Diffuse Phase Transition of the $Sr_{0.3-3y/2}La_yBa_{0.7}Nb_2O_6$ Ceramic System

FIDEL GUERRERO,[a] HARVEY AMORÍN,[b] JORGE PORTELLES,[b,c] JESÚS M. SIQUEIROS[c] & SARA AGUILERA[d]

[a]Facultad de Ciencias Naturales, Universidad de Oriente, Santiago de Cuba 90500, Cuba

[b]Facultad de Física-IMRE, Universidad de la Habana, Vedado, La Habana 10400, Cuba

[c]Centro de Ciencias de la Materia Condensada, Universidad Nacional Autónoma de México, Apartado Postal 2681, Ensenada, Baja California, México, 22800

[d]Departamento de Física, Facultad de Ciencias, Universidad Católica del Norte, Angamos 0610, Casilla 1280, Antofagasta, Chile

Abstract. The effect of Lanthanum cation doping in the diffuse phase transition of the $Sr_{0.3-3y/2}La_yBa_{0.7}Nb_2O_6$ ceramic system is studied for $y = 0.01$, 0.03 and 0.05. For these compositions, the transition temperature T_c shifts towards higher values with increasing frequency and the temperature dependence of the electrical permittivity presents strongly broadened curves which suggest a non Curie-Weiss behavior near the transition temperature for temperatures far from T_c. The diffuse phase transition coefficient (δ) was also determined and its values lead us to conclude that the degree of disorder in the system increases with the presence of the Lanthanum cation. This result is corroborated by calorimetric measurements, where an increase in entropy with the Lanthanum concentration is also found.

Keywords: diffuse-phase transition, LSBN, ferroelectric ceramics

Introduction

A diffuse phase transition (DPT) occurs whenever the following behavior is observed [1]: 1) The transition temperature, as measured from dielectric studies, shows an apparent finite shift towards higher temperatures with increasing frequency. 2) The peak in Tanδ appears at a temperature different from the transition temperature of the material. 3) The normal Curie-Weiss behavior in the permittivity curves is not valid near the apparent Curie temperature but only at temperatures distant from it. 4) The transition temperature, as obtained from pyroelectric measurements, does not coincide with that obtained from the permittivity or Tanδ curves. This behavior may be due to composition fluctuations, thermal fluctuations in Curie regions, structural defects, etc. [2]. In particular, for the Strontium-Barium-Niobate (SBN) system, this effect is very pronounced [3,4] and depends on the Sr/Ba ratio in the system [3].

In previous publications [5,6] it was reported that the dielectric properties of the $Sr_{0.3-3y/2}La_yBa_{0.7}Nb_2O_6$ system for $y = 0.01$, 0.03, 0.05 are modified by the cationic substitution of Sr^{2+} by La^{3+}. By studying the behavior of the density (ρ) and the dielectric permittivity (ε) it is shown that the La^{3+} lie in A sites favoring thus the formation of the LSBN ferroelectric ceramics, where for values of $y \geq 0.05$ a degradation in the dielectric permittivity is observed. A linear decrease in the transition temperature as a function of the La concentration in the samples is also observed [6]. The behavior of the pyroelectric coefficient and the spontaneous polarization of these materials with the Lanthanum cation doping was also analyzed [7] observing an increase of these properties up to a maximum value for the 3% concentration. For the 5% doping, however, the pyroelectric and dielectric properties diminish, due to the apparent existence of a solubility limit of the substituted ions in the SBN solid solution. A decrease of the coercive

field of the LSBN-3% with respect to the LSBN-1% system and the increase of E_c for the LSBN is also observed [7].

Being the SBN a relaxor ferroelectric, the influence of the La doping on the DPT is of great importance. This work is dedicated to the study of the influence of the Lanthanum cation content in the diffuse phase transition (DPT) of the $Sr_{0.3-3y/2}La_yBa_{0.7}Nb_2O_6$ ceramic system.

Experimental Procedure

The composition of the studied system is given by $Sr_{0.3-3y/2}La_yBa_{0.7}Nb_2O_6$ with $y = 0.01$, 0.03 and 0.05, labeled LSBN1, LSBN3 and LSBN5 respectively. The samples were obtained by the traditional ceramic method. The powders were calcined at $900\,°C$ for $2\,h$. The resulting powders were uniaxially die-pressed at $6\,ton/cm^2$ into discs of $10\,mm$ diameter and $1\,mm$ thickness, and sintered at $1400\,°C$ during $5\,h$.

After the sintering process, the dependence of the dielectric permittivity (ε') and the dielectric losses (Tanδ) were measured with a PC controlled bridge (PHILIPS PM6303) at a frequency of $1\,kHz$ using diffused silver electrodes at $750\,°C$. A GR 1615 capacitance bridge was used for measuring the frequency dependent permittivity over the 10–$10^5\,Hz$ range. For calorimetric measurements, the samples were pulverized and data were collected in a differential scanning calorimeter (DSC) (Mettler TA-4000) at a heating rate of $5\,°C/min$.

Results and Discussion

Figure 1 shows the frequency dependence of the temperature of maximum permittivity for all the samples, where the temperatures show a shift towards higher values with increasing frequency, indicating that we are in presence of relaxor-type systems.

Figure 2 shows the dependence of the permittivity and the dielectric losses with temperature, measured at $1\,kHz$ for all the samples. Here we can see that dielectric losses exhibit a peak at a lower temperature than that for the permittivity maxima, and the smallest difference between both temperatures is for the LSBN1 ceramic. The transition temperatures and room temperature permittivities are shown in Table I. Dielectric losses at room temperature for all compositions are also indicated, where the LSBN3 sample
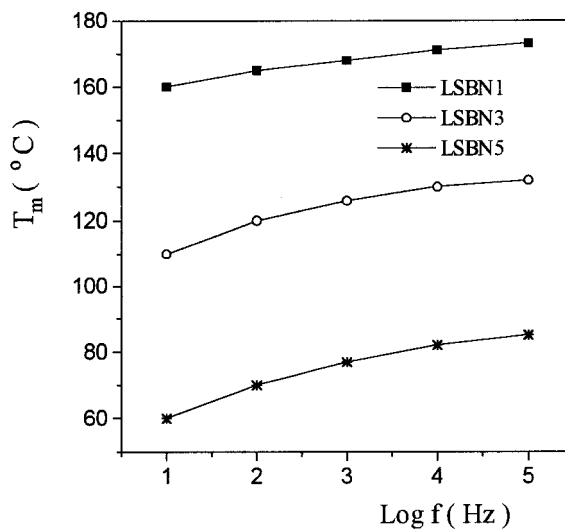

Fig. 1. Frequency dependence of the temperature of maximum permittivity (T_m) in LSBN samples.
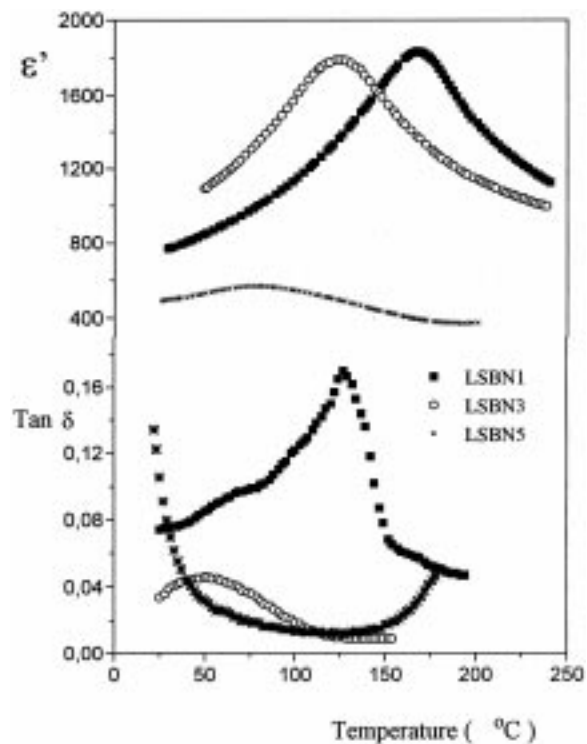

Fig. 2. Permittivity and dielectric losses as functions of temperature for all the samples at a frequency of $1\,kHz$.

exhibits the greater permittivity and the smaller dielectric losses. The permittivity *Vs* temperature curves are strongly broadened suggesting a non Curie-Weiss behavior near the transition temperature.

The behavior of the reciprocal permittivity versus temperature for different compositions, at 1 kHz, is shown in Fig. 3. The curves have been divided in three regions, following the method reported in [1]. The first region governs the behavior of the ferroelectric phase up to the transition temperature T_m. The Curie temperature T_c is obtained in this region by extrapolating the linear data toward the temperature axis. The second region (near the transition temperature) indicates a diffuse phase transition up to

temperature T_o, and the third region displays the linear behavior of $1/\varepsilon$, establishing the validity of the Curie-Weiss law in this paraelectric phase. The Curie-Weiss temperature T_{cw} is obtained over this latter region by extrapolating the data toward the temperature axis.

The difference between the Curie-Weiss temperature and the Curie temperature $(\Delta T = T_{cw} - T_c)$ reveals the nature of the ferroelectric-paraelectric phase transition. In our case ΔT shows an increasing trend with the increase in Lanthanum content, indicating that the phase transition becomes more diffuse. The values of T_c, T_{cw}, T_o and ΔT are shown in Table II.

Assuming a gaussian distribution for the compositional fluctuation and the polarization fluctuation, the reciprocal of the dielectric constant versus temperature obeys a quadratic relation [7]. A general form of this quadratic law (for $\varepsilon > \varepsilon_m$) is

$$\frac{1}{\varepsilon} = \frac{1}{\varepsilon_m} + A(T - T_m)^{\gamma} \tag{1}$$

where

$$A = \frac{1}{2\varepsilon_m \delta^2}$$

and

$$\delta^2 = \frac{(T - T_m)^{\gamma}}{2\varepsilon_m \left(\frac{1}{\varepsilon} - \frac{1}{\varepsilon_m} \right)}$$

where ε is the dielectric constant, ε_m is the maximum dielectric constant, T_m is the transition temperature and T is the operating temperature. In the above expression γ takes values between $1 < \gamma < 2$ [8] and δ is the diffuse phase transition coefficient, which measures the degree of cation disorder in the system.

The slope of the graph of $Ln\left(\frac{1}{\varepsilon} - \frac{1}{\varepsilon_m}\right)$ plotted against $Ln(T - T_m)$ provides the values of γ.

Table I. Transition temperatures from dielectric measurements, room temperature permittivity (ε_{amb}) and room temperature dielectric losses (Tanδ_o) at 1 kHz

Sample	T_m (°C)	$T_{\tan\delta}$ (°C)	ε_{amb}	Tanδ_o
LSBN1	168	127	762	0,074
LSBN3	126	52	965	0,034
LSBN5	77	—	491	0.134
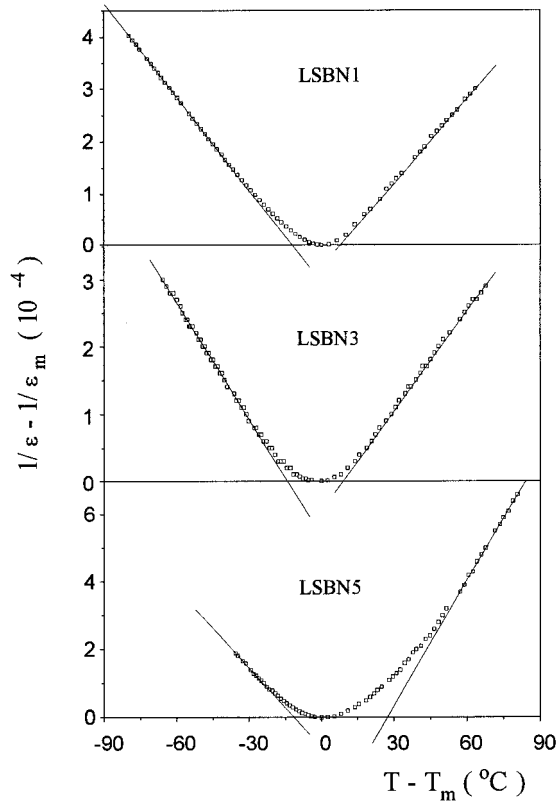
Fig. 3. Temperature dependence of the reciprocal permittivity at 1 kHz for all the samples.

Table II. Different parameters that characterize a diffuse phase transition

Sample	T_c (°C)	T_{cw} (°C)	ΔT ($T_{cw} - T_c$)	T_o (°C)	C (10^{-5})°C	δ (°C)
LSBN1	156	176	20	205	2,18	42
LSBN3	112	135	23	176	2,32	46
LSBN5	66	104	38	—	—	78

The variation of $\text{Ln}\left(\frac{1}{\varepsilon} - \frac{1}{\varepsilon_m}\right)$ as a function of $\text{Ln}(T - T_m)$ for the three studied compositions is shown in Fig. 4 where two regions can be distinguished, one for $\gamma = 1$ and one for $\gamma = 2$. The values of δ were determined from the $\gamma = 2$ region with the use of Eq. 1. The resulting values are given in Table II where an increase in δ with the increase of Lanthanum content can be seen. This result can be explained by taking into account that the substitution of Strontium by Lanthanum gives the doping element more possible accessible locations in the lattice because of (1) intrinsic vacant sites of the SBN system (free vacancies) and (2) empty sites made available upon drawing Strontium. This fact causes more disorder in the material, since now there will be three cations (Ba, Sr and La) to occupy the same A site in the TTB structure of this system. Moreover notice that substitution of Sr^{2+} by La^{3+} must generate further vacancies in the structure (bound vacancy) to preserve electrical neutrality.

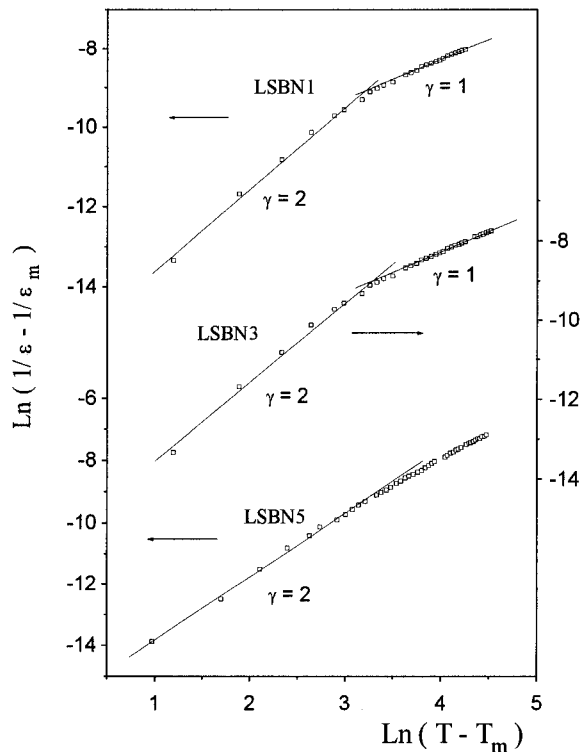In the region where $\gamma = 1$, the Curie-Weiss holds, starting at $T = T_o$. The difference between T_o and T_m

is related to the energy needed for depolarizing all the polar microregions in the paraelectric state, a condition necessary for the Curie-Weiss behavior. This difference increases with the increase in Lanthanum content, reaffirming that the phase transition becomes more diffuse.

In the LSBN5 sample, this second region ($\gamma = 1$) was not as well defined as in the other two compositions. This may be due to an apparent overlapping with a low frequency dielectric dispersion arising, probably, from grain boundary or interface contributions (similar to the results reported for PLZT ceramics in [9]).

By plotting $(T - T_m)/(\frac{1}{\varepsilon} - \frac{1}{\varepsilon_m})$ against temperature, the Curie constant C was obtained as an extrapolation of the horizontal region of this curves and is also shown in Table II.

In previous work [7], a transition temperature obtained from pyroelectric measurements different from that of the maximum permittivity temperature was found.

Measurements of specific heat at constant pressure as a function of temperature produce strongly broadened curves as expected for a diffuse phase transition. The specific heat, the transition heat and the entropy change of the transition are shown in Table III. An increase of these magnitudes with the inclusion of Lanthanum is observed, due to an increase in the disorder of the material.

Conclusions

The effect that the Lanthanum cation produces as doping element in the diffuse phase transition of the $Sr_{0.3-3y/2}La_yBa_{0.7}Nb_2O_6$ ceramic system is studied from dielectric and calorimetric measurements.

The transition temperatures of the samples undergo a shift towards higher values with increasing frequency, evidencing the a relaxor nature of the systems. The dielectric losses exhibit a peak at a temperature lower than that for the permittivity

Fig. 4. A plot of $\text{Ln}(1/\varepsilon - 1/\varepsilon_m)$ against $\text{Ln}(T - T_m)$ for all the samples.

Table III. Differential scanning calorimetric measurements

Sample	Cp (J/gK)	ΔQ (J/g)	ΔS (J/gK)
LSBN1	0.415	14,95	0.051
LSBN3	0.437	16,69	0.057
LSBN5	0.452	19,46	0.073

maxima and the permittivities show strongly broadened dielectric curves which indicate a non Curie-Weiss behavior near the transition temperature, at temperatures distant from it.

The diffuse phase transition coefficient increases with the increase in Lanthanum content, indicating that the Lanthanum rises the degree of cation disorder in the system. This behavior is corroborated by calorimetric measurements, where the entropy of the transition is also increased with the Lanthanum doping.

Acknowledgments

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