Combined wet-chemical process to synthesize 65PMN-35PT nanosized powders

Luis P.S. Santos, Elson Longo, Edson R. Leite*, Emerson R. Camargo

LIEC, Departamento de Química, Universidade Federal de São Carlos (UFSCar), Rod. Washington Luiz km 235, São Carlos SP, CP 676, 13565-905, Brazil

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Abstract

Columbite MgNb\textsubscript{2}O\textsubscript{6} precursors were synthesized by a wet-chemical method by means of the dissolution of Nb\textsubscript{2}O\textsubscript{5}·5H\textsubscript{2}O and magnesium carbonate in a solution of oxalic acid. Pure 65PMN-35PT powders could be obtained by the columbite method with the use of the partial oxalate and oxidant peroxo methods. Powders were characterized by X-ray diffraction and FT–Raman spectroscopy showing that pure 65PMN-35PT are obtained when the powders are calcined up to 800 °C, without any trace of Pb–Nb pyrochlore. Cubic Pb\textsubscript{1.86}Mg\textsubscript{0.24}Nb\textsubscript{1.76}O\textsubscript{6.5} pyrochlore phase is formed by lead loss in the powders calcined at 900 °C and higher temperatures as undoubtedly characterized by Raman spectroscopy.

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1. Introduction

Relaxor-based ferroelectric lead magnesium niobate Pb(Mg\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3} (PMN) when prepared in solid solution with lead titanate PbTiO\textsubscript{3} (PT) has been extensively studied because of its much higher electromechanical response than conventional ceramics [1,2]. However, single-phase perovskite cannot be obtained by the conventional solid state reaction method because of the presence of the pyrochlore phase, which result from the reaction between Nb\textsubscript{2}O\textsubscript{5} and PbO. Swartz and Shrout [3] first succeeded in eliminating the pyrochlore phase by developing the columbite method. Several alternative synthetic routes have been developed for the synthesis of the PMN-PT system, most of them resulting in powders with nanometric size that can show some unique properties [4]. By this way, Gu et al. [2] proposed a columbite inspired route where Nb\textsubscript{2}O\textsubscript{5} particles are firstly coated with magnesium hydroxide followed by the addition of PbO prior to the calcination process. They claimed that the magnesium hydroxide separates physically the niobium from the lead, preventing the formation of the pyrochlore phase. However, it should be mentioned that a magnesium content pyrochlore phase deficient of lead often is obtained at higher temperatures even if pure perovskite phase is synthesized because of the evaporation of the lead.

One of us, developed recently a new synthetic route called “the oxidant peroxo method (OPM)” [5], used to prepare several lead perovskites (e.g. PbTiO\textsubscript{3} and some compositions of PZT) at relatively low temperature with a sharp particle size distribution of nanoparticles. In this study, we synthesized single-phase perovskite 65PMN-35PT by the combined use the OPM method to prepare the PT fraction, the columbite method by means of wet-chemically synthesized nanoparticles of MgNb\textsubscript{2}O\textsubscript{6} and the partial oxalate method. Although the complexity of this combined chemical procedure, we demonstrated that pure PMN-PT nanoparticles can be obtained at low temperatures.

2. Experimental procedure

2.1. Chemicals

Niobium oxide penta-hydrated (Nb\textsubscript{2}O\textsubscript{5}·5H\textsubscript{2}O) 99.9%, CBMM, Brazil; magnesium carbonate (4MgCO\textsubscript{3}·Mg(OH)\textsubscript{2}...
Precipitate were calcined between 700 and 950 °C. Material was filtered, dried, and ground. Amounts of 0.2 g of the particles of the amorphous PT and crystalline MN. This dispersion, resulting in a white precipitate of lead oxalate on was prepared and slowly dropped into the PT–MN–OA dispersion in hot oxalic acid solution resulting in a transparent and colorless solution of Nb–Oxalate complexes. An aqueous solution of peroxo-Ti complexes. An aqueous solution to an aqueous solution of 80 ml of hydrogen peroxide (30%) and 20 ml of ammonia (28%). This solution was kept for 12 h in an ice bath to control temperature until all of the aqueous solvent was slowly eliminated at 80 °C resulting in a white powder that was ground. Small amounts of 0.2 g of the powder were calcined between 700 and 950 °C using sintered alumina boats in a tube type electrical furnace.

2.2. Wet-chemical synthesis of MgNb2O6

Nanosized columbite (MgNb2O6, thereafter referred to as MN) powders were synthesized by the addition of niobium oxide hydrated to an aqueous (0.79 mol l−1) solution of oxalic acid (OA) at mole ratio of Nb:OA = 1:4. The solution was stirred for 3 h at boiling point until all of niobium oxide was dissolved, then the solution was cooled and filtered. The precise niobium content was determined by gravimetric analysis. Magnesium carbonate was added to the solution of Nb-oxalic acid with an excess of 3% in mole to obtain a final composition of Mg:Nb = 1:0.3. The aqueous solvent was slowly eliminated at 80 °C resulting in a white powder that was ground. Small amounts of 0.2 g of the powder were calcined between 700 and 950 °C using sintered alumina boats in a tube type electrical furnace.

2.3. Synthesis of PbTiO3 amorphous precursor by the OPM method

The amorphous PbTiO3 precursor (referred to as amorphous PT) were synthesized as described in detail elsewhere [5]. A precise amount of titanium metal powder was added to an aqueous solution of 80 ml of hydrogen peroxide (30%) and 20 ml of ammonia (28%). This solution was kept for 12 h in an ice bath to control temperature until all of the titanium was dissolved, resulting in a yellow and transparent solution of peroxo-Ti complexes. An aqueous solution of lead nitrate was dropped into the peroxo-Ti solution, precipitating a orange amorphous powder with precise mole ratio of Pb:Ti = 1:1. This powder was collected by filtration, dried for 5 h at 50 °C and ground.

2.4. Synthesis of 65PMN-35PT by the partial oxalate method

To obtain the 65PMN-35PT an aqueous solution of oxalic acid (0.18 mol l−1) was prepared, and the MN columbite and the amorphous PT powders previously prepared were added to the this OA solution. This PT–MN–OA dispersion was stirred by ultrasound for 30 min. A solution of Pb(NO3)2 was prepared and slowly dropped into the PT–MN–OA dispersion, resulting in a white precipitate of lead oxalate on the particles of the amorphous PT and crystalline MN. This material was filtered, dried and ground. Amounts of 0.2 g of this precipitate was calcined between 700 and 950 °C using sintered alumina boats sealed with alumina in a tube type electrical furnace.

2.5. Characterization

All of the powders were characterized by X-ray diffraction using the Cu Kα radiation (Siemens D 5000, Germany) at room temperature, from 15 to 75° in the 2θ range with scan velocity of 0.2°·min−1. Raman spectra were collected at room temperature using a Bruker Reflex 100 Raman spectrometer with Fourier transform. A 1064 nm YAG laser was used as excitation source with its power kept at 90 mW. Raman spectra were decorrelated in the range from 660 to 900 cm−1 after the background removal. It was assumed that the band shapes could be described with symmetrical Gaussian functions. Particle size were estimated from the images obtained by a scanning electron microscope (SEM) Zeiss DSM 940A (Germany).

3. Results and discussion

Pyrochlore phase results from the reaction between lead oxide and niobium oxide [6]. The columbite method bypasses this undesirable situation reacting previously all of the niobium with magnesium, resulting in the MgNb2O6 (MN) columbite phase. Therefore, the best strategy to obtain a single-phase perovskite by means of the columbite method is preparing a high pure MN precursor, e.g. a columbite precursor without any trace of “free” niobium oxide. However, it is necessary high temperatures, often for several hours of heat treatment, to obtain pure MN by the traditional solid-state reaction, which results in big particles partially sintered. This condition does not favor the sequential reaction with lead to form PMN (or PMN-PT even). The use of wet-chemical methods to prepare high pure and reactive columbite precursors have been proposed to overcome this problem [7], however these wet-chemical methods are usually time consuming, relatively expensive and show low final yields.

It is well known that Nb2O5·5H2O can be easily dissolved in hot oxalic acid solution [8,9] resulting in a transparent and colorless solution of Nb-Oxalate complexes, which can be successfully used to prepare several niobate oxide powders with nanometric scale [9,10]. This method shows the advantage to use a simple experimental procedure and cheap and easily handled chemicals at ambient conditions of humidity and pressure. Fig. 1a shows the XRD pattern of the MN powders calcined at 800 °C for 2 h obtained by this "oxalic route". All of the diffracted peaks were indexed following the JCPDS card 33-0875 of the MN phase. However, because of X-ray diffraction is sensitive to the long-range order, it shows a low detection limit for secondary phases. Spectroscopic techniques, on the other hand, are sensitive to the short-range order showing a higher limit of detection, therefore much more appropriate to check traces of free niobium oxide in columbite powders. Fig. 1b shows the Raman spectra of the same MN powder calcined at 800 °C comparing the spectrum of Fig. 1b with that previously reported by Husson et al. [11] and by Camargo et al. [7], one can...
observe that all of the Raman peaks could be assigned as columbite phase.

Fig. 2 shows the XRD patterns of the final 65PMN-35PT powders calcined between 700 and 950 °C for 2 h. Powders calcined at 700 and 800 °C show only the perovskite phase without any evidence of the pyrochlore presence, which were observed in the XRD patterns of the powders calcined at 900 and 950 °C (as indicated by full circles on the peaks at 2θ = 29.4°, 33.8° and 37.1°). The presence of pyrochlore phase only in the powders calcined at higher temperatures suggests that this secondary phase was formed by lead loss during the heat treatment and not by the reaction between lead and niobium. All of the powders were characterized by scanning electron microscopy (SEM), and the representative images of the columbite powder (Fig. 3a) and of the 65PMN-35PT powder calcined at 950 °C/2 h (Fig. 3b) are shown. It is possible to observe the nanometric scale of powders, with particles around of 100 nm.

The calcined powders were also characterized by Raman spectroscopy, and their spectra are shown in Fig. 4. Despite the fact that all of the spectra were collected at room temperature, their peaks are well resolved. Usually, Raman spectra of PMN or PMN-PT show broad peaks with low resolution because of the structural disorder typical of the relaxor materials. Special attention was paid for the range from 700 to 900 cm⁻¹ of the Raman spectrum that can be assigned to Nb-O-Mg stretching mode. The analysis of this region can indicate the presence of pure PMN phase or the presence of magnesium rich pyrochlore [12]. Spectra of the powders calcined at 700 and 800 °C shows only one peak, centered at approx. 785 cm⁻¹, typical of the perovskite phase [13]. On the other hand, it is evident the presence of more than one peak in the spectra of the powders calcined at 900 and 950 °C, what can be interpreted as the presence of the cubic Pb₉₆Mg₃₂Nb₇₆O₆₅ pyrochlore phase.

Since disordered materials are better approximated by Gaussian shape functions [14], Raman spectra were deconvoluted with this function in the range from 660 to 900 cm⁻¹.
Fig. 4. Raman spectra of the 65PMN-35PT perovskite powders calcined at 700, 800, 900 and 950 °C for 2 h.

For the spectrum of the powder calcined at 700 °C (Fig. 5a), two bands were obtained with wavenumbers at 728 and 788 cm⁻¹. Several authors assigned the band at 788 cm⁻¹ as the A₁g vibration mode of the octahedral oxygens in the PMN-like structures, such as the PMN lanthanum doped, the PMN-PT and the PMN itself [14–16]. On the other hand, the second band at 728 cm⁻¹ results from the contribution of the local disorder and distortion induced in the B-site of the perovskites [14,17].

The spectrum of the powder calcined at 950 °C (Fig. 5b) shows a more complex structure, with bands at 711 and 785 cm⁻¹, which can be assigned as the A₁g modes of the PMN-PT as discussed previously, and two additional bands at 742 and 799 cm⁻¹. It is rather difficult to distinguish precisely by XRD the Pb₁ₓMgₐ₋₁ₓNb₁₋₉ₓO₆₂₋₅ pyrochlore from another pyrochlore-type structure without magnesium in their composition, however Wakiya et al. [13] assigned two bands at 745 and 815 cm⁻¹ undoubtedly to the Pb₁ₓMgₐ₋₁ₓNb₁₋₉ₓO₆₂₋₅ pyrochlore phase. The analysis of the spectrum of the powder calcined at 900 °C shows similar result, therefore, it is possible to assign these additional bands in the Fig. 3b to the presence of the Pb₁ₓMgₐ₋₁ₓNb₁₋₉ₓO₆₂₋₅ pyrochlore, in just agreement to that observed in the XRD patterns of the Fig. 3 for the powders calcined at 900 and 950 °C.

Usually, pure PMN or PMN-PT powders are obtained only at calcination temperatures higher than 800 °C for the complete elimination of the pyrochlore phase often formed from the reaction between lead and the “free” (or unreacted) niobium in the columbite precursor. In our case, it was possible to obtain pure perovskite phase at lower temperature (700 °C) because of the MN columbite used was single phase (e.g. without any “free” niobium). Moreover, lead (and titanium) ions could diffuse through the entire nanoparticles, reacting with all niobium and magnesium of the columbite to form perovskite phase. The chemical homogeneity of the final PMN-PT formed could be attested by the formation of the magnesium-content Pb₁ₓMgₐ₋₁ₓNb₁₋₉ₓO₆₂₋₅ pyrochlore when the powders were calcined at high temperatures.

4. Conclusions

The “oxalic route” can be efficiently used to prepare single-phase MgNb₂O₆ (MN) columbite phase with nanometric dimensions. Consequently, pure 65PMN-35PT was obtained by the columbite method when associated to the “oxidant-peroxo” and the “partial oxalate” methods without any trace of the (Pb, Nb) pyrochlore, as observed in the Raman spectra of the powders calcined at 700 and 800 °C for 2h. This low temperature could be a result of the nanometric size of the MN precursor, which reduce the diffusion pathway of the Pb and Ti ions through the MN particle. On the other hand, the magnesium-containing Pb₁ₓMgₐ₋₁ₓNb₁₋₉ₓO₆₂₋₅ cubic pyrochlore was identified by XRD and unequivocally confirmed spectroscopically by the presence of its specific bands in the Raman in the powders calcined at 900 °C, and higher temperatures. This Mg-content pyrochlore was formed by the lead loss during the heat process at high temperature.
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References