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Wet-chemical synthesis of magnesium niobate nanoparticles powders

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Abstract

Nanosized and highly reactive magnesium niobate ($MgNb_2O_6$) powders were successfully synthesized by a new wet-chemical method by means of the dissolution of $Nb_2O_5 \cdot 5H_2O$ and in a solution of oxalic acid followed by the addition of stoichiometric amounts of magnesium carbonate. The Nb–Mg–oxalic acid solution was evaporated resulting in a dry and amorphous powder that was calcined in the temperature range from 200 to 900 °C for 2 h. The crystallization process from the amorphous state to the crystalline $MgNb_2O_6$ was followed by thermal analysis. The calcined powders characterized by FT-Raman spectroscopy, X-ray diffraction (XRD) and their morphology examined by high resolution scanning electron microscopy (HR-SEM). Pure $MgNb_2O_6$, free from the second phases and obtained at 800 °C was confirmed by a combined analysis using XRD and FT-Raman. The average diameter of the particles was calculated from the HR-SEM image as 70 nm approximately. This technique allows a better mixing of the constituent elements and thus a better reactivity of the mixture to obtain pre-reaction products with high purity at lower temperatures and reducing cost. It can offer a great advantage in the PMN-PT formation with respect to the solid-state synthesis.

Keywords: $MgNb_2O_6$; Columbite; Magnesium niobate; Low temperature synthesis; FT-Raman

1. Introduction

In spite of the fact that magnesium niobate ($MgNb_2O_6$) was identified as a potential candidate to be used as microwave dielectric materials [1], it has been widely used as precursor for the synthesis of single-phase relaxor perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) since the success of the route proposed by Swartz and Shrout, known as the columbite method [2]. However, high temperature is often required to form single-phase $MgNb_2O_6$ by the traditional solid-state route. Moreover, if an impure magnesium niobate is used as precursor to prepare PMN, that is a $MgNb_2O_6$ with minor amounts of Nb_2O_5, undesired pyrochlore phase that is deleterious for the relaxor use is always formed by the reaction between lead and the niobium oxide. Therefore, pure $MgNb_2O_6$ is required to obtain pyrochlore-free PMN [3,4]. Several researchers have investigated new alternatives to synthesize reactive and single-phase $MgNb_2O_6$ powders by improved wet-chemical methods [5–8], however different phases are possible in the Mg–Nb–O system [9] and the formation of $MgNb_2O_6$ is not straightforward. Generally, minor amounts of the corundum $Mg_4Nb_2O_9$ phase are formed together to the columbite $MgNb_2O_6$ phase [10–13].

In this work, we are reporting our best results on the synthesis of a highly reactive and single-phase and nanosized columbite $MgNb_2O_6$ powder by means of a new and simple wet-chemical method. Crystalline $Nb_2O_5 \cdot 5H_2O$ was dissoluted in an aqueous solution of oxalic acid followed by the addition of magnesium carbonate, resulting in a stable solution of Nb–Mg ions at the desired mole ratio, which after the total elimination of the aqueous solvent, resulted in an amorphous powder that could be heat treated to obtain the nanometric $MgNb_2O_6$.

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2. Experimental procedure

2.1. Synthesis

Niobium oxide penta-hydrated (99.9%, CBMM, Brazil) was added to an aqueous solution of oxalic acid (OAc, 99.5%, Merck, Brazil) with concentration of 0.79 mol L^{-1}. The amount of niobium was calculated to result in an acid solution with final mole ratio of Nb:OAc = 1:4. This solution was stirred using a magnetic barr for 3 h at boiling point until all of niobium oxide was dissolved. Then, magnesium carbonate (99.9%, Aldrich, USA) was added to the acid solution of Nb–oxalic acid to obtain a final solution with mole composition of Mg:Nb = 1:2. The aqueous solvent was slowly eliminated at 80 °C resulting in a white and dry powder (thereafter referred to as precursor) that was ground with an agate pestle. Small amounts of 0.2 g of this powder were calcined between 200 and 900 °C for 2 h with heating rate of 10 °C min^{-1}, using sintered alumina boats in tube type electrical furnace for the crystallization of the nanosized columbite ($MgNb_2O_6$) powders.

2.2. Characterization

The thermal behavior of the precursor powder was observed by means of dynamic thermogravimetry (TG) and differential thermal analysis (DTA) (Netzsch-STA 409, Germany) in the temperature range from 20 to 1100 °C, with heating rate of 10 °C min^{-1} using a platinum crucible. All of the powders were characterized at room temperature by X-ray diffraction (Rigaku-DMax 2500PC, Japan) using the Cu K α radiation in the 2 θ range from 5° to 75° with 0.2° min^{-1} of scanning velocity. All the diffraction patterns were analyzed by the Rietveld method [14], using FULLPROF program [15]. For the refinements data the following parameters were refined: background coefficients, zero point, half-width, pseudo-Voigt and asymmetry parameters for the peak shape, scale factor, atomic positions, thermal anisotropic factors and unit cell parameters. Raman (Bruker-RFS 100, Germany) and Infrared (FT-IR) absorption (Bruker-Equinox 55, Germany) spectra of the powders were collected at room temperature. A 1064 nm Nd:YAG laser was used to obtain the Raman spectra as excitation source with its power kept at 90 mW. The FT-IR spectra were collected using KBr pallets. Particle size was estimated from the images obtained by high resolution scanning electron microscope (HR-SEM) (Zeiss-Supra 35, Germany).

3. Results and discussion

The use of wet-chemical methods to prepare high pure and reactive columbite precursors has been proposed to avoid undesirable reaction between lead oxide and niobium oxide. This reaction often results in the presence of a pyrochlore type phase [8] which is deleterious on the dielectric behavior of relaxor materials such as the PMN or PMN-PT (that is a solid-solution of $Pb(Mg_{1/3}Nb_{2/3})O_3$ and $PbTiO_3$). Niobium oxide, on the other hand, is a stable and less reactive compound, usually used as niobium source for the synthesis of niobates by solid-state reaction at high temperature. Recently, we demonstrated [16] that it is possible to dissolve $Nb_2O_5 \cdot 5H_2O$ in hot aqueous solution of oxalic acid to obtain a stable solution of Nb–oxalic acid (Nb–OAc) complexes and that this solution can be successfully applied by means of wet-chemical techniques to prepare several niobate oxide powders with nanometric scale. This method shows the advantage to use a simple experimental procedure and chemicals that are cheap, non-toxic and easily handled at ambient conditions of humidity and pressure. Also, the use of $Nb_2O_5 \cdot 5H_2O$ instead of other niobium sources such as chlorides or alkoxides, results in a stable Nb–OAc aqueous solution free from some undesirable ions that are sometimes present when different wet-chemical methods are used. But as a major advantage in our point of view of this route, the Nb–OAc solution allows a precise control on the amount of niobium, since we observed that Nb–OAc aqueous solution could be used as stock solution for long time without loss of stoichiometry or reactivity. Moreover, because of the acid nature of the Nb–OAc, carbonates of several cations (for instance, magnesium, sodium, lithium or rare earth even) that are all insoluble in neutral aqueous solution are allowed to be used, since the carbonate reacts immediately in the acid media to form carbonic gas and water, resulting in a virtually clean solution. Therefore, what we are describing here is a quite flexible method to prepare niobium-composed oxide compound through a simple and efficient route as demonstrated by the synthesis of $MgNb_2O_6$.

Considering that the critical step on the synthesis of the double oxide $MgNb_2O_6$ by every wet-chemical technique is the thermal decomposition of the amorphous precursor, thermogravimetric and differential thermal analysis (TG-DTA) were conducted to understand the thermal behavior of this precursor and the results are illustrated in the Fig. 1. There are two endothermic peaks on the DTA curve at 118 and 256 °C, that may be related to loss of the hydration water and to the decomposition of oxalate group, respectively. These two events are accompanied by a intense weight loss (49.92%) in the TG curve. The small exothermic peaks observed between 390 and 490 °C correspond, probably, to the combustion of the

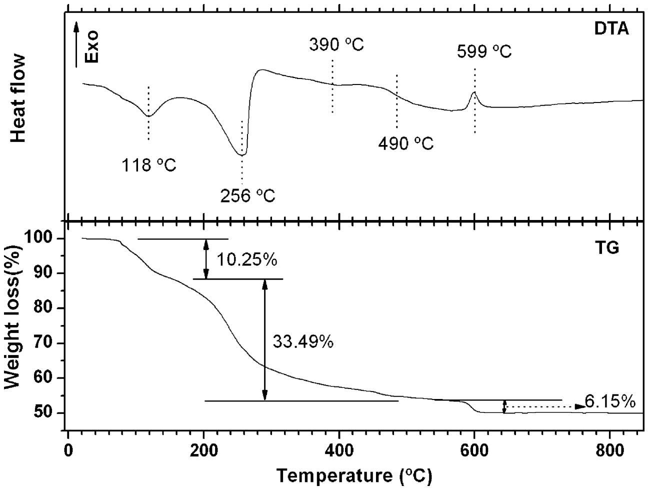

Fig. 1. Thermogravimetric (TG) curve and diferential thermal analysis (DTA) curve of the precipited powder. Heating of 10 °C min^{-1}.

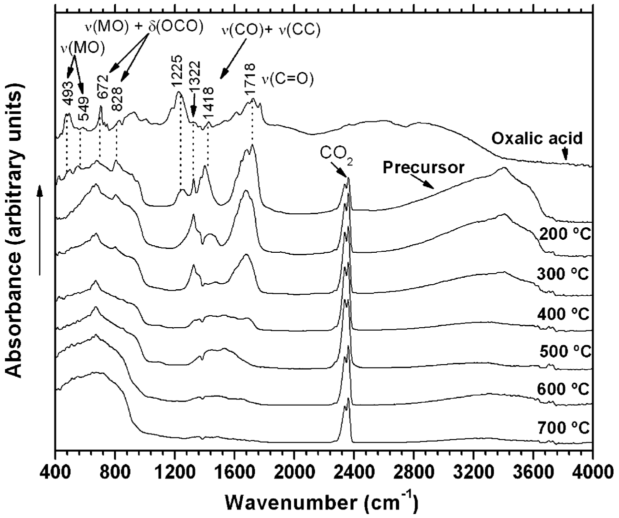

Fig. 2. FT-IR spectra of the precursor amorphous and precursor calcined at different temperatures for 2 h.

remaining oxalate intermediate, whereas the peak centered at 599 °C can be associated to the crystallization of $MgNb_2O_6$. No significant weight loss was observed for temperatures higher than 600 °C in the TG curve, indicating that all oxalate material was decomposed.

Infrared absorption (FT-IR) spectra recorded are shown in Fig. 2. For sake of clarity, the spectrum of pure oxalic acid is also shown in this figure. The large band at approximately 3400 cm^{-1} can be attributed to the water ν(OH) stretching, whereas the band at 2350 cm^{-1} is usually assigned to CO_2 gas adsorbed. The symmetric and asymmetric stretching modes observed at 1225–1718 cm^{-1} are assigned to oxalate modes. Two low intensity bands at 672–828 cm^{-1} are also observed in the spectra and can be attributed to the coordination between metal ions, in this case Nb or Mg with the carboxylate sites of the oxalate ion. Another important information is the wide band

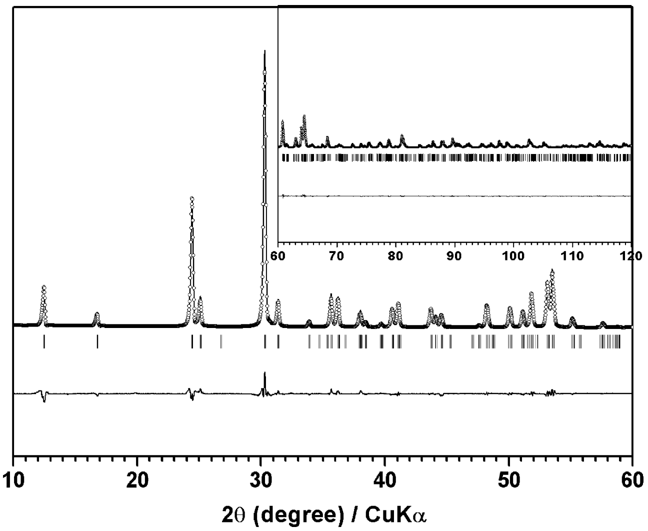

Fig. 4. Observed (continuos line), calculated (open circle), and difference (bottom line) profiles obtained after Rietveld refinement for $MgNb_2O_6$ at 900 °C for 2 h using orthorhombic space group *Pbcn* in the 2 θ range of 10–60°. Inset shows the patterns in the 2 θ range of 60–120°. The series of tick marks indicate the allowed Bragg positions.

Table 1
Refined structural parameters of $MgNb_2O_6$ using orthorhombic space group *Pbcn*

Ions	Positional coordinates			Thermal parameter, *B* (Å^2)
	X	*Y*	*Z*	
Mg^{2+}	0.0000	0.1671(85)	0.25(0)	0.408(0)
Nb^{5+}	0.16(6)	0.318(14)	0.7547(40)	0.408(0)
O^{2-}	0.091(39)	0.394(111)	0.439(139)	0.408(0)
O^{2-}	0.0749(39)	0.1124(108)	0.904(132)	0.408(0)
O^{2-}	0.254(56)	0.1219(95)	0.5833(127)	0.408(0)

$a = 14.1871(2)$ (Å); $b = 5.6996(1)$ (Å); $c = 5.0334(3)$ (Å); $R_{wp} = 13.8$; $R_{exp} = 7.84$; $R_{Bragg} = 4.23$; $\chi^2 = 3.10$.

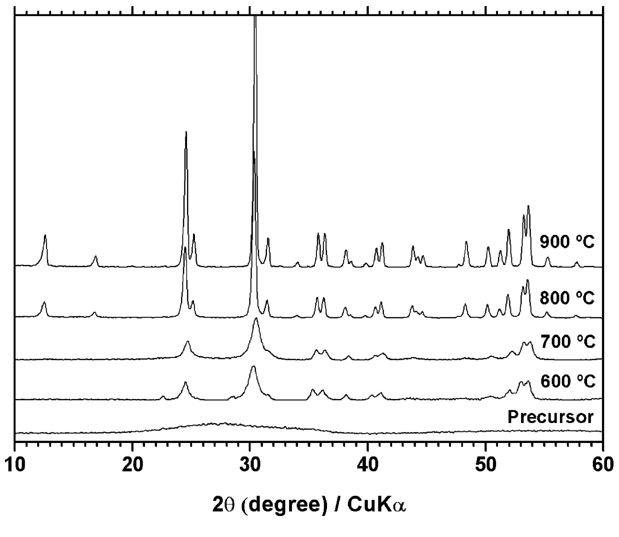

Fig. 3. X-ray diffraction pattern of the precursor powder calcined at different temperatures for 2 h with heating and cooling rates of 10 °C min^{-1}, showing only $MgNb_2O_6$ columbite phase.

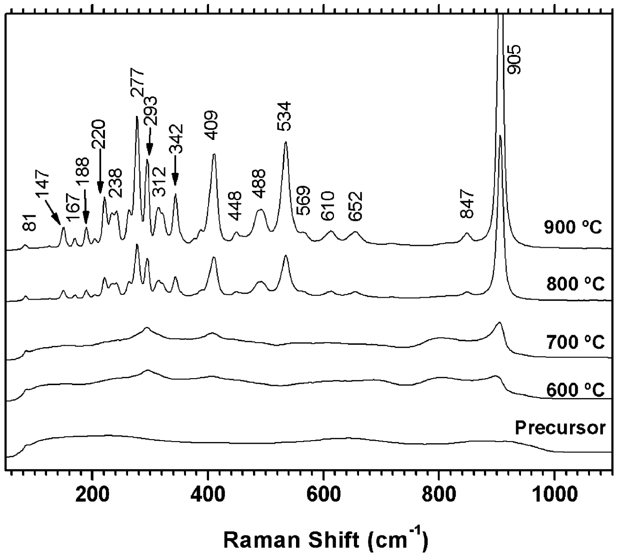

Fig. 5. Raman spectra of the precursor amorphous, precursor calcined at 600, 700, 800 and 900 °C for 2 h.

in the range from 493 to 549 cm^{-1} caused by the interaction of the metal–oxygen vibration, and they become more evident as the calcination temperature is increased [5,17].

Fig. 3 shows the X-ray diffraction patterns collected at room temperature of the precursor amorphous and the patterns of MN powders calcined for 2 h at 600, 700, 800 and 900 °C. Despite the fact that Horowitz [18] reported the formation of the columbite structure at temperatures higher than 800 °C, through the mixture of acetates and oxalates in solution and that Hong et al. [5] suggested the optimum firing temperature for preparation of MN around 850 °C, it is possible to observe in Fig. 3, that the MN phase is formed at temperatures as low as 600 °C, in spite of the low crystallinity of the samples, as indicated by the broad peaks of diffraction. In fact, the samples calcined at 800 °C or higher temperatures show quite well defined diffraction peaks which were all indexed as $MgNb_2O_6$ (JCPDS card 33-0875) phase with orthorhombic structure. This is confirmed by the Rietveld analysis also.

Fig. 4 depicts the observed, calculated and difference profiles in the 2 θ ranges 10–120° for MN powder calcined at 900 °C using orthorhombic space group *Pbcn*. The fit between the observed and calculated profiles is quite satisfactory confirming the orthorhombic structure of MN. The refined structural parameters and various agreement factors are given in Table 1. Differently from the previous reports about the wet-chemical synthesis of MN [5], where the presence of niobium oxide, $Mg_4Nb_2O_9$ and an unknown phase was observed in the samples calcined at 750 °C, after the thermal decomposition of the (Mg, Nb)–citrate-gel, unknown or secondary phases were not observed neither the XRD patterns nor Rietveld refinement, even when the powders were calcined at 700 °C.

It is well known that Raman spectroscopy is a suitable structural analytical technique used to the identification of traces of impurities (secondary phases) at a wide range of ceramic materials when XRD has not enough resolution. Spectroscopic techniques are sensitive to the short-range order

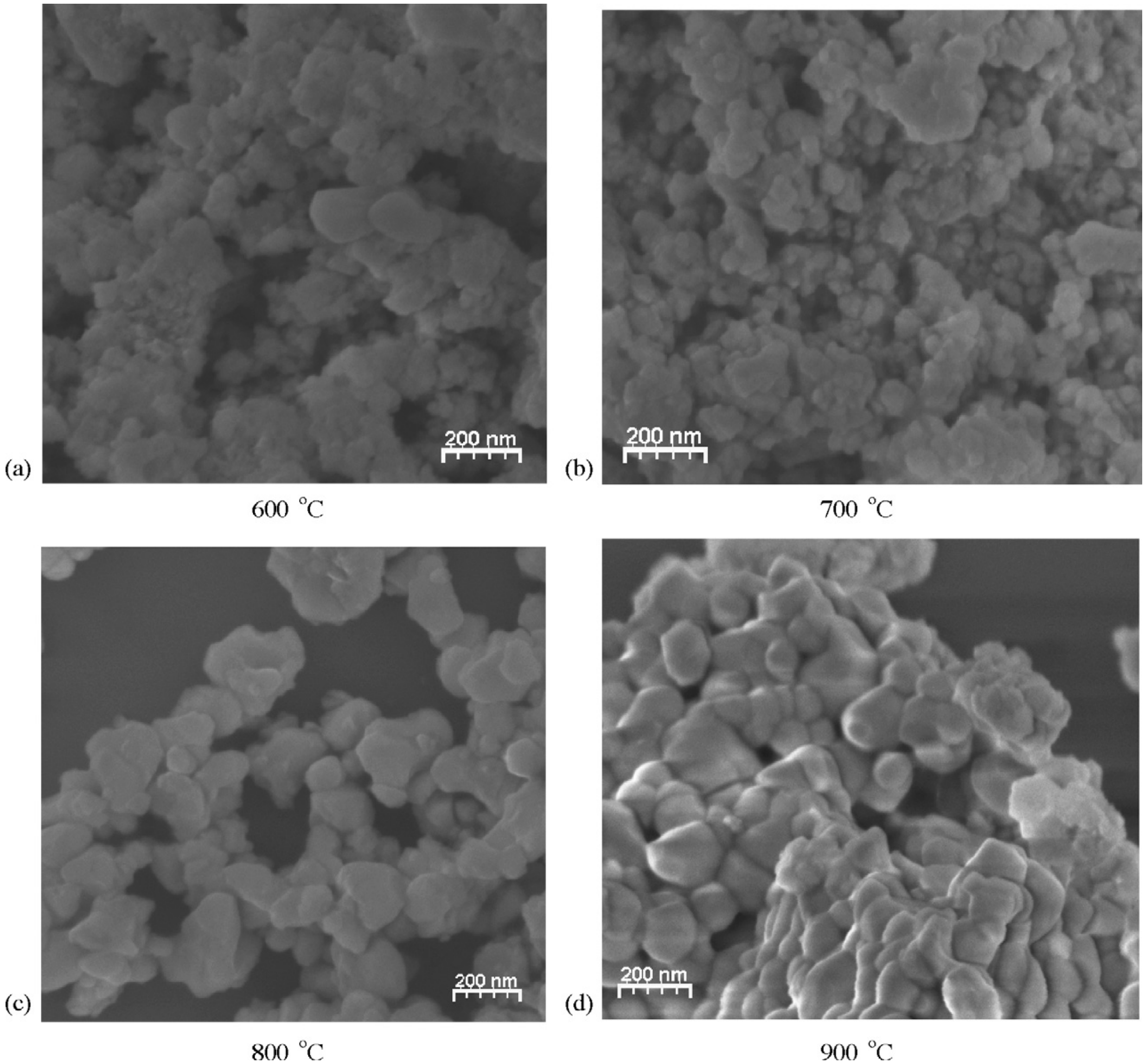

Fig. 6. HR-SEM micrographs of $MgNb_2O_6$ calcined at various temperatures: (a) 600 °C, (b) 700 °C, (c) 800 °C and (d) 900 °C.

showing a higher limit of detection, therefore much more appropriate to check traces of free niobium oxide in columbite powders. Fig. 5 shows Raman spectra collected at room temperature of the precursor amorphous and the powders calcined at different temperatures. In the Raman spectrum of the MN powder calcined at 800 °C for 2 h, no crystalline Nb_2O_5 phase was observed and all peaks in the frequency range were identified as columbite phase [19]. Neither niobium oxide nor magnesium carbonate can be seen in the Raman spectra of the calcined powders (Fig. 5), revealing that Nb_2O_5 has completely reacted with $MgCO_3$. This could be attributed to high reactivity of magnesium and niobium species. These results show also that the disorder structure in the $MgNb_2O_6$ was decreased when increased calcination temperature. This was a consequence of the enhancement in crystallinity of the columbite phase.

HR-SEM micrographs of the $MgNb_2O_6$ powders calcined at different temperatures for 2 h are depicted in Fig. 6. As observed in these images, the particle morphology of the powders is substantially altered with the temperature of calcination. For instance, the powders calcined at 600 and 700 °C have particles that are essentially uniform in size and shape, although forming agglomerates with diameter of approximately 80 nm. On the other hand, it seems that the particles of the samples heat treated at 800 and 900 °C were formed from the coalescence of these agglomerates, resulting in single particles with diameter in the range from 60 to 70 nm approximately, which can be easily observed in the images C and D, respectively. From the structural point of view, it is very interesting to record how the XRD patterns and Raman spectra were modified when the calcination temperature was raised from 700 to 800 °C. When these modifications on the XRD profiles and Raman spectra are cross-linked with the change in the morphology of the particles, as observed in the images of the Fig. 6, it is possible to suggest that the particle size has a strong influence on the structural characteristics of the MN powders.

4. Conclusions

The oxalate route can be efficiently used to prepare single-phase $MgNb_2O_6$ (MN) columnite phase using neither organics nor undesirable halides from an aqueous solution, which is a major advantage over the other methods reported before. A considerable decrease in the calcination temperature (at 800 °C) has been obtained in this study for a formation of these nanopowders without the existence of second phases, as observed in the Raman spectra. The columbite phase is probably formed through a single-step decomposition of an oxalate intermediate, formed during the material calcination. Because of its high reactivity, calcination at temperatures higher than 800 °C results in agglomerated MN powders. This low temperature could be a result of the nanometric size of the MN precursor. Therefore, $MgNb_2O_6$ ultra fine powders prepared by oxalate route may be used as a precursor in the synthesis of PMN free from the pyrochlore phases.

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