Journal of the European Ceramic Society **19** (1999) 1111–1114
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0955-2219/99/$ - see front matter
PII: S0955-2219(98)00384-7

Dielectric Properties of Rare Earth Doped $(Sr,Ba)Nb_2O_6$ Ceramics

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Abstract

The influence of rare earth addition on the microstructure and phase transition of $Sr_{0\cdot61}Ba_{0\cdot39}Nb_2O_6$ ceramics was investigated. $Sr_{0\cdot61}Ba_{0\cdot39}Nb_2O_6$ undoped and doped with 0·3 and 1·0 wt% La_2O_3 and 0·3 wt% Nd_2O_3 were prepared by the conventional ceramic method. Dielectric measurements were performed in order to characterize the phase transition in these ceramics. The addition of RE elements decreased the maximum dielectric constant (ε_{MAX}) and its correspondent temperature (T_{MAX}) and increased the dielectric losses in all studied samples. A peak broadening and an increasingly Curie–Weiss behavior was verified for a La, while an inverse dependence occurred for Nd doping. © 1999 Elsevier Science Limited. All rights reserved

Keywords: sintering, dielectric properties, niobates, tungsten bronze ceramics.

1 Introduction

$Sr_xBa_{1-x}Nb_2O_6$ (SBN) ceramics for $0\cdot25 \leq x \leq 0\cdot75$ form a solid solution with the tetragonal tungsten bronze structure (TTB).[1] These materials can show high pyroelectric coefficients, strong electro-optic effects and photorefractive behavior.[2,3] Ceramics prepared by conventional method with the composition $Sr_{0\cdot3}Ba_{0\cdot7}Nb_2O_6$ doped with 0·1–0·5 wt% La_2O_3, reached high densities when firing temperatures are increased to 1400°C.[4] These materials presented a diffuse phase transition (DPT) in which diffuseness was diminished as the doping concentration was increased. Nishiwaki *et al.*[5] found that rare earth elements (RE) and Li ions increase the transition temperature as the ionic ratio of RE decreases. The authors suggested a structural phase transition, attributed to the combined effects of the pairs of Li and RE ions, which are incorporated into the structure of the ceramics. Using a thermodynamic approach Kuroda *et al.*[6] attributed a special case of second order phase transition for SBN ceramics doped with different RE. The authors proposed that the doping improves the diffuseness of the phase transition, independent of the dopant used.

In this work a study of dielectric properties of $Sr_{0\cdot61}Ba_{0\cdot39}Nb_2O_6$ ceramics (SBN61), doped with La and Nd is presented. The effect of rare earth elements on the structural parameter, microstructure and characteristics of the phase transition have been investigated.

2 Experimental Procedure

Ceramics of $Sr_{0\cdot61}Ba_{0\cdot39}Nb_2O_6$ (SBN61), undoped and doped with La and Nd, were prepared by the conventional mixed oxides method. The precursors $[Ba(NO_3)_2$, Nb_2O_5 and $SrCO_3]$ were mixed for 2 h in a ball mill containing distilled water and zirconia balls. The mixture was calcined in air at 1200°C for 3 h. To the calcined powder 0·3 and 1·0 wt% La_2O_3 and 0·3 wt% Nd_2O_3 were added. Discs with 5 mm in diameter were prepared by uniaxial and isostactic cold pressing, these were fired for 3 h at 1350°C. XRD patterns of the sintered ceramics (not presented) were obtained at room temperature, by using a rotatory anode Rigaku X-ray diffractometer (CuK_α radiation and Ni filter).

Dielectric measurements were made after sputtering gold electrodes on the disc faces. These measurements were made as a function of the temperature and frequency using a HP4194A impedance gain/phase analyzer interfaced with a microcomputer. The measurements were performed over the temperature range of $-100°C < T < 300°C$ by heating at a constant rate of $3°C\ min^{-1}$.

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Micrographs were taken with a JEOL JSM 5800LV scanning electron microscope.

3 Results and Discussion

Figure 1 presents the SEM micrograph of the undoped and doped SBN61 ceramics. No segregated phase was observed, an indication that practically all RE elements are incorporated into the SBN61 structure. In Fig. 1(C), SBN61 with 0·3 wt% La_2O_3 had anomalous grain growth; this effect could not be explained based on our results.

Figure 2 presents the theoretical (calculated using XRD patterns) and relative densities of the ceramics. The results of Fig. 2 show that the relative density first decreases, for doping with 0·3 wt% of La_2O_3 and Nd_2O_3, and then increases for higher concentrations of the RE elements.

The temperature dependence of the dielectric constant and the dissipation factor at 1 MHz are shown in Fig. 3 for undoped and doped SBN61 ceramics. The temperatures of maximum dielectric constant (T_{max}) are in good agreement with those

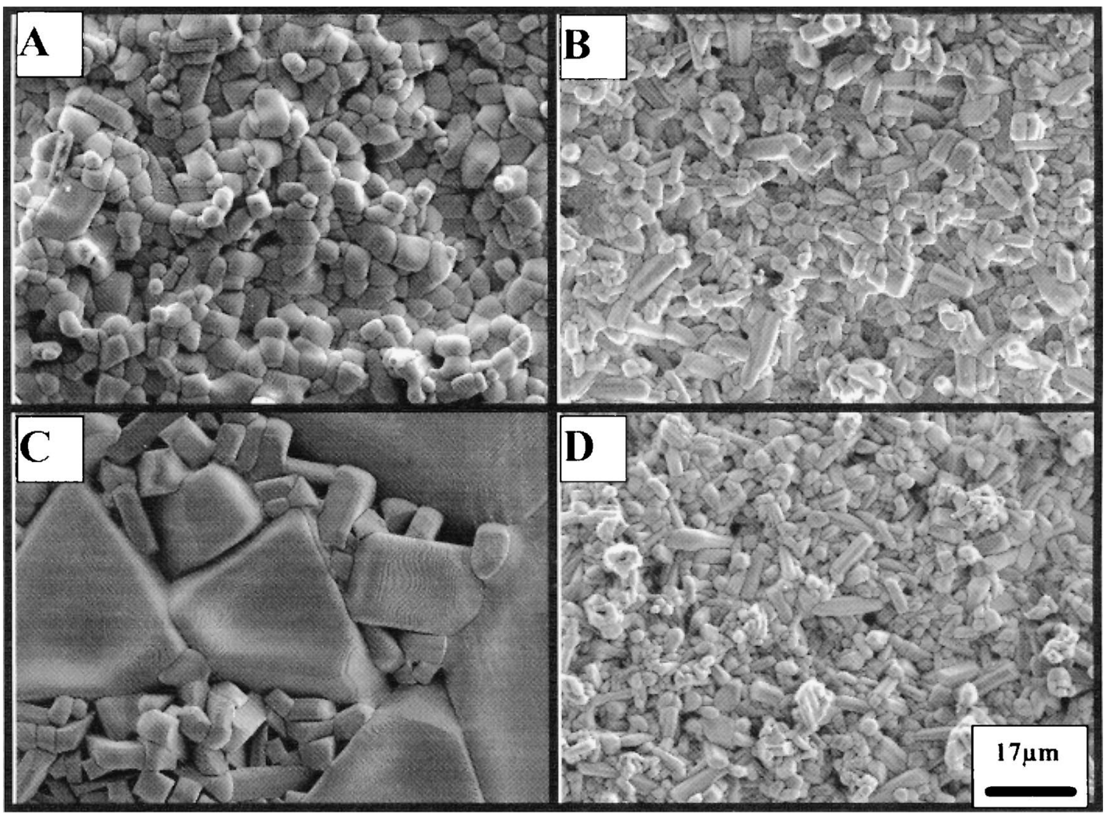

Fig. 1. SEM micrographs for $Sr_{0.61}Ba_{0.39}Nb_2O_6$ ceramics: undoped (A) and doped (B) 0·3 wt% Nd_2O_3, (C) 0·3 wt% La_2O_3 and (D) 1·0 wt% La_2O_3 (2000×).

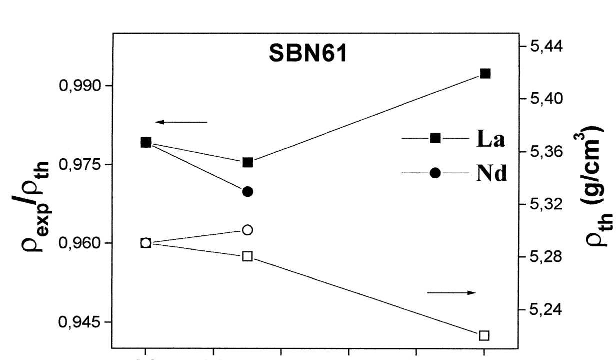

Fig. 2. Theoretical (ρth), calculated using XRD patterns, and relative (ρ_{exp}/ρth) densities as a function of the rare earth (La_2O_3 or Nd_2O_3) doping in SBN61 ceramics.

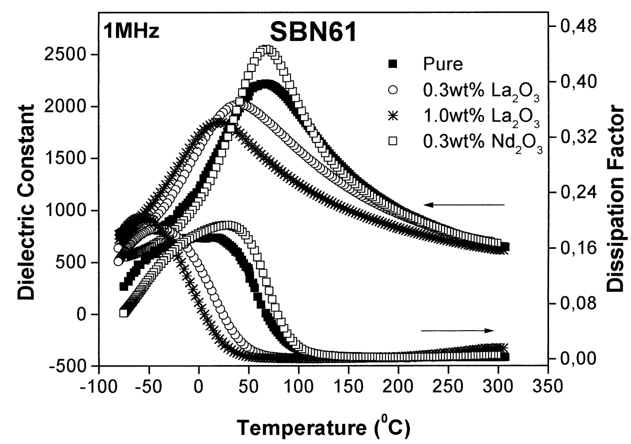

Fig. 3. Temperature dependence of the dielectric constant and dissipation factor at 1 MHz for undoped and La_2O_3 or Nd_2O_3 doped SBN61 ceramics.

found for SBN60 doped with Li and other RE elements.[7] The transition temperature for undoped SBN61 ceramic is 61°C, lower than that reported for a SBN60 single crystal,[8,9] at 88°C. This difference is probably due to the effect of the grain size on T_{max} in SBN ceramics, as reported by Jimenez *et al.*,[9] which can decrease the distortion of the unit cells in SBN ceramics. The lattice parameters obtained for SBN61 single crystals are $a = 12{\cdot}452$ Å and $c = 3{\cdot}938$ Å.[10] The lattice parameters obtained by us are $a = 12{\cdot}545$ Å and $c = 3{\cdot}935$ Å. Comparing the curves in Fig. 3 it can be seen that the maximum dielectric constant, and its respective temperature, decreases as the La_2O_3 content increases. An inverse dependence was observed for the dissipation factor. For all SBN61 doped ceramics the temperature of the phase transition was smaller than that of undoped SBN61.

To determine the characteristics of the phase transition in the ceramics the experimental results were fitted using eqn (1).

$$\varepsilon' = \frac{\varepsilon'_{MAX}}{1 + \left(\frac{T - T_{MAX}}{\delta}\right)^{\gamma}} \qquad (1)$$

where γ is the diffuseness exponent of the phase transition, δ the peak broadening and ε_{MAX} the maximum dielectric constant. In eqn (1) $\gamma = 1$ represents normal Curie–Weiss behavior, while $\gamma = 2$ corresponds to a diffuse phase transition. For fitting only high temperature results, experimental data were taken at least 5°C above T_{max}. Assuming a diffuse phase transition ($\gamma = 2$), as reported by Portelles *et al.*,[4] the high temperature experimental data could not be well fitted. The results for the diffuseness, peak broadening, T_{max} and ε_{max} are shown in Fig. 4. The addition of La_2O_3 decreased T_{max} and ε_{max}, while an inverse dependence was observed for doping with Nd_2O_3. Figure 4 also shows that peaks become broader as the RE element content increases. Similar behavior was reported by Kubota *et al.*[6] On the other side the character of the phase transition showed an evolution, from diffuse to Curie–Weiss behavior (γ diminishes), as the RE element content increases.

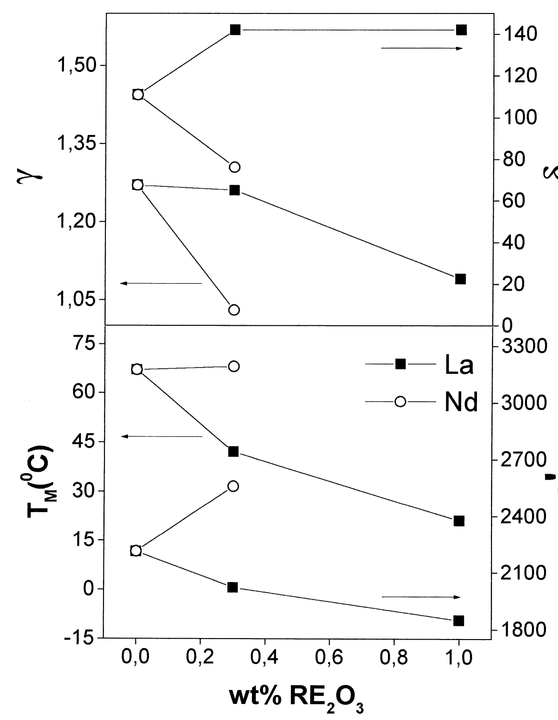

Fig. 4. Phase transition characteristics (diffuseness γ, peak broad δ, maximum ε_{max} and temperature T_{max} of maximum dielectric constant) as a function of the rare earth (La_2O_3 or Nd_2O_3) doping in SBN61 ceramics

The response of the γ parameter is unclear. This is in contrast to the response in perovskite ceramics, like PLZT, where increasing impurities content increases both γ and δ.[11]

4 Conclusions

$Sr_{0{\cdot}61}Ba_{0{\cdot}39}Nb_2O_6$ undoped and doped with 0·3 and 1·0 wt% La_2O_3 and 0·3 wt% Nd_2O_3 were prepared by conventional ceramic methods. SEM examination showed that practically all RE elements were incorporated to the SBN structure. Dielectric measurements found that La_2O_3 doping causes peak broadening decreases ε_{max} and T_{max} and increases the dielectric losses in all studied ceramics. There was a tendency to approach a Curie–Weiss behavior for a La content higher than 0·3 wt%. An inverse dependence of these parameters was observed for doping with 0·3 wt% Nd_2O_3.

Acknowledgements

The authors would like to thank Dr Y. Mascarenhas IF/USP-São Carlos for X-ray facilities and CNPq for financial support.

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