



Ferroelectric Properties of the $\text{La}_{0.03}\text{Sr}_{0.255}\text{Ba}_{0.7}\text{Nb}_{2-y}\text{Ti}_y\text{O}_{6-y/2}$ Ceramic System*

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Abstract. The study of the dielectric properties of the stoichiometric Titanium doped $\text{Sr}_{0.255}\text{La}_{0.03}\text{Ba}_{0.7}\text{Nb}_2\text{O}_6$ ceramics prepared according to the formula $\text{Sr}_{0.255}\text{La}_{0.03}\text{Ba}_{0.7}\text{Nb}_{2-y}\text{Ti}_y\text{O}_{6-y/2}$ is reported. A single phase compound is observed for low Ti content ($y < 0.1$) in the XRD spectra, being isostructural with the SBN phase. For high Ti concentrations ($y > 0.1$), the XRD patterns show, besides the SBN phase reflections, several small peaks associated with an additional phase present in the ceramics. A possible liquid phase sintering is analyzed. Strongly broadened dielectric curves are obtained in dielectric measurements, where the transition temperature decreases with the Titanium content. The diffuse phase transition coefficients are calculated, corroborating that Titanium increases the diffuse character of the transition in the monophasic region.

Keywords: dielectric properties, diffuse phase transition, ferroelectric ceramics

1. Introduction

Tetragonal Tungsten Bronze (TTB) ferroelectric oxides have received considerable attention for many years. Among these materials we find the $\text{Sr}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$ (SBN) solid solution system, having numerous applications, particularly in the area of pyroelectric infrared detection [1], electro-optics [2] and photorefractive optics [3]. The ferroelectric properties in the SBN system have been improved by the addition of small amounts of different ions [4–6] to produce the modified/unmodified SBN, which is one of the best materials for pyroelectric applications [7]. In the TTB structure of this system, the AI and AII crystallographic sites are occupied by Sr^{2+} and Ba^{2+} in a random way, while the Nb^{5+} cations occupy the BI and BII sites [8].

The SBN system has been extensively studied in single crystal form [1,9]. In recent years ferroelectric

ceramic materials have become important as substitutes for single crystals in various device applications, because of their low cost and ease of fabrication.

The influence of small amounts of lanthanum in the properties of the SBN ceramics was reported in previous work [4,10,11]. The present paper is mainly concerned with the study of ferroelectric properties in $\text{Sr}_{0.255}\text{La}_{0.03}\text{Ba}_{0.7}\text{Nb}_{2-y}\text{Ti}_y\text{O}_{6-y/2}$ (LSBNT) ceramics, where the results lead us to believe that Ti^{4+} cations substitute Nb^{5+} cations in the B sites of the TTB structure.

2. Experimental Procedure

The raw materials BaCO_3 , SrCO_3 , La_2O_3 , Nb_2O_5 and TiO_2 with high purity grade (> 99.9%) were used for the preparation of $\text{Sr}_{0.255}\text{La}_{0.03}\text{Ba}_{0.7}\text{Nb}_{2-y}\text{Ti}_y\text{O}_{6-y/2}$ samples, where y took the values 0.01 (LSBNT1), 0.03 (LSBNT3), 0.05 (LSBNT5), 0.1 (LSBNT10), 0.2 (LSBNT20) and 0.5 (LSBNT50), using the conventional ceramic technique. The powers were mixed in

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an agate mortar with ethyl alcohol for 2 h and calcined at 1100°C for 2 h. The resulting powders were uniaxially die-pressed at 612 Mpa into discs of 10 mm diameter and 1 mm thickness, and sintered at several temperatures in air for 1 and 5 h.

After the sintering process, the density of the samples was calculated by measuring their volume and weighing them. The temperature dependence of the dielectric constant was measured using an RLC bridge (PHILIPS PM 6303) at a frequency of 1 kHz. Silver electrodes deposited by a diffusion technique were used for the experiments.

The sintered samples were examined by XRD using CuK α radiation and a 0.05°/step. The analysis to identify the crystalline phases in the samples was performed from the obtained reflections by means of the PC-APD software.

3. Results and Discussion

In previous work [4] it has been reported that lanthanum ions can substitute for strontium in AI sites of the SBN solid solutions, the excess of positive charges introduced by the substitution, must be balanced by strontium vacancies to preserve electrical neutrality [12]. Similarly, we must expect that in substituting Nb⁵⁺ by Ti⁴⁺, Ti ions will preferentially lie in the B sites, attending to the similar ionic radii and electronegativity of these cations and therefore, oxygen vacancies must also appear to preserve electrical neutrality.

Figure 1 shows the X-ray diffraction spectra of samples with different Ti contents, after sintering at 1200°C during 5 h. A single phase compound is observed from LSBNT1 (Fig. 1(a)) to LSBNT10 (Fig. 1(b)) samples, being isostructural with the SBN phase. For LSBNT20 (Fig. 1(c)) however, besides the SBN phase reflections, the corresponding XRD pattern shows several small reflections associated with an additional phase identified as Ba₆Nb₉Ti₇O₄₂ (BNT) present in the ceramic. This result suggests that there must be a solubility limit when titanium is being incorporated into the LSBN structure, giving rise to a polyphasic compound. This fact is corroborated with the LSBNT50 sample (Fig. 1(d)), where X-ray diffraction spectra show the presence of the SBN and BNT phases.

The dependence of the relative density (with respect to the LSBN system, previously reported in

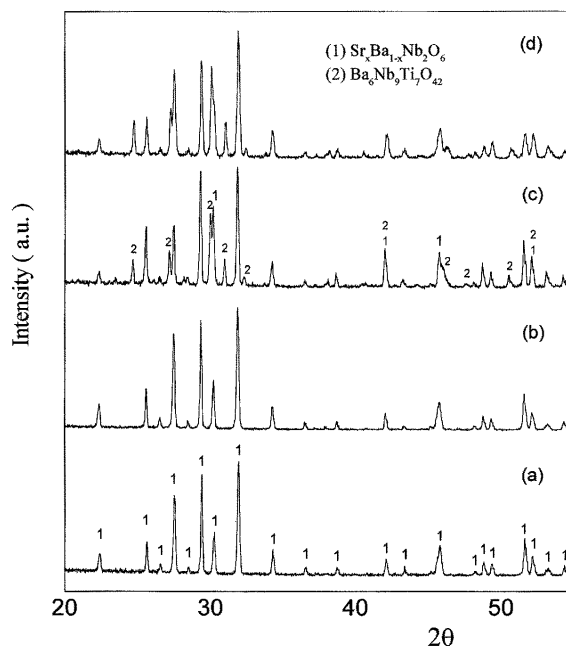


Fig. 1. XRD patterns of the Sr_{0.255}La_{0.03}Ba_{0.7}Nb_{2-y}Ti_yO_{6-y/2} ceramics for y = (a) 0.01 (LSBNT1), (b) 0.1 (LSBNT10), (c) 0.2 (LSBNT20) and (d) 0.5 (LSBNT50) after sintering at 1200°C during 5 h (1) SBN, (2) Ba₆Nb₉Ti₇O₄₂ (BNT) phases. XRD patterns after sintering show from y = 0.01 (LSBNT1) to 0.1 (LSBNT10) a single phase compound isostructural to the SBN phase, while for higher titanium content another phase is present in the material.

[13]) of the monophasic compositions (LSBNT1 to LSBNT10) is given in Fig. 2 as a function of sintering temperature at 1 and 5 h. A maximum value showing relative densities higher than 90% is observed at about 1250°C for all compositions sintered during 1 h. Meanwhile, for the samples sintered for 5 h, the maximum with relative densities higher than 95% shifts to 1200°C with increasing Ti content. We should point out that the sintering process performed at 1400°C resulted in samples melted thoroughly. On the other hand with the increase of Ti content, the material density is increased. In such a case two possibilities arise: (1) an eutectic reaction of the material in the presence of titanium, or (2) the synthesis of a new phase melting at the applied sintering temperature. Although further studies are to be performed, the first possibility is the more feasible since this process is also present in those samples from LSBNT1 to LSBNT10 which do not show any additional phases from XRD analysis. In any case, the incorporation of

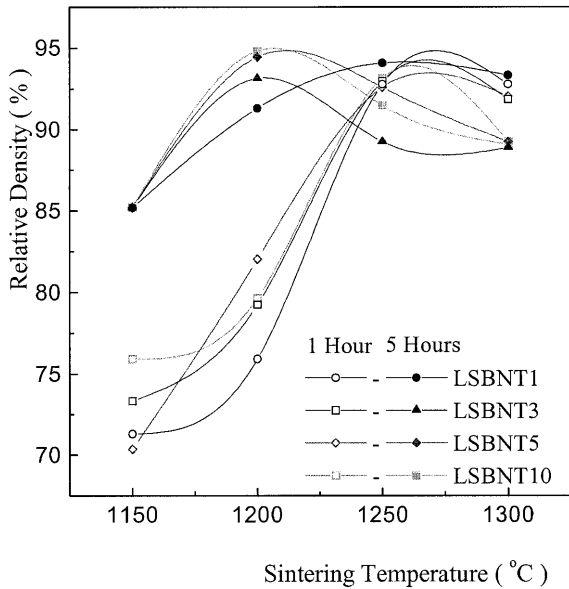


Fig. 2. Relative density as a function of the sintering temperature in monophasic samples (LSBNT1 to LSBNT10), sintered during 1 and 5 h. It is clearly visible for the 5 h sintered samples, that the maximum density with relative values higher than 95% shifts to lower temperatures with increasing Ti content, indicating a possible liquid phase sintering process.

titanium into the LSBN system leads to a liquid phase sintering which improves the mass transfer process and degree of densification during sample firing.

Figure 3 illustrates the temperature dependence of the dielectric permittivity for those compositions sintered at 1200°C during 5 h. These samples show the greater densities and the highest permittivity values. This result agrees with that previously reported for the LSBN system [11], that is, the lower the volume fraction of porosity the higher the permittivity.

Moreover, the dielectric curves show strongly broadened peaks, suggesting the existence of a transition temperature distribution in the ceramics. This behavior arises from the uncertainty in the occupancy of the A sites by the Sr^{2+} , Ba^{2+} and La^{3+} ions, in the partially filled lattice, provoking a fluctuation in the composition of the grains. In deed, for the LSBNT system, this effect should also include the B site uncertainty of the Nb^{5+} and Ti^{4+} ions.

The behavior of the Curie temperature with the increase of Ti content is given in Fig. 4. This

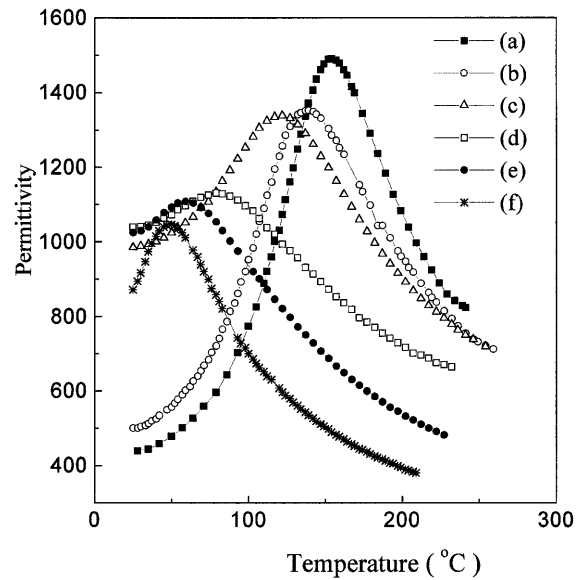


Fig. 3. Temperature dependence of the permittivity for $\text{Sr}_{0.255}\text{La}_{0.03}\text{Ba}_{0.7}\text{Nb}_{2-y}\text{Ti}_y\text{O}_{6-y/2}$ ceramics, with $y =$ (a) 0.01, (b) 0.03, (c) 0.05, (d) 0.1, (e) 0.2 and (f) 0.5, after sintering at 1200°C during 5 h. Strongly broadened dielectric curves are obtained in all cases and the Curie temperature decreases with the increase of titanium content.

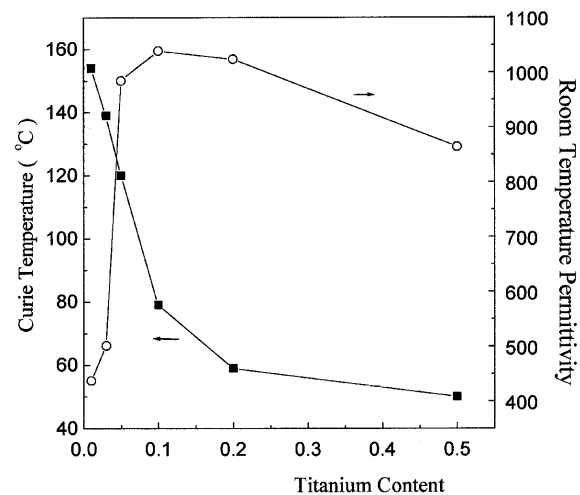


Fig. 4. Behavior of the Curie temperature and room temperature permittivity with the increase of Ti content in samples sintered at 1200°C during 5 h. The Curie temperature shows a strong linear decrease over the composition region where the samples are monophasic. In the region where the system presents more than one phase (according to the XRD), the variation of the Curie temperature is less pronounced. A maximum in room temperature permittivity is observed for 0.1 of Ti content.

parameter shows a steep linear descent over the composition region (until 0.1 of Ti content) where the samples are monophasic, according to our XRD observations. However, in the region where the system presents more than one phase (according to the XRD), the variation of the Curie temperature is less pronounced. A similar result was obtained by Ravez et al. in oxifluoride systems [14]. This fact may be associated with the deviation from stoichiometry of the expected system due to the appearance another phase, which has a direct influence in the phase transition process.

The decrease of the Curie temperature with increasing titanium concentration, may be explained by the increase of the structural disorder due to the presence of several ions located in the same crystallographic sites (B sites). This disorder reduces the binding forces of the ions in the lattice, provoking a decrease of the potential barrier and, consequently, the thermal energy needed to destroy the spontaneous polarization leading the system to the paraelectric state.

The inverse permittivity vs. temperature curves do not follow a Curie–Weiss law, fulfilling rather a relationship of the type:

$$\frac{1}{\varepsilon} - \frac{1}{\varepsilon_{\max}} = \frac{(T - T_c)^2}{2 \cdot \delta^2 \cdot \varepsilon_{\max}}$$

where ε is the permittivity, T_c is the Curie temperature and δ is the diffuse phase transition coefficient. The above mentioned expression gives the structural disorder degree of the system and is related to the distribution of polar microregions in the paraelectric state.

Using this expression, the value of δ in each curve was calculated and reported in Table 1. An increase of

δ is found with the rise of Ti content over the monophasic region ($y < 0.1$), reaffirming that the inclusion of Ti enhances the structural disorder, increasing therefore the diffuse character of the transition. At the same time, Fig. 4 shows an improvement of the room temperature permittivity up to 0.1 of Ti content.

Table 1 summarizes the principal ferroelectric properties of the studied materials and, in general, all the properties change with the Ti content. The LSBNT10 is the composition where the material becomes polyphasic and can be considered as a reference from which changes of the material properties of all the other compounds are measured.

4. Conclusions

We have obtained the $\text{Sr}_{0.255}\text{La}_{0.03}\text{Ba}_{0.7}\text{Nb}_{2-y}\text{Ti}_y\text{O}_{6-y/2}$ ceramic system at different concentrations of titanium cation, where the Nb^{5+} was substituted by Ti^{4+} in such a way that oxygen vacancies must appear to preserve electrical neutrality. A single phase compound is observed for low Ti content ($y < 0.1$) in the XRD spectra, being isostructural with the SBN phase. For high titanium concentrations ($y > 0.1$), the XRD patterns show, besides the SBN phase reflections, some small peaks associated with an additional phase present in the ceramic. The incorporation of titanium into the LSBN system leads to a liquid phase sintering, with relative densities higher than 95% of the theoretical density. Permittivity measurements show strongly broadened dielectric curves for all compositions, indicating the diffuse character of the transition. The Curie temperature values show a strong linear decrease over the composition region (up to 0.1 of Ti content) where the samples are monophasic, according to our XRD observations.

Table 1. Relevant ferroelectric properties of the $\text{Sr}_{0.255}\text{La}_{0.03}\text{Ba}_{0.7}\text{Nb}_{2-y}\text{Ti}_y\text{O}_{6-y/2}$ ceramic system, sintered at 1200°C during 5 h. T_c is the Curie temperature, ε_{RT} is the room temperature permittivity, $\text{Tan}\delta_{\text{RT}}$ is the room temperature dielectric loss, ε_{\max} is the maximum permittivity and δ is the diffuse phase transition coefficient

Titanium content	Density (g/cm ³)	T_c (°C)	ε_{RT}	ε_{\max}	$\text{Tan}\delta_{\text{RT}}$	δ (°C)
0.01	4.93	154	437	1490	0.019	61
0.03	5.03	139	501	1352	0.014	64
0.05	5.10	120	985	1338	0.010	68
0.1	5.12	79	1039	1130	0.005	86
0.2	5.25	59	1024	1108	0.006	82
0.5	5.24	50	864	1046	0.010	55

While in the region where the system presents more than one phase, the variation of the Curie temperature is smaller. The diffuse phase transitions coefficient was calculated, reaffirming the rise of the structural disorder with the increase in Ti content in the monophasic region.

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