ELSEVIER

Ceramics International 27 (2001) 509–515

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Seeding of PMN powders made by the Pechini method

A.A. Cavalheiro [a], C.R. Foschini [a,*], M.A. Zaghete [a], C.O. Paiva-Santos [a], M. Cilense [a], J.A. Varela [a], E. Longo [b]

[a] *Instituto de Química, UNESP, PO Box 355, 14801-970, Araraquara, SP, Brazil*
[b] *Departamento de Química, UFSCar, PO Box 676, 13560-900, São Carlos, SP, Brazil*

Received 18 May 2000; received in revised form 9 September 2000; accepted 15 October 2000

Abstract

The partial oxalate method, with the columbite route, associated with the Pechini method, was used to obtain a very fine ceramic powder at low temperature. Using this route it was possible to obtain a very reactive powder and to synthesize a lead magnesium niobate (PMN) powder with up to 100% of perovskite phase at a lower temperatures than the PbO melting point. The influence of the $BaTiO_3$ and $PbTiO_3$ seeds in the phase formation, along with time and temperature during the PMN calcination, was also investigated. The amount of 2% of $BaTiO_3$ seeds promoted PMN powder formation with 100% of perovskite phase and a very narrow particle size distribution. © 2001 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

Keywords: C. Ferroelectric; D. Perovskite; Columbite; PMN; Seed particles

1. Introduction

The lead magnesium niobate (PMN) is a classical relaxor ferroelectric. The perovskite phase with $Pb(Mg_{1/3}Nb_{2/3})O_3$ composition, exhibits a broad range transition of dielectric constant, with temperature as a function of frequency, in its maximum dielectric constant [1]. As being a lead basis ceramic, the PMN shows a low sintering temperature (~1000°C) which reduces its production cost. Relaxor effect and the electrostrictive properties allied with the high dielectric constant ($K_m > 20{,}000$) are important factors to increase the volumetric efficiency of the capacitors, turning the PMN into a material of great industrial interest [2].

The amount of perovskite phase formation is a direct function of the synthesis process utilized. By conventional mixing of oxides, there is the formation of pyrochlore, which is a stable phase and degrades the dielectric properties of PMN ceramics, since it shows a lower dielectric constant ($K_m < 130$) [3,4]. Swartz and Shrout [5] established a direct relation between the pyrochlore phase formation and the chemical reactivity among the niobium, magnesium and lead oxides. The authors demonstrated that a pre-reaction between MgO and Nb_2O_5, for $MgNb_2O_6$ phase formation, named columbite, followed by the reaction with PbO enables obtaining PMN powders with amount of perovskite phase content higher than 98% [5,6]. The intermediate columbite phase should have a single crystalline phase with high surface area to increase the reactivity during the reaction with PbO and to form a higher perovskite PMN phase quantity. This method is known as columbite route [7–11].

The chemical methods have been intensely investigated for providing the stoichiometry and microstructural control, getting better final properties to the electronic ceramics [12]. In this context, Anderson coworkers proposed a new way involving polymeric synthesis [13,14]. This method enables a perfect chemical homogeneity in the mixture of cations, leading to higher reactive powders and with a higher quantity of perovskite phase at lower synthesis temperatures. The ratio between B′ and B″ in the perovskite phase $A(B',B'')O_3$ must be well controlled, since the general properties of the material strongly depend on this relation. It is possible to guarantee a high precision in this cationic relation since it involves aqueous solutions of the former cations, which leads to materials with better properties.

The final characteristics of the PMN polycrystalline ceramic can also be changed using additives, increasing T_m to values close to room temperature or stabilizing the perovskite phase [15–19]. The addition of Ti^{+4}

---

* Corresponding author. Tel.: +55-16-2016641.
E-mail address: foschini@iq.unesp.br (C.R. Foschini).

PII: S0272-8842(00)00109-7

minimizes the PbO volatilization due to $PbTiO_3$ preferential formation [16], while the addition of Ba^{+2} ions cause the stabilization of the perovskite phase [15–19]. Besides, the addition of $BaTiO_3$ (BT) or $PbTiO_3$ (PT) seeds, of the cubic perovskite structure can improve the PMN perovskite phase formation through the energy barrier reduction to the perovskite phase nucleation. The extrinsic nucleation caused by the epitaxial effect of seeds can lead to narrow particle size distribution powders [20].

The homogeneity among $MgNb_2O_6$ (MN) and PbO particles and the synthesis conditions are of great importance to perovskite phase formation [21]. The partial oxalate method allows obtaining a more homogeneous powder with a lower amount of secondary phases, leading to better final PMN ceramic properties. The PbO excess added during the PMN synthesis, in the reaction between MN and PbC_2O_4, aims to compensate the loss of PbO by volatilization during calcination and sintering. Nonetheless, this excess also could promote the formation of a higher quantity of agglomerated powder [22].

In this work the influence of calcination condition in the PMN powder morphology with 3 wt.% PbO excess, using a method that consists of the association of the Partial Oxalate with the Pechini's Method, through the columbite route was investigated. The effect of BT and PT seeds addition in the PMN perovskite phase amount and in the powder morphology was also investigated.

2. Experimental procedure

2.1. Chemical synthesis

Two citrate solutions were prepared separately. The niobium citrate was prepared from a precipitate of niobium hydrated oxide, previously prepared by the addition of an ammonium hydroxide solution into a niobium oxalate ammoniacal complex solution dissolved in citric acid, until a pH 9–10 was reached. After the complete homogenization of this solution, ethylene glycol was added, with a constant stirring, followed by heating at 80–100°C, to promote the polyesterification reaction. The magnesium citrate was prepared by dissolving the magnesium basic carbonate in an aqueous solution of citric acid polyesterified in ethylene glycol at 80–100°C. The molar ratio metal: citric acid: ethylene glycol used was 1:4:16 for both solutions. The molar ratio between niobium and magnesium mixed was gravimetrically determined as being 2:1. After homogenization the final solution was heated at 250°C yielding a high viscous polyester resin. The residual organic matter was subsequently eliminated at 400°C for 2 h. This powder was milled and calcined at 900°C for 2 h forming a very homogeneous, reactive and with a well-controlled stoichiometry MN powder.

This MN powder was milled with zirconia balls in an isopropyl alcohol medium for 1 h. The lead oxalate was then precipitate onto the MN particles by adding a diluted solution of oxalic acid in a MN suspension of lead nitrate. The mixture was pre-calcined and calcined at several temperatures with airflow. The seeds used were added during the co-precipitation step.

2.2. Materials characterization

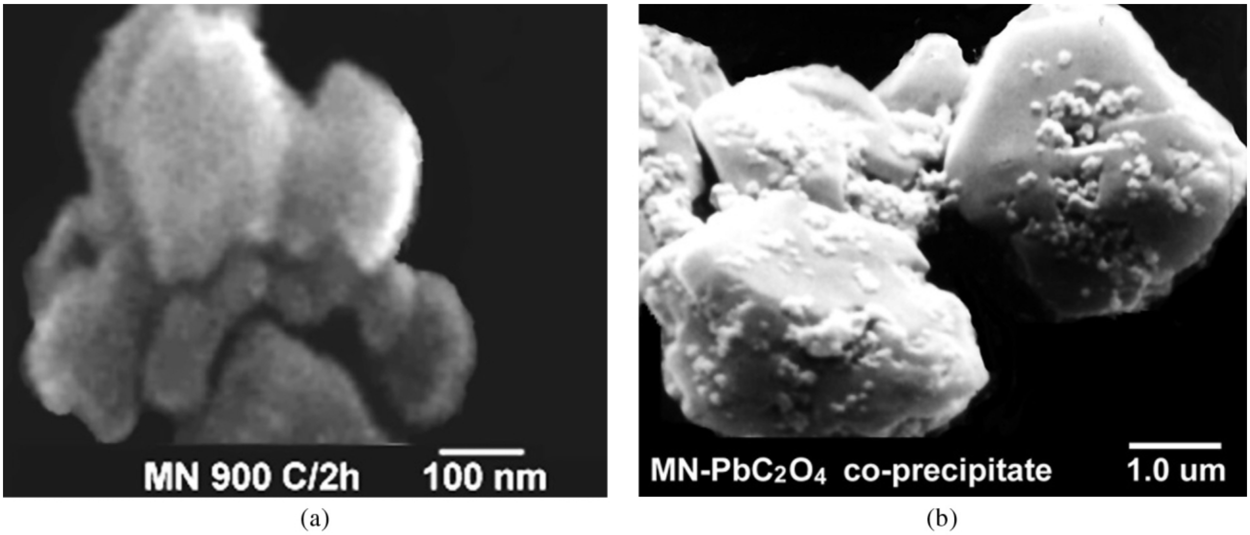
Powders were analyzed by X-ray diffraction (XRD) for phase formation, using a Siemens D5000 diffractometer at 50 kV and 100 mA using Cu K_α radiation with a step size of $(2\theta) = 0.03°$ and 1 s per step. To calculate the amount of perovskite phase the FIT/SOCA-BIM- Siemens Diffrac AT — version 3.1 software was utilized. The integrated intensities of the perovskite (110) peak $\left(I_{P_e}\right)$ and the (111) peak of PbO phase (I_{PbO}) were used to calculate the percentage of perovskite phase according to the equation: $\%Pe = 100.I_{P_e}/(I_{Pe} + I_{PbO})$. If other phases were present, besides the PbO phase, the most intense peak of each of these phases was considered as being that of the PbO phase, for calculation.

The powder morphology was analyzed using a Topcon SM300 scanning electron and a Phillips CM200 transmission electron microscopes. The sample powders were prepared by ultrasonic treatment of the powder dispersion in a 1 wt.% polyvinyl alcohol aqueous solution. The surface areas were determined by the nitrogen adsorption/desorption technique (ASAP 2000-Micromeretics) using the BET method.

3. Results and discussion

After calcination at 900°C for 2 h, the surface area measured in the MN powder was 13.2 m^2/g. The energy released during the organic matter combustion promotes the powders agglomeration and the aggregates formation due to the partial sintering of particles. The surface area increases 18% after milling (15.6 m^2/g), improving the contact among MN particles and the lead oxalate co-precipitated favoring the homogeneity of PMN powder after calcination. In Fig. 1 the micrograph of MN particles after milling (Fig. 1a) and the co-precipitated of MN-PbC_2O_4 (Fig. 1b) are shown. The MN particles present dimensions of ~100nm and the MN-PbC_2O_4 co-precipitated, 4 μm. This relation between the MN particles and co-precipitates favors a good contact and allows the later reaction in the solid state for PMN formation.

The TG/DTA simultaneous analysis for MN-PbC_2O_4 (Fig. 2) indicates that the combustion of lead oxalate occurs at 320°C, forming $PbCO_3$. The carbonate decomposition in PbO occurs approximately at a higher temperature (360°C) due to energy released during the combustion and the relatively low thermal stability.



(a) (b)

Fig. 1. SEM photographs for MN powder: (a) after milling and (b) PbC_2O_4 co-precipitated MN powder.

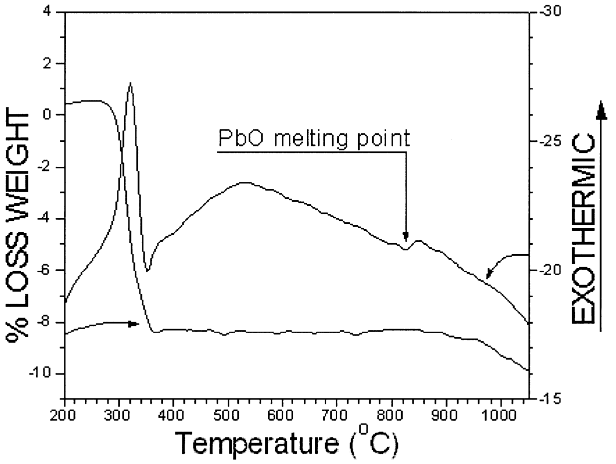
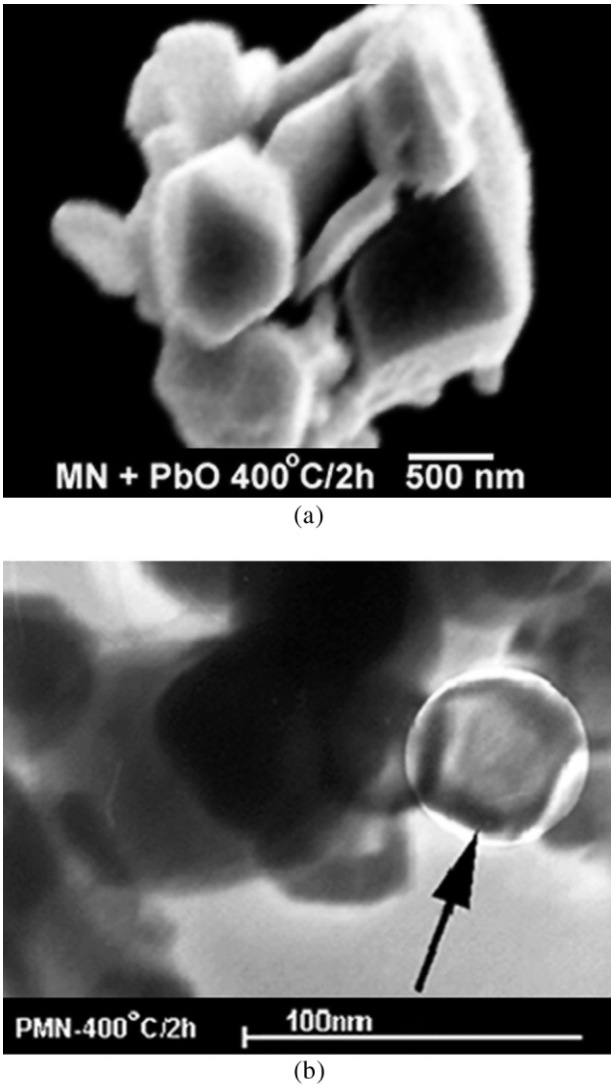


Fig. 2. TG/DTA curves for PbC_2O_4 co-precipitated MN powder.

Increasing the temperature up to 820°C, the solid-state reaction occurs between PbO and MN. The broad exothermic peak in the DTA curve represents that reaction, which has a maximum at 520°C. Close to the PbO melting point (850°C), a weight loss begins associated to this phase volatilization. Thereafter the perovskite phase decomposition starts. This analysis allowed determining the pre-calcination temperature and calcination of the lead oxalate precipitate. The pre-calcination was done in a glass beaker at 400°C for 2 h, since the thermal analysis indicate that at this temperature it is possible to eliminate all organic material. The calcination was done inside alumina crucibles using a furnace at 700, 750 and 800°C in the range from 1 up to 5 h, with the aim of obtaining a crystalline PMN phase at a temperature just bellow the decomposition of perovskite phase.

In Fig. 3a and b the scanning and transmission electron micrographs respectively can be seen for the intermediate obtained during the pre-calcination at 400°C/2 h.



(a)

(b)

Fig. 3. (a) SEM and (b) TEM photographs for PbC_2O_4 co-precipitated MN powder pre-decomposed at 400°C for 2 h.

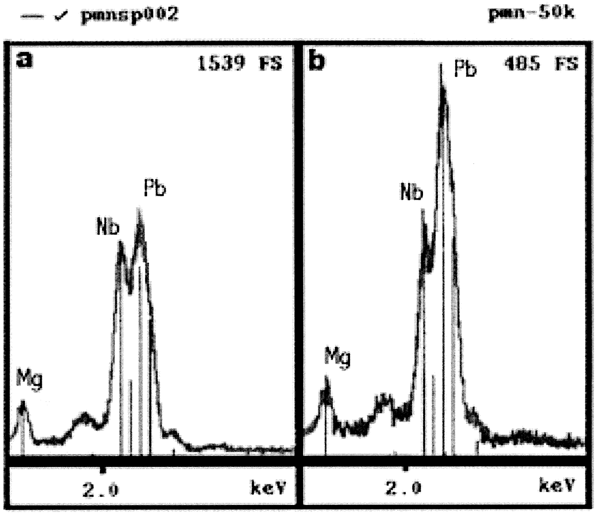


Fig. 4. EDX spectra for: (a) altogether particles and (b) hexagonal particle spotted.

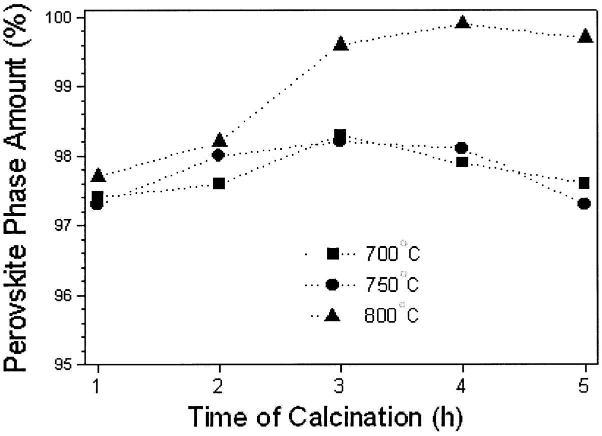
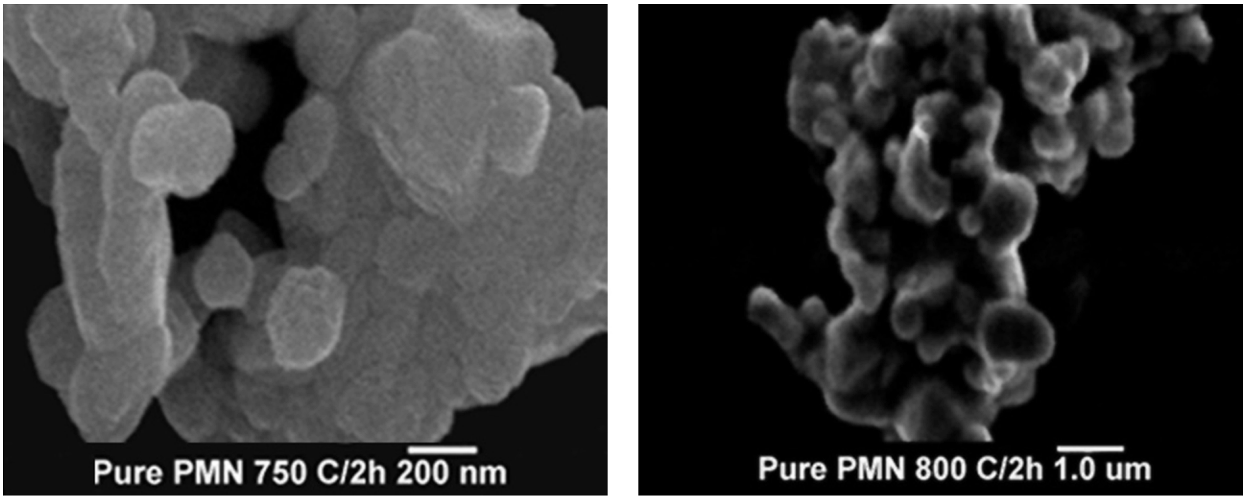


Fig. 5. Perovskite phase amount versus calcination time for pure PMN powders.

In these analysis particles with three different morphologies were found. The XRD results allowed the identification of cubic particles as being the Perovskite $Pb_3MgNb_2O_9$ (JCPDS: 27-1199) and the Pyrochlore $Pb_{1.38}Nb_{1.71}$ $Mg_{0.29}O_{6.39}$ (JCPDS: 37-0071) phases. The other two morphologies, octahedral and hexagonal phases were not directly identified with any diffraction peaks of PbO–MgO–Nb_2O_5 system. In the scanning electron micrograph (Fig. 3a) of pre-calcined powders at 400°C, it was possible to observe particles with the three morphologies coexisting. The secondary emission spectrum (Fig. 4), referring to image 3b, allowed establishing a relation among the oxides of the PbO–MgO–Nb_2O_5 system for the general set of particles (Fig. 4a) and for the selected particle with the hexagonal plate shape (Fig. 4b). There is a lower Pb/Nb relation in the spectrum of Fig. 4a than in the spectrum of Fig. 4b, what allowed verifying that the hexagonal plate shape particles have a composition with a high lead concentration. In the selected particle composition, the contribution of the other particles, around and/or bellow it should also be considered. Nonetheless, the composition found to the general set of particles, part of the lead is due to hexagonal lead particles. This is coherent to the relation Pb/Nb/Mg of 3/2/1 PMN phase.

The calcined powder at 400°C was milled in agate mortar and screened in 0.18 mm and then calcined from 700 to 800°C temperature range from 1 to 5 h. In the X-ray diffraction it was possible to identify peaks related to perovskite phase and PbO with orthorhombic structure (JCPDS: 05-0570). The cubic pyrochlore phase was identified in the pure calcined powders for periods higher than 3 h. In Fig. 5 the amount of the perovskite phase content is presented.

After 3 h calcination, in any temperature, the low amount of perovskite phase is due to the uncompleted



(a) (b)

Fig. 6. SEM photographs for pure PMN powders calcined for 2 h at: (a) 750°C and (b) 800°C.

reaction between MN and PbO. At temperatures lower than 800°C the perovskite phase concentration remained around 98% to any calcination time. The decreasing of perovskite phase amount beginning at 4 h of calcination is due to the decomposition caused by PbO loss via volatilization. At 800°C, the amount of perovskite phase increases along with calcination time up to 4 h, reaching 99.8%. The perovskite decomposition phase occurs with only 5 h calcination, what was associated with the faster particle growing, reducing the volatilization loss. This can be verified by the scanning electron micrographs in Fig. 6. In the calcined powder at 750°C/2 h (Fig. 6a) the particles show 5 times lower dimensions than in the calcined powder at 800°C/2 h (Fig. 6b).

The effect of 1–3% of BT and PT seeds addition in the amount of perovskite phase can be observed in Fig. 7. In all diffraction of this system only perovskite and PbO phase were indicated. The amount of perovskite phase grows along with calcination time, except for the PT seeded powders calcined at 750°C, where the amount of perovskite phase varies as a function of calcination time. This indicates that the seeds of BT and PT promote the perovskite phase stabilization. The

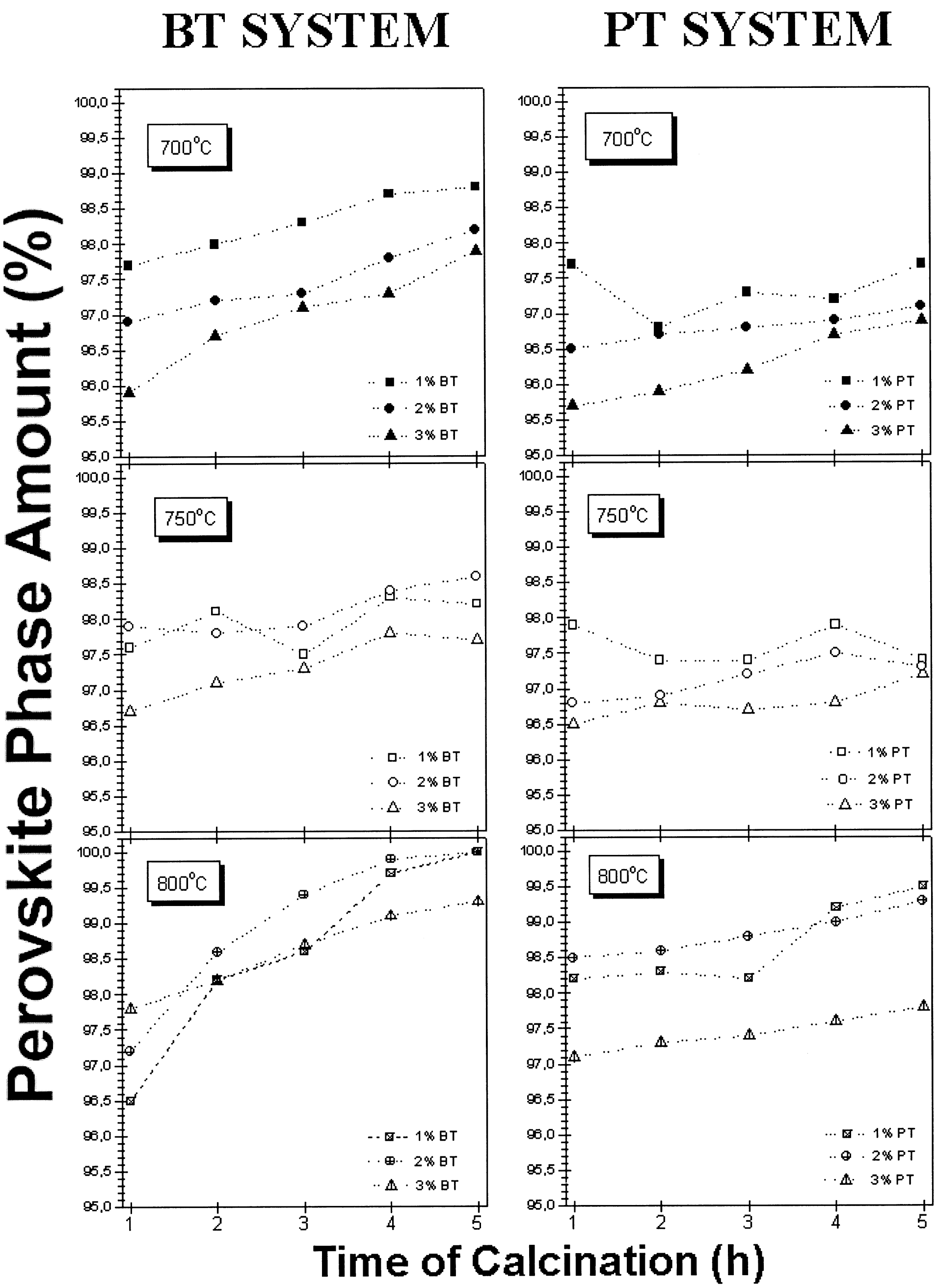


Fig. 7. Perovskite phase amount versus time of calcination for BT and PT seeded PMN powders.

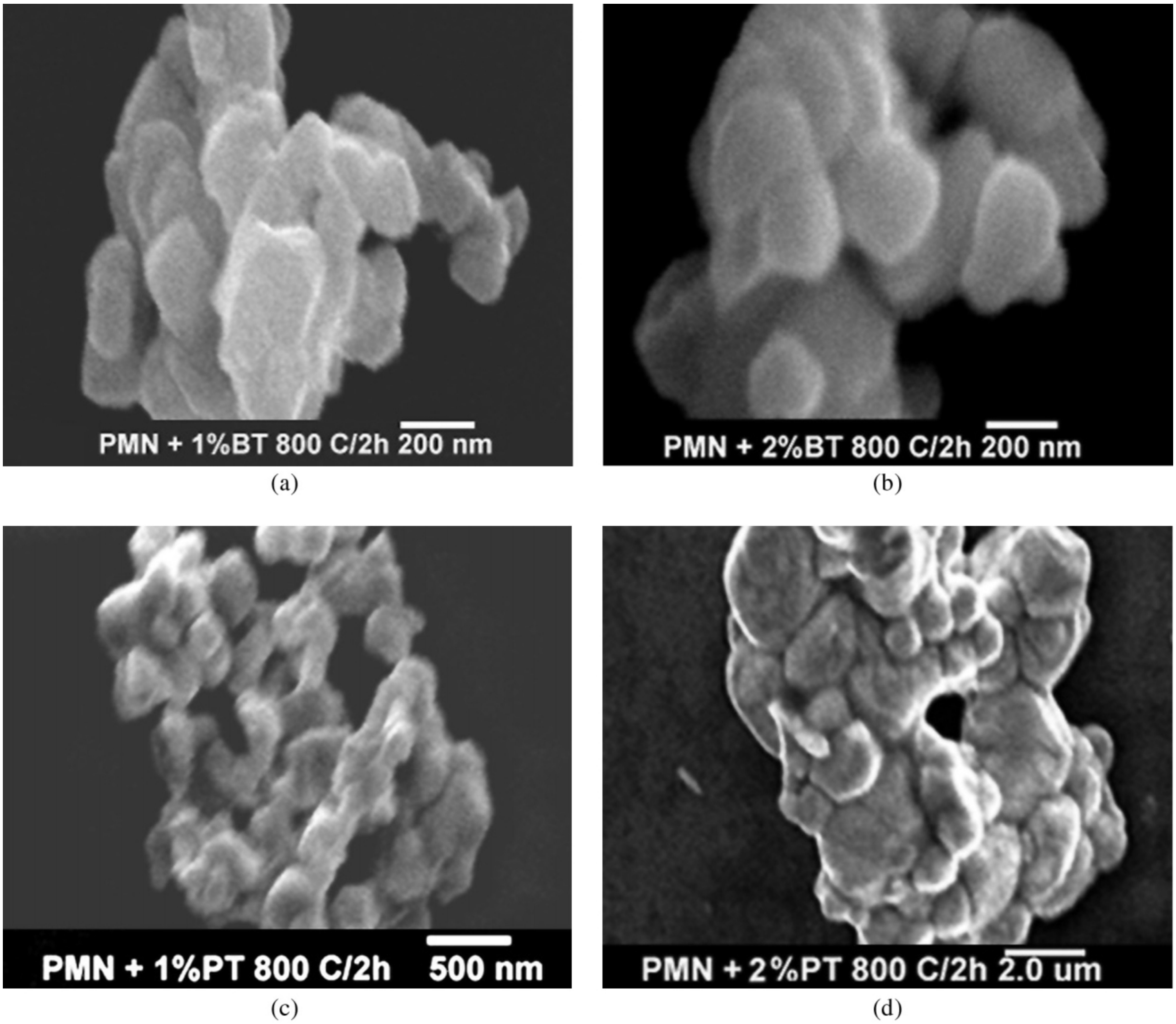


Fig. 8. SEM photos for PMN powders calcined at 800°C/2 h seeded with: (a) 1%BT; (b) 2%BT; (c) 1%PT; (d) 2%PT.

increase in the seed concentration leads to reduction of perovskite phase amount for both cases. However, at 800°C beginning at 2 h of calcination and concentration of 2%BT, higher amounts of perovskite phase in the seeded systems was obtained. For PT seeding, the 2% concentration and calcination at 800°C up to 3 h led to best results. At 5 h calcination, the 1 and 2%BT concentrations allowed PMN powder with 100% of perovskite phase. For PT seeds, the obtaining of 100% perovskite phase was not possible in any investigated condition. This could be related to the higher amount of lead in PMN-PT system. For this system, a lower PbO excess and a higher time and/or higher calcination temperature could result in 100% perovskite phase.

The scanning electron micrographs to the PMN powders with 1 and 2% of BT seed addition calcined at 800°C for 2 h are showed in Fig. 8. The particle size is the smallest investigated in this work. With 2% of seed (Fig. 8b) the powder gets a lower range of particle size distribution due to the effect of extrinsic nucleation introduced by seeds.

For PT seeding, a strong increase in the PMN particle size proportional to its concentration was observed. For 1% PT (Fig. 8c) the particles have dimensions around 500nm, while for 2% (Fig. 8d) there is an increase to around 2 μm. The reduction effect of particle size distribution was not observed as in the BT seeding. Another effect in the seeded powders morphology with PT is the increasing of the agglomerate size and this could be attributed to a higher lead content.

4. Conclusions

The Pechini's Method enabled obtaining of a $MgNb_2O_6$ single phase with a high surface reactivity. The association between Partial Oxalate and Pechini's Methods allowed obtaining a PMN powder with perovskite phase amount close to 100%. Temperatures just bellow the PbO melting point promoted the formation of a higher perovskite phase quantity. The role of BT and PT seeds added to PMN powders was also studied and it was observed that the seeds stabilize the perovskite phase along the calcination time. The PMN powder with 2% of BT seeds, calcined at 800°C for 5 h showed a narrow particle distribution with 100% of perovskite phase.

Acknowledgements

The authors acknowledge the financial support from FAPESP, CNPq and FINEP/PADCT, Brazilian research agencies.

References

[1] A.A. Bokov, Ferroelectrics 131 (1992) 49–53.
[2] J.M. Smith, L.E. Cross, Ferroelectrics 01 (1970) 137–140.
[3] M. Lejeune, J.P. Boilot, Ceram. Int. 8 (2) (1982) 119–122.
[4] M. Lejeune, J.P. Boilot, Ceram. Int. 8 (3) (1983) 99–103.
[5] S.L. Swartz, T.R. Shrout, Mater. Res. Bull. 17 (1982) 1245–1250.
[6] J. Chen, A. Gorton, H.M. Chan, M.P. Harmer, J. Am. Ceram. Soc. 69 (12) (1986) 303–305.
[7] H. Horowitz, J. Am. Ceram. Soc. 71 (5) (1988) 250–251.
[8] H.C. Wang, W.A. Schulze, J. Am. Ceram. Soc. 73 (4) (1990) 825–832.
[9] C.-H. Lu, J.-T. Lee, J. Ceram. Soc. Japan 103 (11) (1995) 1122–1128.
[10] A.A. Cavalheiro, M.A. Zaghete, J.A. Varela, Cerâmica 292–293 (45) (1999) 56–60.
[11] N.-K. Kim, Mater. Lett. 32 (1997) 127–130.
[12] Y. Narendar, G.L. Messing, J. Am. Ceram. Soc. 80 (4) (1997) 915–954.
[13] H.V. Anderson, M.J. Pennel, J.P. Guha, Adv. in Ceram. 21 (1987) 91–98.
[14] M.P. Pechini, US Patent 3 330 697, 11 July 1967
[15] L.F. Francis, D.A. Payne, J. Am. Ceram. Soc. 74 (12) (1991) 3000–3010.
[16] O. Bouquin, M. Lejeune, J.P. Boilot, J. Am. Ceram. Soc. 74 (5) (1991) 1152–1156.
[17] S.J. Butcher, N.M. Thomas, J. Phys. Chem. Solids 52 (7) (1991) 595–601.
[18] S.M. Pilgrin, M. Massuda, A.E. Sutherland, J. Am. Ceram. Soc. 75 (7) (1992) 1970–1974.
[19] L.J. Lin, T.B. Wu, J. Am. Ceram. Soc. 73 (5) (1990) 1253–1256.
[20] P. Ravindranathan, S. Komarmeni, R. Roy, J. Am. Ceram. Soc. 73 (4) (1990) 1024–1025.
[21] A.A. Cavalheiro, M.A. Zaghete, C.O.P. Santos, J.A. Varela, E. Longo, Mater. Res. 2 (4) (1999) 255–260.
[22] S.M. Gupta, A.R. Kulkarni, J. Mater. Res. 10 (1995) 953–961.