Formation of the La$_{0.03}$Sr$_{0.255}$Ba$_{0.7}$Nb$_{2-y}$Ti$_y$O$_{6-y/2}$ ferroelectric ceramic system

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The study of the formation of the Sr$_{0.255}$La$_{0.03}$Ba$_{0.7}$Nb$_{2-y}$Ti$_y$O$_{6-y/2}$ ferroelectric ceramic system and the influence of the sintering conditions and titanium concentration on the densification process is reported. A single-phase compound is observed for low titanium content ($y \leq 0.1$) in the XRD spectra, being isostructural with the tetragonal tungsten bronze SBN phase. For high titanium concentrations ($y > 0.1$) the XRD patterns show, besides the tetragonal phase reflections, several small peaks evidencing an additional phase in the compound. This second phase was identified as isostructural to hexagonal Ba$_6$Nb$_9$Ti$_7$O$_{42}$. The grain size shows a linear increase with titanium content in the region of monophasic compositions and a possible liquid phase aided sintering process is analyzed. © 2000 Kluwer Academic Publishers

1. Introduction
Strontium-Barium Niobate (SBN) solid solutions have proved to be very useful in many applications such as pyroelectric detectors [1, 2], photorefractive materials [3] and electro-optic [4] and surface acoustic wave (SAW) [5] devices. Since the production of materials in single crystal form is usually very expensive [6], the design and production of ferroelectric ceramics [7] and, in particular SBN [8–10], has drawn increasing interest. The ease of fabrication, chemical and mechanical stability and the possibility of optimization of their properties by ion substitution in their crystalline structure, are some of the advantages of polycrystalline ceramics [11, 12].

Many investigations on the dielectric properties of ferroelectric ceramics such as permittivity, pyroelectricity and aging have shown them to be strongly dependent on the fabrication process [9, 12]. Even though the properties of the ceramics are often similar to those of single crystal materials [8, 9], their behavior is strongly conditioned by the grain morphology and grain boundaries, which contribute additional effects that must be considered [13]. The selection process of the sintering parameters that will produce the ceramic with the best properties becomes very important [14, 15]. The modification of the SBN system by rare earth and/or other elements strongly affects the material properties, including their transition temperature [16, 17]. In particular, the dielectric and pyroelectric properties can be optimized for room temperature applications [17, 18]. On the other hand, the addition of specific impurities in certain ferroelectric ceramics may produce the conditions that favor a fast densification process [14, 15]. In previous work, the influence of small amounts of lanthanum in the sintering of SBN based ceramics has been reported [11, 19]. Here, the effect of titanium content on the formation process of the Sr$_{0.255}$La$_{0.03}$Ba$_{0.7}$Ti$_{2-y/2}$O$_{6-y/2}$ (LSBNT) ceramic system is presented.

2. Experimental procedure
High purity grade (>99.9%) BaCO$_3$, SrCO$_3$, La$_2$O$_3$, Nb$_2$O$_5$ and TiO$_2$ raw materials were used for the preparation of Sr$_{0.255}$La$_{0.03}$Ba$_{0.7}$Ti$_{2-y/2}$O$_{6-y/2}$ samples, where $y$ is 0.01 (LSBNT1), 0.03 (LSBNT3), 0.05
(LSBNT5), 0.1 (LSBNT10), 0.2 (LSBNT20) and 0.5 (LSBNT50), trough the conventional ceramic technique. The powders were mixed in an agate mortar with ethyl alcohol for 2 hours and calcined at 1100 °C for 2 hours. The resulting powders were uniaxially de-pressed at 612 Mpa into discs of 10 mm diameter and 1 mm thickness, and sintered for several temperatures in air for 1 and 5 hours.

The density of the sintered samples was calculated by directly measuring their volume and weight them. The sintered samples were examined by X-ray diffraction (XRD) using Cu Kα radiation and a 0.02 °/step. The analysis of the obtained reflections by means of the PC-APD software and the 1997 PDF Database [20], allowed us to identify the crystalline phases present in the samples. The microstructure was observed using a Jeol JSM-5300 Scanning Electron Microscope (SEM) and the mean grain size was determined by the line intersection method [14].

3. Results and discussion

Fig. 1 shows the XRD patterns for samples with different compositions sintered at 1250 °C for 5 hours. All the reflection peaks on the XRD patterns of the LSBNT1 and LSBNT10 samples coincide with those reported in the literature for SBN, that is, a tetragonal tungsten bronze (TTB) structure [21]. Similar patterns were obtained for intermediate compositions, indicating that for low titanium content monophasic compounds, isostructural with SBN, were produced.

In the LSBNT20 sample, beside the reflections corresponding to the TTB system, several small peaks appear evidencing an additional phase in the compound. Such additional peaks are better defined in the XRD patterns of the LSBNT50 sample (see Fig. 1). The increment of the titanium content in the compound results in an enhancement in the intensity of the peaks of the additional phase. This second phase was identified as isostructural to the hexagonal Ba₆Nb₉Ti₇O₄₂ (BNT) reported in the 1997 PDF Database [20]. This result suggests the existence of a solubility limit in the substitution of niobium by titanium in the TTB structure of the LSBN system, producing a polyphasic material for titanium concentrations above y = 0.1, as can be seen in the XRD patterns.

In accordance to the kinetics of crystallization of the Sr₂₅La₀₃Ba₀₇Nb₂₋ₓTixO₅₊ₓ system as a function of firing temperature shown in Fig. 2, where equal molar amounts of titanium and niobium are used, the second phase seems to be generated from the TTB structure as the material is being processed. In this graphical sequence, it is seen how the TTB phase develops initially at a temperature of 1000 °C, with the peaks associated to the hexagonal phase being very small, and without the presence of the intermediate compounds of the SBN phase (BaNb₂O₆ and SrNb₂O₆) in the XRD spectrum. For higher firing temperatures the hexagonal phase peaks start growing, while the TTB phase peaks become smaller as the temperature is increased. Finally, the hexagonal phase fully develops at 1200 °C. All this facts suggest that the hexagonal phase grows at the expense of the TTB phase and not through intermediate compounds during the firing process.

The microstructure of the samples sintered at temperatures lower than 1250 °C shows a high density of interconnected pores indicative of an early stage in the sintering process, as can be seen in Fig. 3a for the LSBNT1 sample sintered at 1200 °C for 1 hour. The grain size is around 1 μm in all cases and a slight decrease in the porosity is observed with the increase in titanium concentration. Fig. 3b–e shows the microstructure of the LSBNT1, LSBNT5, LSBNT10...