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Phase Evolution and Densification Behavior of PBN Ceramics

C. V. do Carmo, R. N. de Paula, J. M. Póvoa, D. Garcia and J. A. Eiras*

Universidade Federal de Sao Carlos, Departamento de Física, Grupo de Cerâmicas Ferroelétricas
13.565-905, Sâo Carlos/SP, Brasil

Abstract

$(Pb_{1-x}Ba_x)Nb_2O_6$ ceramics were prepared by conventional oxide mixture for studies on phase evolution and densification behavior. Formation mechanisms were examined by X-ray diffraction (XRD) for samples isothermally fired at several temperatures and by differential thermal analysis/thermogravimetric analysis (DTA/TGA). The analysis showed phase evolution distinct for each composition, although temperatures above 1200°C formed compositions with similar XRD patterns, which present tetragonal and orthorhombic forms of PBN phase. Dilatometric studies of ceramics bodies, from those high temperature calcined powders, revealed that substitution of Ba for Pb enhances the densification rate, mainly for the powders whose needle shape particles were broken by grinding. The densification of Pb-richest composition was more affected by the phase transformation rhombohedral-tetragonal (high temperature), only detected by shrinkage measurements. © 1999 Elsevier Science Limited. All rights reserved

Keywords: powders: solid state reaction, grain size, niobates, tungsten bronze ceramics

1 Introduction

Lead barium niobate $(Pb_{1-x}Ba_x)Nb_2O_6$ has a tungsten-bronze type structure[1] and in its single-crystal form has large piezoelectric and electro-optic coefficients.[2–4] Especial attention has been devoted to the region with $x \approx 0{\cdot}40$, where a ferroelectric–ferroelectric phase transition near 100°C results in the 90° switching of polar axes, which is interesting for memory applications.[5] However, there are still some restrictions to use these materials in polycrystalline form. It was suggested that single phase PBN can be formed only after calcination of the powders at temperatures as high as 1240°C. Besides high temperatures for calcination, the densification of conventionally fired compacts is hard, due to the formation of large and elongated grains, the presence of several intragrain pores, originating the appearance of many cracks in sintered bodies.[6–9] Thus, the understanding of the sequence of reactions during powder calcination and their densification behavior can be extremely important, to enable the sintering of dense and pore-free PBN ceramic bodies, interesting for several electromechanical applications.

In this work is presented a study about sequence of reactions and densification behavior for $(Pb_{1-x}Ba_x)Nb_2O_6$ system, with $x = 0{\cdot}30$, $0{\cdot}40$ and $0{\cdot}44$, prepared through conventional ceramic methods. The discussion is based on results of DTA/TGA, DRX and dilatometric measurements.

2 Experimental Procedure

The starting materials PbO (99·9%), Nb_2O_5 (99·5%) and $Ba(NO_3)_2$ (99^+%) were weighted following the batch formula $(Pb_{1-x}\ Ba_x)Nb_2O_6$, with $x = 0{\cdot}30$, $0{\cdot}40$ and $0{\cdot}44$ (hereafter denominated PBN70/30, PBN60/40 and PBN56/44, respectively). The reagents were mixed in a ball-mill in isopropilic alcohol using polyethylene pots and ZrO_2 balls. After drying, the powders were uniaxially pressed in pellets and calcined for 2 h, at temperatures ranging between 600°C and 1200°C. The calcined compacts were crushed to further X-ray diffraction (XRD) analysis. XRD patterns of the calcined powders were obtained at room temperature, by using a rotatory anode X-ray diffractometer with CuK_α radiation and Ni filter.

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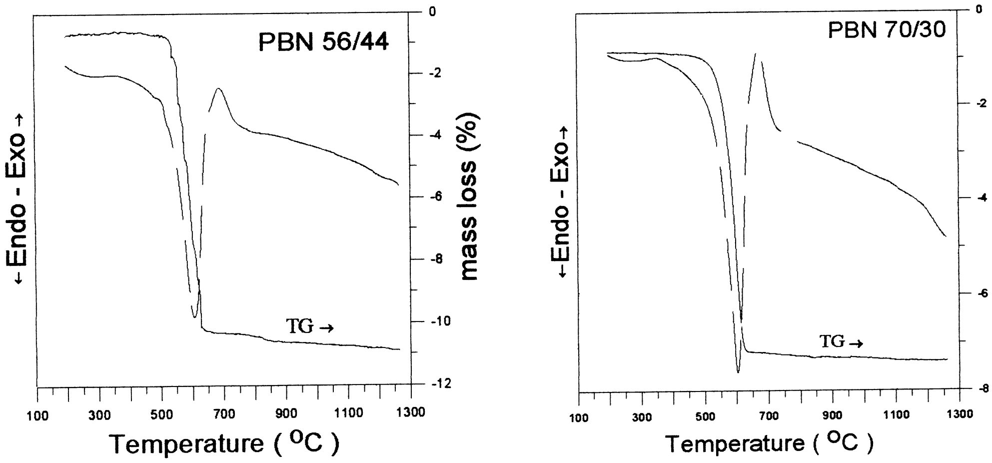
*To whom correspondence should be addressed. Fax: +55 16 261 4835; e-mail: eiras@power.ufscar.br



(A) **(B)**

Fig. 1. DTA/TGA for a ternary mixture of PbO–$Ba(NO_3)_2$–Nb_2O_5 containing different ratios Pb/Ba: (A) 56/44; and (B) 70/30.

Prior to calcination the reaction temperatures were investigated by DTA/TG analysis, heating the powders mixture at a constant rate of 10°C/min up to 1200°C. A portion of the powders calcined at 1200°C was ball-milled for 10 h in isopropilic alcohol using ZrO_2 balls. Both powders (ground and non-milled) were cold pressed in samples with dimensions of 8×1×1 mm for dilatometric studies. The linear shrinkage versus temperature, by heating up to 1350°C with a constant-rate of 10°C min^{-1} was monitored for studies of densification behavior. The densities of fired samples were measured by Archimedes method, at room temperature.

3 Results

Figure 1 shows simultaneous DTA/TGA representative curves for the mixed oxides. The DTA versus T plot shows for all composition a sharp endothermic peak around 600°C, accomplished by a mass change, followed by an exothermic peak (around 650–700°C) where practically no mass loss was observed. Except for the composition with $x = 0{\cdot}30$, which presents at ≈1170°C a little slope change in the DTA/TG, no further reactions were observed by heating up to 1250°C. Additional DTA/TG measurements (not presented) were performed in PbO–Nb_2O_5 and $Ba(NO_3)_2$–Nb_2O_5 mixtures. It was found that $PbNb_2O_6$ (PN) phase is formed by an endothermic reaction at 630°C, with no associated mass change. Otherwise DTA/TGA analysis for the $Ba(NO_3)_2$–Nb_2O_5 mixture showed an endothermic peak at 640°C (assigned to the decomposition of barium nitrate), with a corresponding change in the TG curve and a broader exothermic peak extended up to 1000°C [associated to the formation of $BaNb_2O_6$ (BN) phase]. Based on these results the DTA/TGA curves of

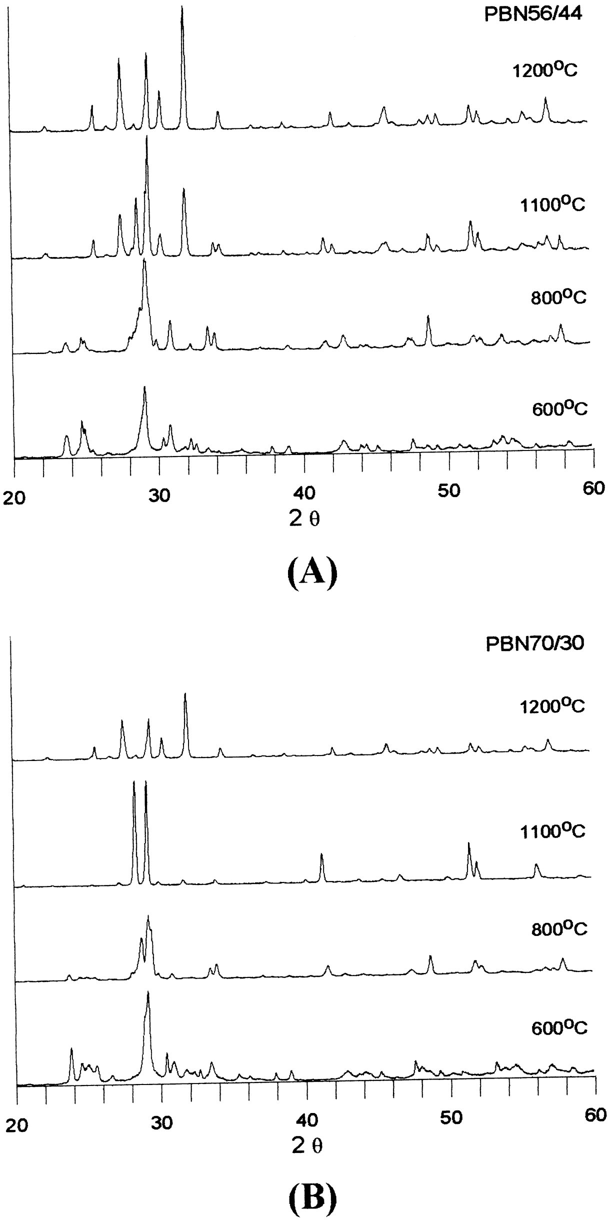


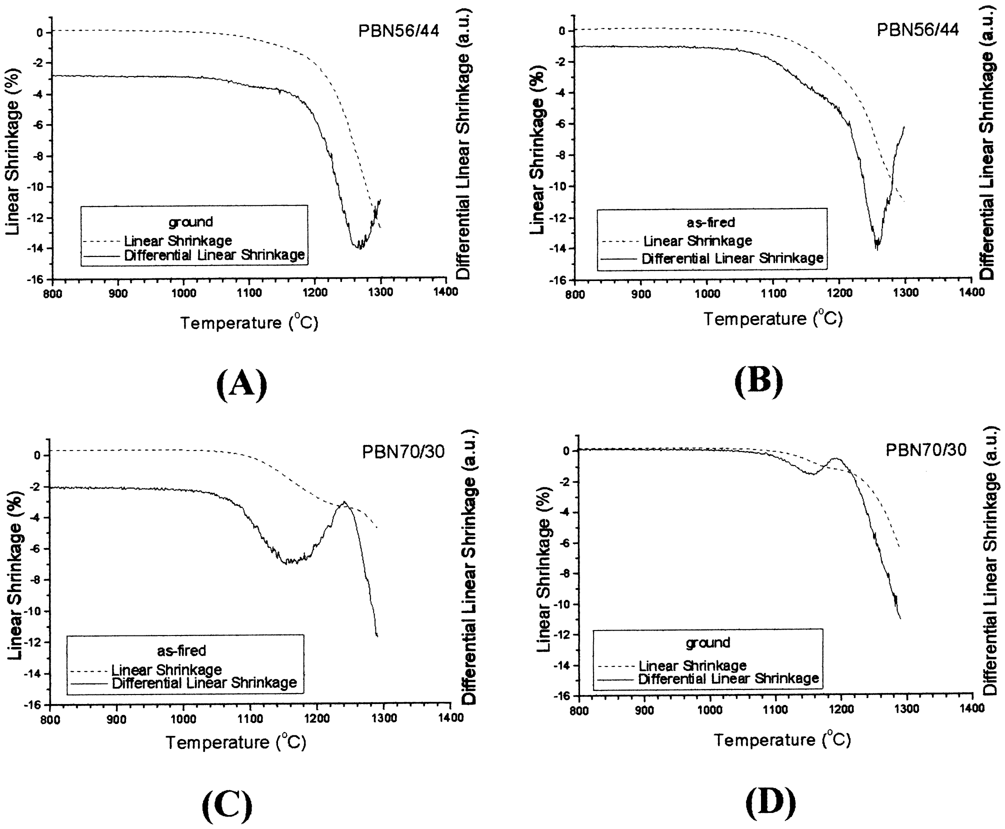
Fig. 2. DRX patterns as a function of the calcination temperature for (A) PBN 56/44 and (B) PBN 70/30 powders [(1) PBN56/44, orthorhombic; (2) PBN 56/44 rhombohedric; (2) $Pb_3Nb_4O_{13}$; (3) $BaNb_2O_6$; (5) $Ba_5Nb_4O_{15}$; (6) Nb_2O_5; (7) BaO].

PbO–$Ba(NO_3)_2$–Nb_2O_5 mixtures (Fig. 1) can be understood as follows: the endothermic peaks (around 600°C) correspond to the simultaneous formation of Pb rich PBN phase and decomposition of barium nitrate, while the exothermic peak is related to the formation of Ba-rich PBN phase. The presence of PbO or PN phase apparently lowered the temperature and the range of temperatures in which barium and niobium react. The observed weight losses match the expected theoretical losses for NO_2 elimination, which increases with Ba content.

Figure 2 shows the XRD patterns for powders calcined for 2 h between 600°C and 1200°C. It is observed that intermediate phases (3)-$Pb_3Nb_4O_{13}$ (P_3N_4), (4)-$BaNb_2O_6$ and (5)-$Ba_5Nb_4O_{15}$ (B_4N_5) are formed between 600 and 800°C. At 800°C continuous reaction of Nb_2O_5 reaches nearly complete formation of PBN. This sequence is similar to that reported by Fang *et al.*[10] for solid solutions of strontium barium niobate (SBN). Possibly, PbO phase acts to decrease the reaction temperature for the system PbO–BaO–Nb_2O_5 as predicted by DTA/TG analysis. In fact, this may be due to formation of Pb-rich and Ba-rich PBN phases instead of PN and BN phases.

The calcination temperature of 1100°C was enough to react completely the oxides into a single phase for the composition $x = 0{\cdot}30$ [Fig. 2(B)]. The pattern shows a structure tungsten-bronze with rhombohedral form (paraelectric) as presented by PN when prepared at temperatures between 800°C and 1200°C.[11] XRD pattern for the composition with $x = 0{\cdot}44$ [Fig. 2(A)], calcined at 1100°C, presented a mixture of two phases of tungsten-bronze structure, with rhombohedral and tetragonal (majoritarily) symmetry. A similar result was observed for $x = 0{\cdot}40$. After calcination at 1200°C, all compositions presented apparently a quite identical XRD pattern. It seems by the change of XRD patterns, for the powder with $x = 0{\cdot}30$ calcined at 1100°C and 1200°C [Fig. 2(B)], that a rhombohedral to orthorhombic phase transition occurs, indicating a similar polymorphism as observed for lead metaniobate. Probably, this phase transition is related to the change of the slope in the DTA curve [Fig. 1(A)] at 1170°C. For the compositions near the MPB region, Pb-rich PBN phase portion changes from rhombohedral to orthorhombic form, mixing with the tetragonal form of Ba-rich PBN phase. Due to a coexistence of tetragonal and orthorhombic phases, for the $x = 0{\cdot}40$ and $x = 0{\cdot}44$ compositions, it was not possible to determine the cell parameters of the individual phases. DRX patterns refinements are in progress.

Figure 3 shows the percentage of linear shrinkage ($\Delta L\%$) and its differential linear shrinkage ($d(\Delta L\%)/dT$) curves, as a function of the temperature, for samples prepared with powders calcined at



(A) (B)

(C) (D)

Fig. 3. Percentage of linear shrinkage (ΔL%) and its differential linear shrinkage (d(ΔL%)/dT) curves, as a function of the temperature for PBN70/30: (A) as-fired and (B) ground and for PBN56/44: (C) as-fired and (D) ground powders.

Table 1. Linear shrinkage and relative apparent densities of PBN samples, fired under constant-rate heating treatment up to 1300°C

Ba Content	*Linear shrinkage (%)*		*Relative density (%)*	
(at%)	As-fired powder	Grinded powder	As-fired powder	Grinded powder
0·30	5·0 6·5		70·1	79·6
0·40	10·5 1·5		84·2	89·2
0·44	11·0 13·0		86·9	93·2

1200°C [as fired Fig. 3(A) and (C), milled for 10 h Fig. 3(B) and (D)]. The shrinkage plots [Fig. 3(A) and (C)] reveal that the densification is significantly increased by Ba content and by grinding the powders [Fig. 3(B) and (D)]. The change of the slope in the $(d(\Delta L\%)/dT)$ curves, around 1150°C, is more pronounced for compositions with less Ba content and for samples prepared with the as-fired powders. Similar behavior, observed by Kimura *et al.*[9] in compacted $(Pb_{1-x}Ba_x)Nb_2o_6$ (x = 0·0, 0·15 and 0·30) powders of rhombohedral symmetry, was related to a phase transformation of these compounds, from rhombohedral (paraelectric) to the tetragonal (paraelectric) symmetry. It is then presumed from our dilatometric studies there is a portion of the rhombohedral phase, not detected by our preliminary DRX analysis, which transformed to tetragonal form during heating forward 1200°C, delaying the densification. In compositions with higher Ba content, where the phase transformation occurs at lower temperatures, particles possess majority high temperature tetragonal form, then the effect of phase transformation is reduced, resulting in higher densities of the compacts (Table 1).

Table 1 sums up the results obtained for all compositions. The higher densities were obtained for samples prepared with ground powders. These results are consistent with the expectation that needle shape particles (as observed in as-fired powders) hinder the densification, while in milled powders, where the needle shapes particles were broken by grinding, the densification was enhanced.

4 Conclusions

The sequence and temperature of reactions in the ternary $PbO–Ba(NO_3)_2–Nb_2O_5$ mixtures were investigated by XRD, thermal and dilatometric analysis. The experimental results showed that the presence of PbO or a compound formed by $PbO–Nb_2O_5$ enhanced the reactivity of barium with the other components, diminishing the interval temperature of reaction. XRD patterns obtained in powders fired at 1200°C were similar for all $Pb_{1-x}Ba_x)Nb_2O_6$ (x = 0·30, 0·40 and 0·44) compositions, presenting a coexistence of tetragonal and orthorhombic forms of PBN phase. Substitution of Ba for Pb or milling the needle shape particles of the powders enhances the densification rate.

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