

Sintering Characteristics of the LSBN Ceramics and Influence of the Lanthanum Content

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Abstract

SBN-30 ceramics doped stoichiometrically with 1, 3 and 5% of La, i.e. the $\text{Sr}_{0.3-3y/2}\text{La}_y\text{Ba}_{0.7}\text{Nb}_2\text{O}_6$ system (LSBN) were obtained. The influence of La content and the sintering characteristics were studied by X-ray diffraction (XRD) and thermo-electric analysis (TEA). When the La concentration is 0.05, various reflections XRD shifted to higher angles. The density increases linearly with $\ln t$, where t is the sintering time and the values of the maximum of permittivity curves rose monotonously with t for 1 and 3%, with a strong dependence on the porosity. The dynamics, diffusion of the porous respond to a mechanism of D4 type with $k_D = 0.0017$ and 0.0016 for 0.01 and 0.03, respectively. For 0.05 a lower decrease of the porosity with sintering time was found, and the maximum values of the permittivity remained constant. The dielectric properties of the ceramic start to deteriorate in this case. © 1998 Elsevier Science Limited. All rights reserved

1 Introduction

$\text{Sr}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$ (SBN) series of compounds crystallize in the tetragonal–tungsten–bronze crystal structure forming a solid solution in the range of $0.25 \leq x \leq 0.75$.¹ They exhibit very good ferroelectric properties, electro-optic characteristics with large electro-optic coefficient, and photorefractive effects, these compounds receive an increasing attention as a potential photorefractive medium for three-dimension holographic data storage.² Moreover, the SBN system possess excellent pyroelectric properties with fast response time.³

The difficulty in growing large crystals with good homogeneity is the major obstacle for practical applications of this excellent material.⁴ The applications of SBN materials in the mentioned areas have been thoroughly investigated for ceramics.^{4,5} However, these require a very precise control of microstructure and the composition; that is the details of sample preparation as the addition of dopants, the sintering atmosphere, and the firing conditions. A large amount of papers have been reported in this topic.^{6,7}

The addition of small amounts of rare-earth and other ions have been a usual way to change the microstructure of the compounds, in some cases with an increase of the diffusion and densification rates⁶ and in others with an increase of the grain growth.⁸

The Lanthanum adding SBN ceramics has helped, for example, to decrease the SBN transition temperature, improving therefore the dielectric and pyroelectric properties of the material at room temperature.^{9,10} Furthermore, the lattice parameters shift with the increase of Lanthanum content.¹¹

The present paper is concerned with the effects of the sinterization conditions and the influence of the Lanthanum content in the $(\text{Sr}_{0.3-3y/2}\text{La}_y\text{Ba}_{0.7})\text{Nb}_2\text{O}_6$ ceramic system.

2 Experimental Procedure

The composition of the studied system is given by $\text{Sr}_{0.3-3y/2}\text{La}_y\text{V}_{y/2}\text{Ba}_{0.7}\text{Nb}_2\text{O}_6$ where V stand for the vacancies at the Sr–Ba sites. The samples were prepared via the conventional ceramic technique by mixing high purity reagents (BaCO_3 , SrCO_3 , La_2O_3 and Nb_2O_5) with $y = 0.01$, 0.03 and 0.05 in

a agate mortar with ethyl alcohol for 2 h. The powder were pre-fired for 2 h at 900°C, pressed into disks with a diameter of 10 mm at 612 Mpa, and sintered at 1400°C with sintering time between 1 and 5 h.

After sintered, the density of specimens were measured by calculating the specimen volume from its dimensions and by weighing it. The temperature dependence of the dielectric permittivity was measured with a RLC bridge (TESLA BM509) at a frequency of 1 kHz, coupling at a PC-micro-computer, using silver electrodes deposited by a diffusion technique. Crystalline phases were identified by XRD using $\text{CuK}\alpha$ radiation with increase 0.05°/step.

3 Results and Discussion

3.1 Sintering process

The general characteristic of $\text{Sr}_{0.285}\text{La}_{0.01}\text{Ba}_{0.7}\text{Nb}_2\text{O}_6$ ceramic samples as a function of thermal history are summarized in Table 1.

X ray diffraction of the ceramic shown in Fig. 1 corresponds to sintering time of 2, 3 and 4 h. In all cases a compound single phase are observed belonging to the SBN phase.

The dependence of the density versus sinterization time of $\text{Sr}_{0.285}\text{La}_{0.01}\text{Ba}_{0.7}\text{Nb}_2\text{O}_6$ ceramic was shown in.¹² The density increases linearly with logarithm of time, as predicted by Coble's model.¹³ The densification rates calculated at several times from the slope of the curve decrease from 0.66 with correlation coefficient $r = 0.994$ for 1 to 3 h to 0.015 with $r = 0.993$ for 3 to 5 h. This indicates that densification rate reduces.

The maximum values of the permittivity increase monotonously with sintering time. In general, the increase of the permittivity have three major causes: (1) dopants content increase;¹⁴ (2) grain size increase and (3) the decreasing of the porosity.¹⁵ The first cause was eliminated because shifts in Curie temperature are not observed (Table 1).

To analyze the other two cases, the real values of the permittivity without porosity were calculated, using Wiener's mixture rule and assuming that the porosity is not interconnected,¹⁵ we have:

Table 1. Processing conditions and general characteristics

Firing condition	Density $\times 10^3$ (Kg m^{-3})	Permittivity (ϵ)	Curie temperature ($^{\circ}\text{C}$)
1400°C 1 h	3.82	1183	172
2 h	4.60	1290	170
3 h	5.33	1670	171
4 h	5.37	1697	171
5 h	5.41	1832	170

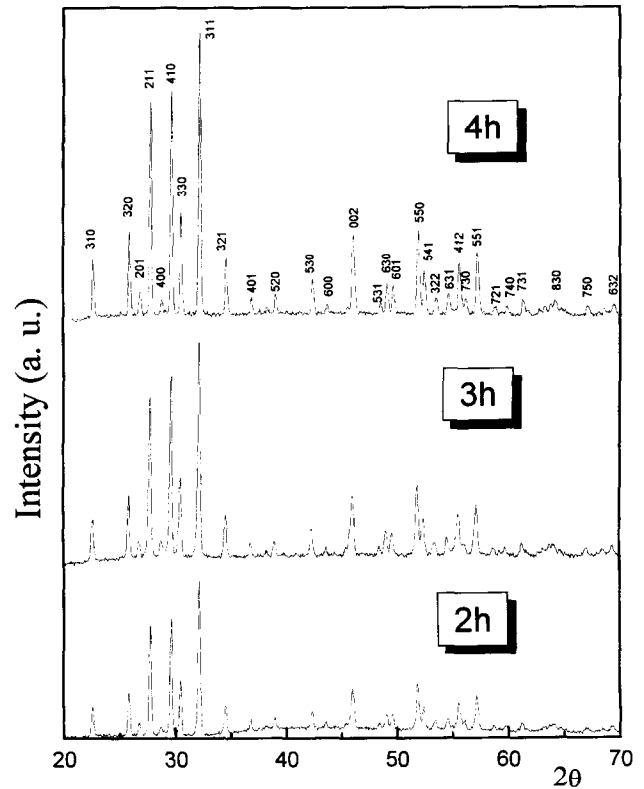


Fig. 1. XRD of $\text{Sr}_{0.285}\text{La}_{0.01}\text{Ba}_{0.7}\text{Nb}_2\text{O}_6$ ceramic sintered for 2, 3 and 4 h.

$$\epsilon_T = \epsilon_M \left(1 + \frac{1}{2} V \right) / D \quad (1)$$

where ϵ_T and ϵ_M are the value of the permittivity without porosity and the measured, respectively, V is the volume fraction of porosity for phase two, which is assumed to be constituted of spheres

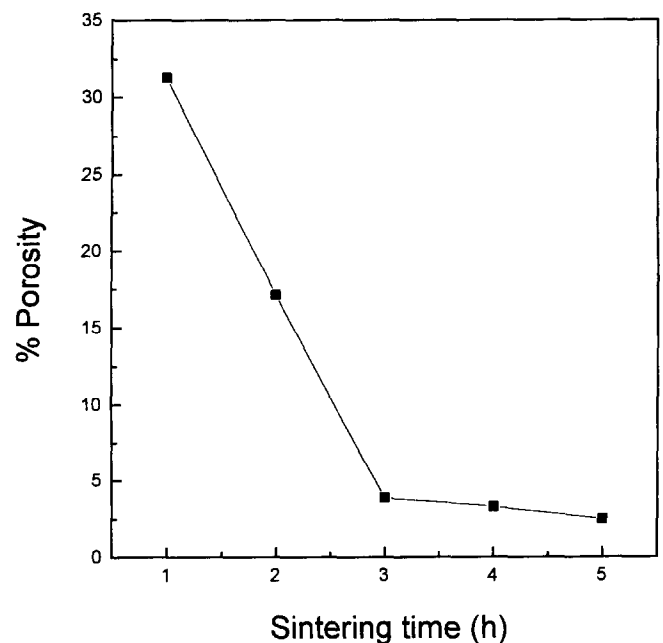


Fig. 2. Porosity with sintering time for $\text{Sr}_{0.285}\text{La}_{0.01}\text{Ba}_{0.7}\text{Nb}_2\text{O}_6$ ceramic.

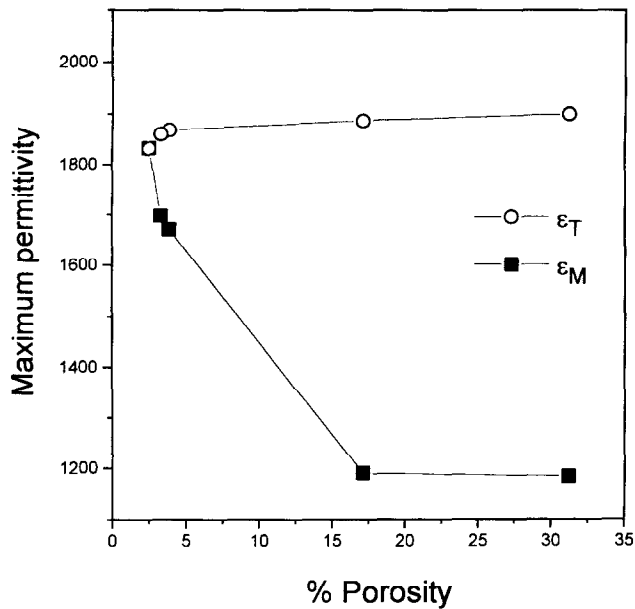


Fig. 3. Porosity dependence of maximum real and measured permittivity for $\text{Sr}_{0.285}\text{La}_{0.01}\text{Ba}_{0.7}\text{Nb}_2\text{O}_6$ ceramic.

embedded in a matrix of phase one, and D is the rate between the measured and theoretical density.

The decrease in porosity observed with a sintering time is shown in Fig. 2. This behavior was explained by Coble's model,¹³ where it describes the intermediate and final stages of sintering of single phase crystalline solids by bulk diffusion of vacancies from pores to grain boundaries. Values below 5% of the porosity were obtained for 3 h and more.

The maximum values of the real and measured permittivity in function of the porosity are plotted in Fig. 3, which shows ϵ_T constant and ϵ_M decrease. These suggest that the grain size is constant in this time range and indicate that the differences in these permittivities were due only to the porosity. This result is according to a Nishiwaki *et al.*⁴ report on grain size constant for SBN-30 ceramic until 24 h of sintering.⁴

The possible mechanisms of transport of matter has been reported in Ref. 16. It is known that above 1000°C the initiation of the sintering processes

begin, with mechanisms of the volume and grain boundary diffusion. In order to carry out this study we have used the maximum values of the permittivity with porosity, and defined the parameter α_i :

$$\alpha_i = [\epsilon(t_i) - \epsilon(t_o)] / [\epsilon(t_f) - \epsilon(t_o)] \quad (2)$$

where t_i , t_o and t_f are interest, initial and end times respectively. These α_i values in function of the sintering time are a sigmoidal-shaped curve. Using linear regression method we found that dynamic diffusion of the porous responds to a D4 type mechanism,¹⁷ according to the equation:

$$[(1 + \alpha)^{\frac{1}{3}} - 1]^2 = k_D t_s \quad (3)$$

where k_D is the equilibrium constant and its value is $K_D = 0.0017$ with standard deviation of 0.0018 and $r = 0.986$.

3.2 Influence of the Lanthanum content on sintering characteristics

The influence of La content on sintering characteristics was studied for 0.01, 0.03 and 0.05. The effect of the La cation on the XRD lines of sintered ceramics is, when La content is increased, that various reflections shift to a higher angles as shown in Table 2.

Figure 4 shows the variation of crystal structure with La cation in 2θ for the major shift reflections. It is suggested that it has strong dependence on La concentration above 0.03 in SBN ceramic.

In the Fig. 5 it is shown the dependence of the density on La content for 1, 3 and 5 h of sintering time. Decrease of the density for all composition is observed, this indicates that with the increase of La dopant, in the range estimated, the diffusion rate and densification are reduced. This behavior may be explained, because the vacancies introduced by doping are bound to the impurity ions and can not move freely through the crystal to expedite mass transfer. These bound vacancies reduce the

Table 2. XRD of LSBN phase with various La content sintered for 3 h

hkl	0.01			0.03			0.05		
	2θ	$d(\text{\AA})$	I/I_o	2θ	$d(\text{\AA})$	I/I_o	2θ	$d(\text{\AA})$	I/I_o
310	22.60	3.934	40	22.55	3.943	42	22.80	3.899	40
420	32.10	2.788	100	32.10	2.788	100	32.25	2.776	100
321	34.50	2.600	41	34.45	2.603	39	34.65	2.589	49
401	36.75	2.446	36	36.75	2.446	30	36.90	2.436	36
002	45.95	1.975	47	45.95	1.975	34	46.35	1.959	57
322	53.35	1.717	32	53.40	1.716	30	53.70	1.707	40
412	55.50	1.656	41	55.50	1.656	39	55.85	1.646	52
332	56.05	1.641	31	56.10	1.639	30	56.40	1.631	38
242	57.15	1.612	45	57.10	1.613	42	57.20	1.610	50

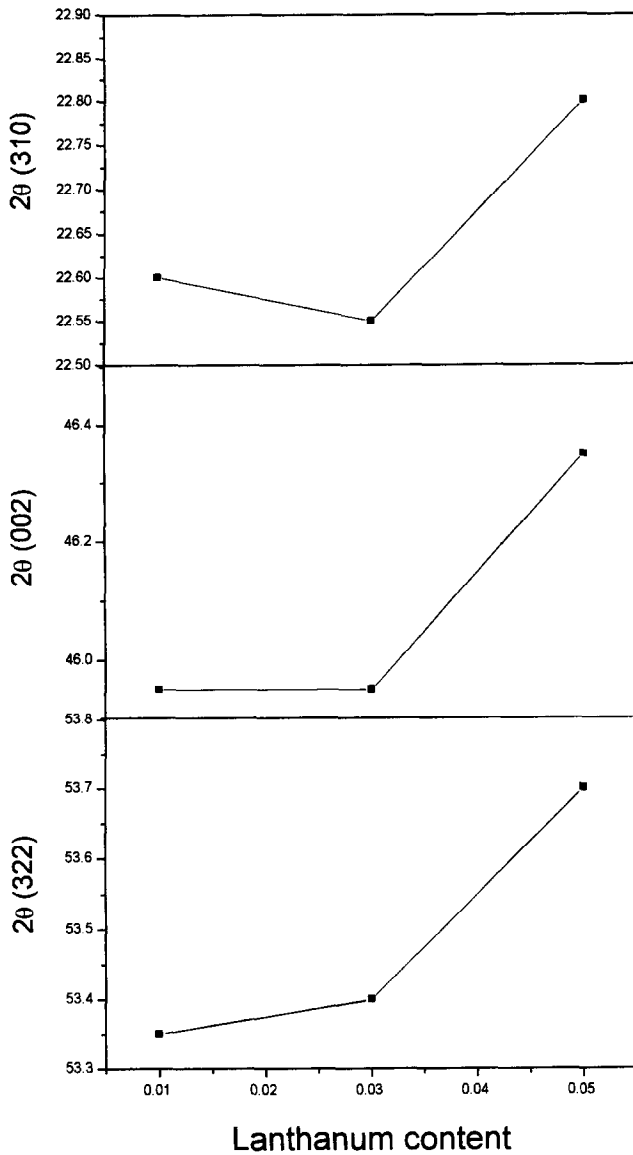


Fig. 4. Major shift reflections with La content for $Sr_{0.3-3y/2}La_yBa_{0.7}Nb_2O_6$ ceramics system.

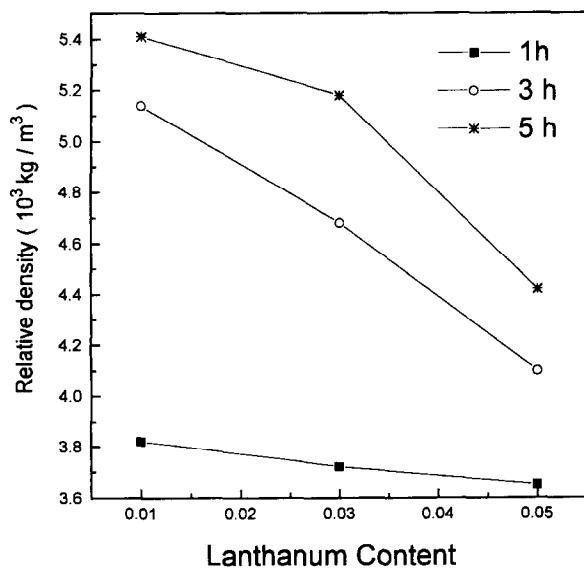


Fig. 5. Dependence of relative density with La content for $Sr_{0.3-3y/2}La_yBa_{0.7}Nb_2O_6$ ceramics system.

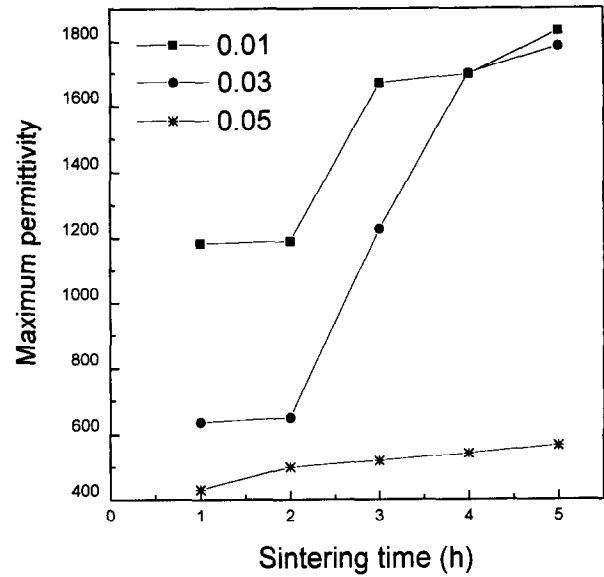


Fig. 6. Maximum permittivity with sintering time for $Sr_{0.3-3y/2}La_yBa_{0.7}Nb_2O_6$ ceramics system.

concentration of unbound vacancies and retard the diffusion.⁶ The maximum values of the permittivity for 0.03 composition of La content for different sintering time are below the obtained in 0.01 La content as shown in the Fig. 6. This result can be explained using the model of decreasing of movement of the grain boundary.⁶ The porosity has the same behavior, but with higher values, (Fig. 7). The mechanism of move of the porous from the bulk to grain boundary also responds to diffusive processes of D4 type. $K_D = 0.0016$ with standard deviation of 0.0023 and $r = 0.988$.

In the case of 0.05 La cation concentration, the maximum values appreciated of the permittivity is almost constant at about 600 and below 0.01 and 0.03 La content. Low decrease of the porosity was

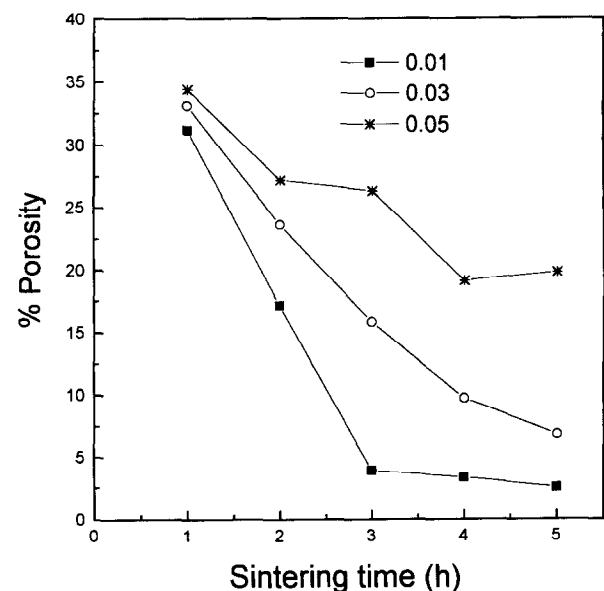


Fig. 7. Porosity with sintering time for $Sr_{0.3-3y/2}La_yBa_{0.7}Nb_2O_6$ ceramics system.

found. This result can be explained assuming that an amorphous phase exists, according to Randall *et al.*¹⁸ The ceramic microstructure is a mixture of parallel and series intergranular boundaries, where the series boundaries could dominate the permittivity owing to the small volume fraction of glassy phase existing with amorphous nature, implying a low permittivity relative to ferroelectric grain.

4 Conclusions

The densification rate calculated at several times from the slope of the dependence of the density versus sinterization time of $\text{Sr}_{0.285}\text{La}_{0.01}\text{Ba}_{0.7}\text{Nb}_2\text{O}_6$ ceramic decrease from 0.66 for 1 to 3 h to 0.015 for 3 to 5 h. The maximum values of the permittivity for the former composition rose monotonously with sintering time due to decrease of the porosity. The influence of La content on sintering characteristics suggests that this system has strong dependence on La concentration. The dynamics of the diffusion of porous respond to a mechanism of the D4 type with $K_D = 0.0017$ and 0.0016 for 0.01 and 0.03 of the La amount, respectively.

For the case of 0.05 La cation concentration the permittivity is lower than 0.01 and 0.03 La content and remains almost constant with sintering time, besides porosity remain above 20%. The dielectric properties of the ceramic start to deteriorate.

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