


# EFFECT OF ATMOSPHERE ON THE PEROVSKITE PHASE STABILITY OF 0.87PLMN-0.13PT POWDERS

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## ● Resumen

En este estudio, polvos del compuesto perovskita 0.87 (Pb, La) (Mg, Nb) O<sub>3</sub>-0.13PbTiO<sub>3</sub> o mejor conocido como PLMN-13PT, fueron producidos por el método de la columbita en diferentes atmósferas (oxígeno, nitrógeno y argón) con el fin de lograr la estabilidad de la fase perovskita. La formación de la fase fue investigada por difracción de rayos X, análisis termogravimétrico y microscopía electrónica de barrido. La influencia de las atmosferas de oxígeno y argón en la etapa de calcinación fue similar y dio lugar a una estabilidad adecuada de la fase perovskita en los polvos PLMN-13PT, entretanto, a atmosfera de oxígeno fue considerada como ideal por causa da menor pérdida de masa del material durante dicho proceso. Del mismo modo, el polvo calcinado en atmosfera de nitrógeno mostró una cantidad no apropiada de la fase de pirocloro, siendo totalmente descartado el uso de esta ultima atmosfera en el proceso de calcinación.

Palabras clave: perovskita, formación de fase, control de atmósfera, materiales ferroeléctricos, PLMN-PT.

## ● Abstract

In this study, powders of the perovskite compound 0.87(Pb,La)(Mg,Nb)O<sub>3</sub>-0.13PbTiO<sub>3</sub>, or PLMN-13PT, were produced by the columbite method in various atmospheres (oxygen, nitrogen and argon), in order to achieve perovskite phase stability. The phase formation was investigated by X-ray diffraction, thermogravimetric analyses and scanning electron microscopy. The influence of the oxygen and argon calcining atmospheres was similar and led to adequate perovskite phase stability in the PLMN-13PT powders. However, the powder calcined in nitrogen showed an unwanted amount of the pyrochlore phase.

Keywords: perovskite phase formation, atmosphere control, ferroelectric materials, PLMN-PT.

## ● Introduction

Lead-based magnesium niobate ceramics, such as PMN and PMN-PT, belong to the class of relaxor ferroelectric materials, exhibiting good dielectric and electrostrictive properties /1-3/. The conventional mixed oxide method for the synthesis of PMN-based ceramic powders usually cannot avoid the formation of paraelectric pyrochlore phases that are detrimental to the electrical and optical properties /4/.

Various alternative techniques, used to suppress the formation of undesirable pyrochlore-type phases in the synthesis of lead-based magnesium niobate ceramics, have been reported; for example, mechanical activation /5/, sol-gel method /6/ and co-precipitation method /7/.

Nevertheless, a well-known two-step solid-state reaction, proposed in the early 1980s by Swartz and Shroud /8/, is still a reasonably low-cost method to prepare single-phase PMN-based ceramics. This

method, known as the columbite method, starts with the precalcination of a mixture of MgO and Nb<sub>2</sub>O<sub>5</sub> to form MgNb<sub>2</sub>O<sub>6</sub> which has a columbite structure. This magnesium niobate is then made to react with PbO.

It is well known that processing conditions affect the amount of pyrochlore-type phase in PMN-based ceramics and powders. Cavalheiro et al. /9/ showed that PMN powders contain two types of pyrochlore phase, depending on the PbO content added during heat treatment.

Although more aggregated particles are formed, excess PbO prevent the Nb/Mg ratio increasing significantly in the perovskite structure, reducing the amount of pyrochlore phase in the powder. Lejeune and Boilot /10/ studied dependence of the reactivity of magnesium and ferric oxides on other phases, belonging to the binary system PbO- Nb<sub>2</sub>O<sub>5</sub>, and concluded that the formation of a pyrochlore phase could not be completely eliminated. Moreover, it was proposed that the formation of PMN is directly dependent on the reactivity of magnesium oxide with lead and niobium oxides. Joy and Sreedhar /11/ proposed the use of the precursor Mg<sub>4</sub>Nb<sub>2</sub>O<sub>9</sub> in place of MgNb<sub>2</sub>O<sub>6</sub> for the preparation of pyrochlore-free PMN by the columbite method, because a minor amount of free Nb<sub>2</sub>O<sub>5</sub> in the precursor may be the reason for the formation of small amounts of pyrochlore phase during the synthesis of PMN perovskite.

More recently, Wongmaneerung et al /12/ found that, by using suitable two-stage sintering techniques, dense and pure perovskite PMN ceramics can be successfully derived from a corundum B-site precursor. On the other hand, the dielectric, piezoelectric and electrostrictive properties of PMN can be enhanced by the addition of ferroelectric PbTiO<sub>3</sub> (PT).

The formation of a solid solution by the addition of more ionic compounds such as PbTiO<sub>3</sub>, has been ascribed to the increase the tolerance factor and electronegativity difference, leading to stabilization of the perovskite structure /13/. With the aim of improving the optical and electro-optical properties, La has been added to the system PMN-PT; however, La-doped PMN-PT materials show less perovskite-phase stability.

Investigations revealed that enhanced pyrochlore formation accompanies the enhanced B-site cation ordering, with increasing La content in the PLMN-PT system /14/. While a reasonable number of papers refer to the preparation of PMN perovskite /5-12/, there are no reports in the literature on the formation of the perovskite phase under different calcinations atmospheres, for powders based on lead magnesium niobate with La.

Controlling the atmosphere can also be a key factor information of the desired phase and to enhance the chemical reaction kinetics, since the atmosphere can remove contaminants and volatiles, transfer heat to the powder and beneficially contribute to the stoichiometric equilibrium /15/. Therefore, in the case of PMN-based ceramic powder, atmosphere control during the solid state reaction could help in attaining perovskite phase stability, although to the best to our knowledge, no report has been published about the effect of the atmosphere on the perovskite phase stability in PMN-based powders.

The purpose of the present work, then, was to study the effect of atmosphere on the perovskite-phase in formation of 0.87[Pb<sub>(1-y)</sub>La<sub>y</sub>(Mg<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>]-0.13PbTiO<sub>3</sub> powders prepared by the columbite method.

### Experimental procedure

The powder was synthesized by the columbite or two-stage calcining method [8]. The batch formula was 0.87[Pb<sub>(1-y)</sub>La<sub>y</sub>(Mg<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>]-0.13PbTiO<sub>3</sub> PLMN-13PT, with y=0.01. Lanthanum oxide, La<sub>2</sub>O<sub>3</sub> (Aldrich, >99 % purity), niobium oxide, Nb<sub>2</sub>O<sub>5</sub> (Alfa Aesar 99,9+ % purity), lead oxide, PbO (MGK 99 %) and titanium oxide, TiO<sub>2</sub> (Alfa Aesar, 99,8 % purity) were used.

The magnesium carbonate hydroxide pentahydrate, (MgCO<sub>3</sub>)<sub>4</sub>Mg(OH)<sub>2</sub>·5H<sub>2</sub>O (Aldrich 99 % purity), was carried up to 1 100 °C, for 4h, to drive off CO<sub>2</sub> and H<sub>2</sub>O and obtain the correct amount of MgO for a stoichiometric reaction with Nb<sub>2</sub>O<sub>5</sub>.

In the first stage, MgO and Nb<sub>2</sub>O<sub>5</sub> powders were ball-milled and prereacted at 1 100 °C for 4 h, in air, to form the columbite phase (MgNb<sub>2</sub>O<sub>6</sub>). In the second stage, the synthesized MgNb<sub>2</sub>O<sub>6</sub> (MN) was

ball-milled in isopropanol, for 24 h, with appropriate amounts of PbO, TiO<sub>2</sub> and La<sub>2</sub>O<sub>3</sub> and heated at 900 °C, for 4h, in various gas atmospheres (oxygen,

nitrogen and argon), at a controlled pressure of 200 kPa. This preparation is summarized in the flow-chart in figure 1.

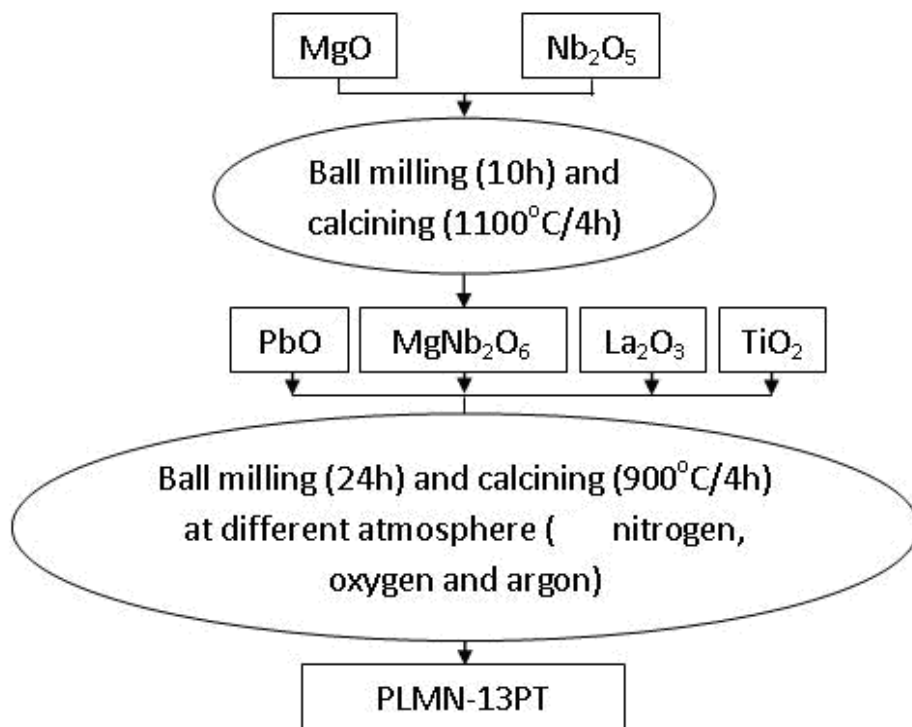


Fig. 1 Preparation route for the PLMN-13PT powders by the columbite method at different gas atmosphere applied in this work.

The reaction sequence of the uncalcined powders, during heat treatment was investigated by thermal gravimetric and differential thermal analysis (TG and DTA, respectively), with a heating rate of 10 °C/min, in the same atmospheres used during calcination (flowing at 5cm<sup>3</sup>/min), using a Netzsch Simultaneous Thermal Analysis system (STA 409 ET). The phase formation was identified by X-ray diffraction analysis (XRD), using a Rigaku diffractometer, with CuK $\alpha$  radiation used a scan rate de 0,2 °C/min at room temperature. The particle size and morphology of the powders were investigated by scanning electron microscopy (SEM), with a Jeol JSM 5800 LV microscope.

## ● Results and discussion

The morphology of PLMN-13PT powder calcined under various atmospheres was examined in SEM micrographs as can be seen in the figure 2. The calcined particles had almost the same morphology. In general, were irregular in shape, with a size of approximately 1  $\mu$ m, similar to the particle size reported by Panda and Sahoo /8/ in the preparation of PMN powder by a chemical route. Secondary phases cannot be seen in BEI micrographs (not shown here).

The results of TGA and DTA experiments conducted on PLMN-13PT powder in flowing nitrogen argon and oxygen are shown in figures 3 and 4, respectively. The TGA and DTA curves

recorded from the powder produced in argon atmosphere were quite similar to those produced in oxygen. In general, similar patterns are observed in the curves shown in figure 3.

The powders prepared in argon, oxygen and nitrogen atmospheres (and analyzed in the same gas) demonstrated three distinct regions of weight loss. The first region occurs below 270 °C, the

second loss between 270 °C and 370 °C and the third, showing a continuous and homogeneous weight loss, between 370 °C and 1 000 °C for the powders calcined in argon and nitrogen atmospheres and between 650 °C and 1 000 °C for the powder calcined in oxygen. This is expected in theory, because the gas flow can transfer some of the mass to the atmosphere, as reported by German /15/.

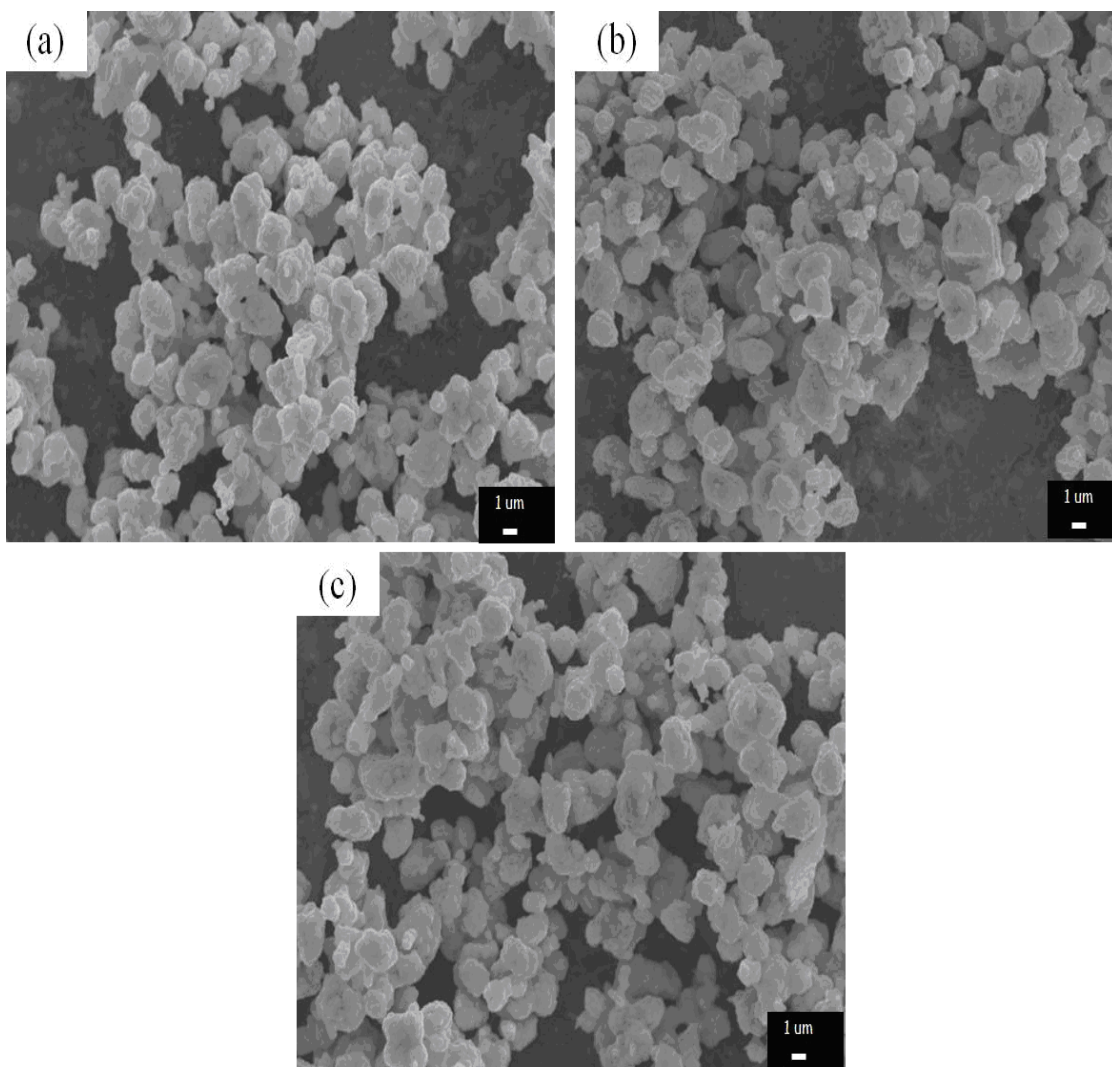


Fig. 2 SEM micrographs of PLMN-13PT calcined powders at 900 °C, for 4h, at (a) oxygen (b) nitrogen and (c) argon atmosphere.



It can be seen in the curves of the figure 3 that after 370 °C, the powder calcined in nitrogen suffers the greatest weight loss; this is understandable, because this atmosphere

reducing facilitates the removal of oxides such as PbO. The used of the oxygen atmosphere prevents the loss of PbO, resulting in a smaller weight loss.

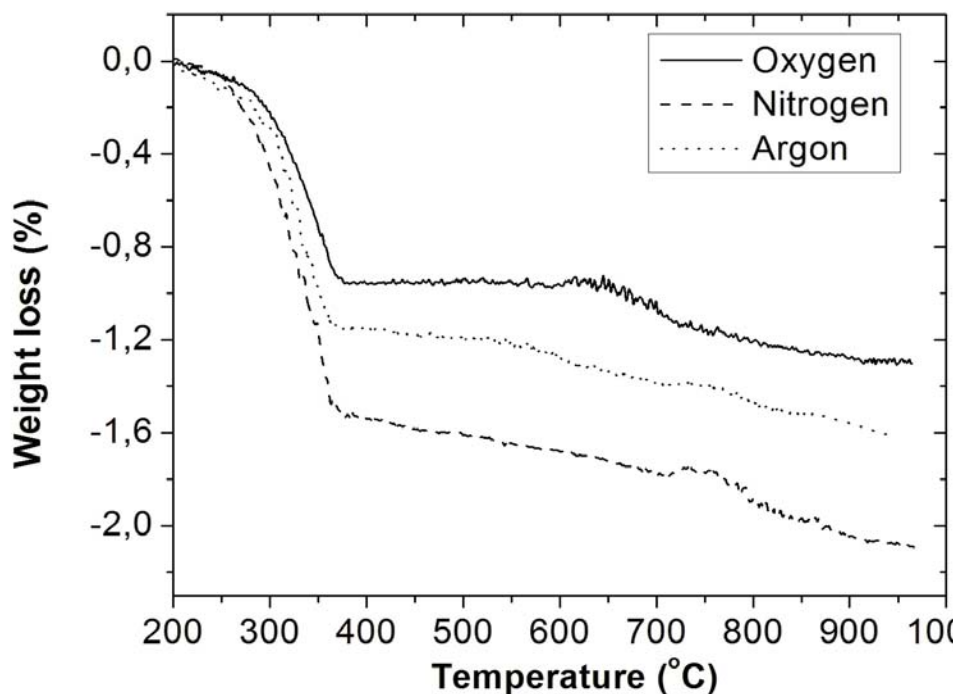


Fig. 3 TGA curves of PLMN-13PT calcined powders in oxygen, nitrogen and argon atmosphere.

In the DTA curves in figure 4, an endothermic peak ( $T_1$ ) can be seen in the range 300 °C –380 °C and other endothermic peak ( $T_2$ ) in the range 700 °C–750 °C. The peak at  $T_1$  is believed to relate to the elimination of organic residues from the solvent and water /16, 17/.

The second peak, between 700 °C and 750 °C, may be caused by formation of the perovskite phase, due to the reaction between PbO and  $MgNb_2O_6$ , when the columbite method is used. This peak can also be attributed to PbO volatilization, as suggested by Ianculescu, Kim *et al.* /18, 19/. In the curve that corresponds to the powder calcined in nitrogen, two more peaks can be seen. The first peak, near 400 °C, can be attributed to the formation of a cubic  $Pb_3Nb_4O_{13}$  phase, as reported by Mergen *et al.* /20/.

The same peak was also observed by Bouquin and Lejeune /21/, for the pyrochlore  $Pb_3Nb_4O_{13}$  between 500 °C and 600 °C, during formation of PMN perovskite. The other peak, near 900 °C,  $T_3$  can be attributed to the formation of pyrochlore phase, probably due to PbO vaporization from PMN, as it was reported by Kim *et al.* /19/, when studying the effect of the atmosphere on the chemical stability of PMN pellet in air, that PbO vaporization caused PMN to decompose into a pyrochlore. Peak  $T_3$  can also be observed in the curve for the powder calcined in an argon atmosphere, but that peak is weaker.

The XRD patterns from PLMN-13PT powder calcined in the three atmospheres are presented in figure 5. The main peaks show a predominant cubic perovskite structure (JCPDS 391488), then a pyrochlore phase (JCPDS 330769) and other secondary phases, such as PbO (massicot) and  $MgNb_2O_6$  (orthorhombic structure).

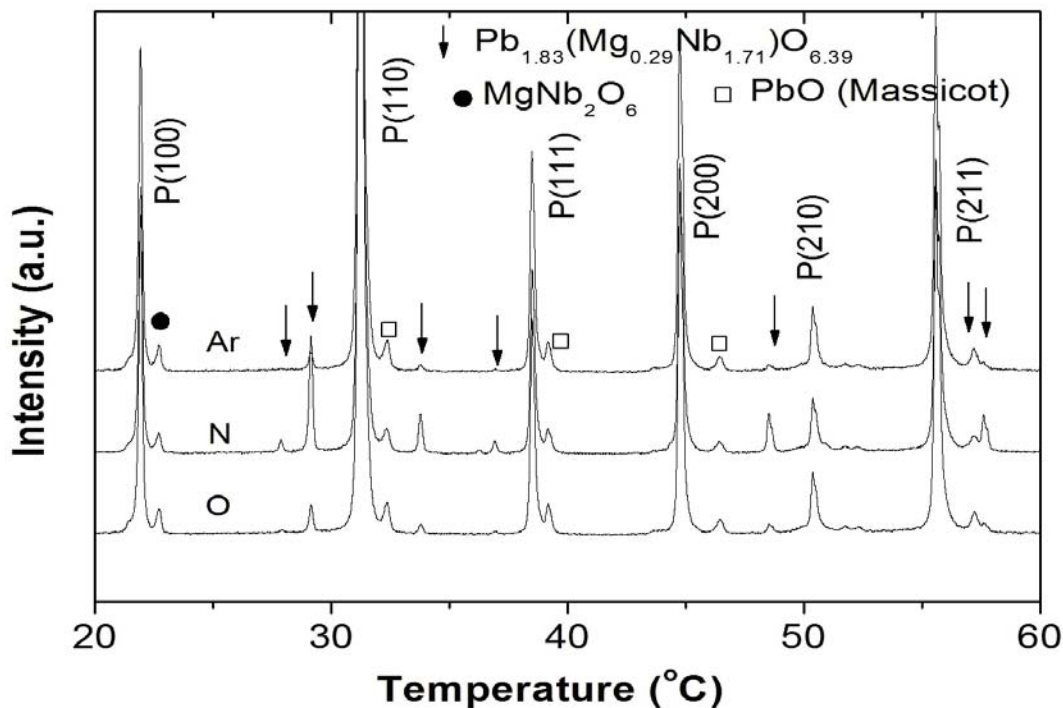


Fig. 4 DTA curves of PLMN-13PT calcined powders in oxygen, nitrogen and argon atmosphere.

In particular, the peaks corresponding to  $Nb_2O_5$  (bcc structure) and  $MgO$  (hcp structure) are not observed, revealing that  $Nb_2O_5$  has completely reacted with  $MgO$ . The pyrochlore phase is present in all cases; however, the intensities of pyrochlore lines are much higher in the powder calcined in a nitrogen atmosphere.

This possibly indicates that inert and oxidizing atmospheres facilitated the stabilization of the perovskite phase, as they suppressed the loss of lead oxide in appreciable amounts, to form the pyrochlore phase, as suggested in the analysis of the DTA and

TG. These results confirm that the atmosphere can be considered to take part in the calcining process /15/.

Table 1 shows the fraction of pyrochlore and other secondary phases formed in the PLMN-13PT powders when calcined in each atmosphere. These data were calculated with the following equation:

$$\% phase = \frac{I_{phase}}{(I_{phase} + I_{perov})} \times 100\%$$

where  $I_{phase}$  and  $I_{perov}$  are the intensities of the most intense peaks for the phase to be calculated and the perovskite phase, respectively.

TABLE 1. SECONDARY PHASE CONTENTS FOR PLMN-13PT POWDERS CALCINED IN DIFFERENT ATMOSPHERES

Atmosphere	Pyrochlore phase (%)	Other phases (%)
Oxygen	3	3
Nitrogen	10	1
Argon	2	3

In table 1, it can be seen that the powder calcined in nitrogen contained the greatest amount of pyrochlore and a smaller amount of other secondary phases. This agrees with the DTA measurement, in which there was more evidence of the formation of the pyrochlore phase in powder calcined in nitrogen, possibly because a nitrogen atmosphere allows the pyrochlore phase to be formed by decomposition of the PLMN-PT perovskite phase, as a consequence of PbO volatilization during sintering. For the powders calcined in oxygen and argon atmospheres, it can be seen that no significant difference exists between the generation of secondary phases in the two cases.



## Conclusion

*X-ray diffraction patterns of PLMN-13PT powders, synthesized by the two-stage calcining (columbite) method, indicated the cubic perovskite phase for powders calcined in oxygen, argon and nitrogen atmospheres, although a percentage of the pyrochlore phase and other secondary phases were also detected.*

*The result showed that oxidizing and inert atmospheres favored the formation of the perovskite phase, which reached 98 % when the samples were calcined in O<sub>2</sub> or Ar at 900 °C for 4h. The oxidizing atmosphere inhibits the release of oxygen needed in the perovskite phase. However, the nitrogen was detrimental to the formation of the perovskite structure, since it allowed the release of oxygen and affected the formation of the perovskite structure.*

*Argon and oxygen atmospheres are thus adequate in the calcining process of PLMN-13PT powders. However, oxygen atmosphere is associated with a smaller weight loss.*

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