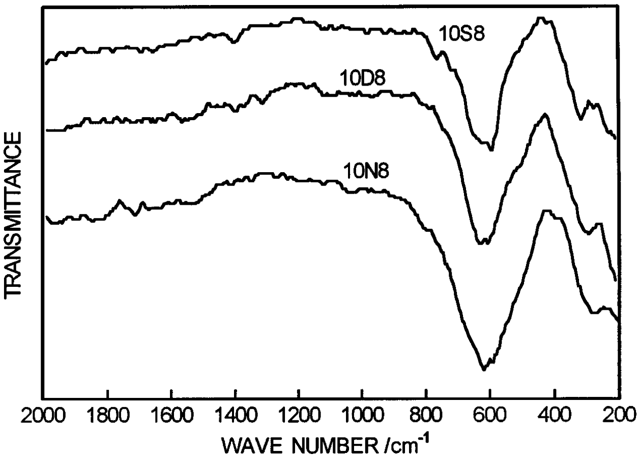

FIG. 7. Infrared spectrum of calcined powders at 800 °C for 1 h.

before the nucleation of $PbZr_xTi_{1-x}O_3$ (PZT) phase.[10,22] These two carbonates have different reactivities that lead to formation of nonhomogeneous PZT phase. In the same way, the formation of PMN phase by decomposition of the polyester containing Pb, Mg, and Nb can also lead to the formation of PM and PN carbonates. PM carbonate is more stable than PN carbonates which can lead to preferential decomposition of the latter, favoring the formation of P_3N pyrochlore phase, especially for long time at low temperature calcination (700 °C). This is in agreement with the results of this study (Fig. 4).

The use of seed $BaTiO_3$ particles as well as stoichiometric Ba/Ti solution seems to favor the decomposition of these mixed carbonates leading to the maximization of the perovskite phase formation.[26]

IV. CONCLUSIONS

From results of this study it is concluded that both $BaTiO_3$ seeds and stoichiometric Ba/Ti solutions favor the formation of PMN perovskite phase. The existence of PN and PM carbonate phases for temperatures below 800 °C seems to limit the perovskite phase formation for pure PMN composition.

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