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Electrical Properties of the Titanium Modified SBN Ceramic System

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Abstract. The electrical properties of the $Sr_{0.3}Ba_{0.7}Nb_2O_6$ system modified with different concentrations of titanium, following the general formula $Sr_{0.3}Ba_{0.7}Nb_{2-y}Ti_yO_{6-y/2}$ for charge compensation, are studied. The investigation is carried out in samples prepared by the conventional ceramic method. The X-ray diffraction analysis shows tetragonal tungsten bronze monophasic compounds in all cases. Dielectric measurements show a typical ferroelectric behavior with diffuse phase transition, where the transition temperature and the maximum permittivity decrease with increasing titanium content. The remanent polarization is obtained from hysteresis measurements in the ferroelectric region, while at high temperatures, two processes (a conductive and a ferroelectric process) are overlapping. The diffuse character of the ferroelectric-paraelectric phase transition is also studied and the diffusivity coefficient calculated in all cases.

Keywords: Ferroelectric ceramics, diffuse phase transition, doped SBN

Introduction

In the Tetragonal Tungsten Bronze (TTB) $Sr_{1-x}Ba_x$-Nb_2O_6 (SBN) system, the ferroelectric, optical and pyroelectric properties strongly depend on the Sr/Ba ratio [1, 2]. The $Sr_{0.5}Ba_{0.5}Nb_2O_6$ (SBN 50/50) system has been, perhaps, the most investigated composition, because of its large dielectric response at room temperature [1–3]. However, there are reports of great interest over a wide composition range of SBN solid solutions in which the addition of other cations has been particularly useful in improving the ferroelectric properties [4–6]. In the specific case of the La-doped SBN 30/70 system, a lowering in the transition temperature and an increase of the diffuseness and the pyroelectric response at room temperature has been reported [7–9]. The former is probably provoked by the substitution of Sr^{2+} by La^{3+} in the crystallographic A sites of the TTB structure. The present work is mainly concerned with the study of the electrical properties of the $Sr_{0.3}Ba_{0.7}Nb_{2-y}Ti_yO_{6-y/2}$ (SBNT) ceramic system, where the Ti^{4+} cation is incorporated into the SBN30/70 substituting the Nb^{5+} at the crystallographic B sites.

Experimental Procedure

The ceramic samples were elaborated by the conventional ceramic method, starting from raw materials (oxides and carbonates) of high purity grade. Mixtures of the type $0.3\ SrCO_3 + 0.7BaCO_3 + yTiO_2 + (1 - y/2)Nb_2O_5$, with $y = 0.01,\ 0.03,\ 0.05,\ 0.07$, were prepared in an agate mortar for 2 h. The resulting powders were calcined at 1100°C for 2 h and then uniaxially die-pressed at 612 Mpa into discs of 10 mm diameter and 1 mm thickness. Sintering was performed at 1250°C during 5 h.

To follow the phase evolution of the ceramics as niobium is substituted by titanium, X-ray diffraction (XRD) study of the sintered samples was performed at room temperature in a JEOL diffractometer with Cu K_α radiation, where a qualitative behavior of the phase formation is obtained. For dielectric and

hysteresis measurements, silver electrodes were deposited on both surfaces of the sintered disk-shaped samples. Capacitance measurements were then carried out from room temperature to 250°C in an LCR meter (Philips PM6303) working at a frequency of 1 kHz. The hysteresis loop measurements were performed using a modified Sawyer-Tower circuit and displayed in a memory oscilloscope (Tektronix 210). A Eurotherm controller was used for measurements with temperature.

Results and Discussion

Considering that the valences of titanium and niobium cations are 4+ and 5+ respectively, the substitution of Nb by Ti to form the $Sr_{0.3}Ba_{0.7}Nb_{2-y}Ti_yO_{6-y/2}$ dielectric structure will demand a charge compensation mechanism to achieve electrical neutrality. Generation of oxygen vacancies during the formation process will lead to a stable structure from the beginning and will be favored over other mechanisms such as free charge compensation. XRD analysis provides the basic information on the phase evolution of the $Sr_{0.3}Ba_{0.7}Nb_{2-y}Ti_yO_{6-y/2}$ (SBNT) ceramic system. The results indicate that for the SBNT compositions under study the system is TTB monophasic, where the reflections appear to correspond to those found in the $Sr_{0.3}Ba_{0.7}Nb_2O_6$ (SBN 30/70) crystalline phase [10, 11].

Figure 1 shows the temperature dependence of the permittivity (ε) for all the studied samples. The permittivity curves show broad phase transitions in all cases. This is a typical behavior of ferroelectric materials with diffuse phase transition (DPT) [12]. The existence of polar microregions above the average transition temperature, provoking the DPT character, is mainly a consequence of composition and local polarization fluctuations [13, 14]. Above the transition temperature (around 150°C, see Fig. 1(b), the tanδ curve shows an increase possibly due to a conduction mechanism, involving perhaps, space-charge or interfacial polarization effects [15, 16].

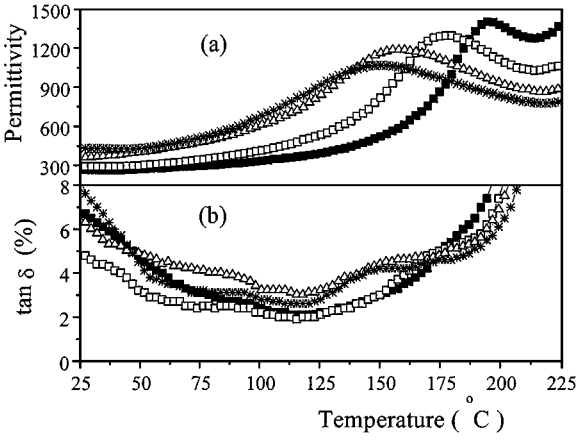

Fig. 1. Temperature dependence of (a) permittivity and (b) dielectric losses for $y =$ (■) 0.01, (□) 0.03, (△) 0.05 and (∗) 0.07 of titanium content.

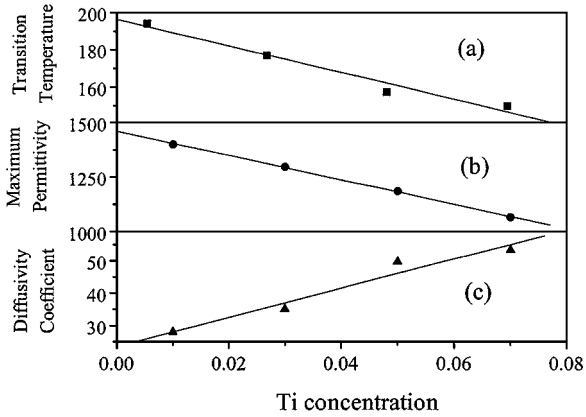

Fig. 2. Titanium content dependence of (a) transition temperature (■), (b) maximum permittivity (●) and (c) diffuseness coefficient (▲).

In Fig. 1(a) it is also observed that both, transition temperature (T_m) and the maximum permittivity (ε_m) $\equiv \varepsilon(T_m)$, decrease with increasing titanium content. Figure 2(a) and (b) show clearly these variation, where both parameters decrease linearly over the studied composition range. Although no evidence for complete incorporation of the titanium into the TTB structure of the SBN system is obtained, from the linear behavior of T_m with titanium concentration it is inferred that an increasing percentage of titanium is incorporated as the initial titanium content increases.

Figure 3 shows the variation of the remanent polarization with Ti concentration, obtained at room temperature from hysteresis measurements. Due to dielectric breakdown, it is difficult to saturate the polarization in the SBNT system at room temperature that is why, to reach saturation of polarization, measurements had to be made at higher temperatures (near and below the transition temperature). It can be seen (for an applied electric field of 20 kV/cm) that the remanent polarization increases with the titanium content, in good

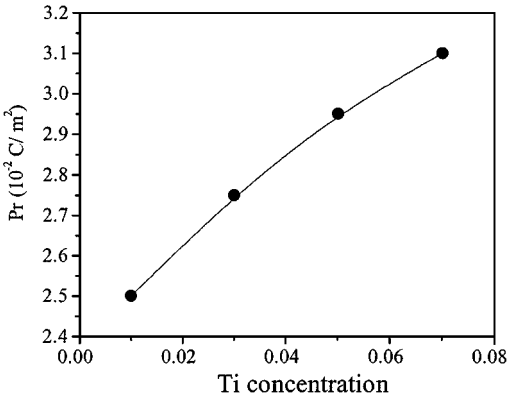

Fig. 3. Dependence of the remanent polarization with Ti concentration measured at 2 MV/m, obtained at room temperature from hysteresis measurements.

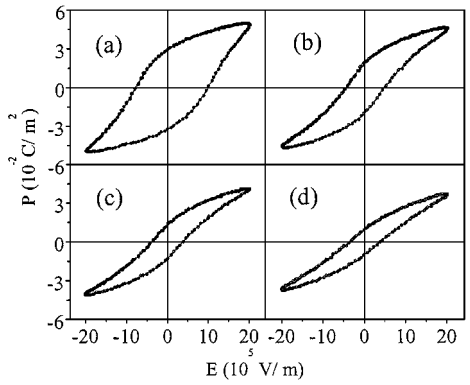

Fig. 4. Variations of the hysteresis loop with temperature measured at 2 MV/m, (a) 25°C, (b) 130°C, (c) 150°C and (d) 170°C for the composition $y = 0.07$ of titanium content.

agreement with the behavior of the room temperature permitivity [11]. This fact suggests that the substitution of niobium by titanium enhances the polarization of the material, for the same maximum applied electric field, in this way improving its ferroelectric behavior.

However, this behavior of the remanent polarization is very different from that obtained from pyroelectric measurements [17, 18]. Here, it must be taken into account that the hysteresis measurements were performed without reaching saturation of polarization; therefore a comparative study would be inappropriate. On the other hand, thermally stimulated current influences the pyroelectric contribution measurements, since different relaxation mechanisms are overlapping in the curve [18]. The pyroelectric contribution was in this case experimentally cleaned for the determination of pyroelectric parameters due only to ferroelectric dipoles [18]. The increasing behavior of the remanent polarization (from hysteresis measurements) and the room temperature permittivity [11] when the titanium concentration is raised is probably associated to the lowering of the ferroelectric-paraelectric transition temperature, leading to an enhancement of room temperature ferroelectric properties. A value of the remanent polarization obtained from hysteresis measurements is meaningful only when saturation of polarization is reached. From pyroelectric measurements, a decrease of the remanent polarization with titanium concentration was obtained [17]. It is therefore evident that titanium doping lowers the total dipole moment per unit volume of the material.

Figure 4 shows the hysteresis loops for $y = 0.07$ Ti concentration. The polarization and the coercive field decrease with temperature. Moreover, above the transition temperature (150°C in this case), there exists a slim-loop hysteretic behavior characteristic of materials with DPT. The slim-loop behavior of DPT-type ferroelectric materials has been interpreted in terms of interacting nanopolar regions embedded in a paraelectric matrix [14]. This model would seemingly be applicable in this case to the slim-loop region above 150°C. For $y = 0.01$ titanium concentration (seeFig. 5) the hysteresis loops practically do not change until 100°C, while above 160°C, the loops become of the elliptical type, probably due to the overlapping of two processes, the ferroelectric polarization and the conductive processes (see tanδ curves in Fig. 1(b). The form of the loop at 195°C (see Fig. 5(d) shows that above the transition temperature, nanopolar regions are still present,

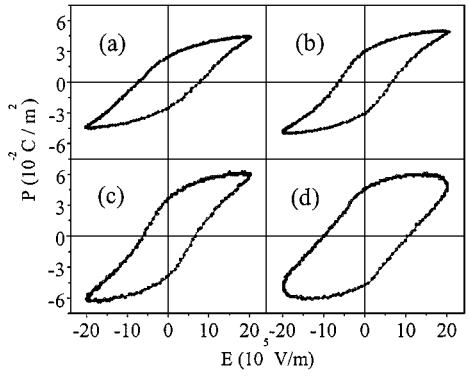

Fig. 5. Variations of the hysteresis loop with temperature measured at 2 MV/m (a) 25°C, (b) 100°C, (c) 150°C and (d) 195°C for the composition $y = 0.01$ of titanium content.

together with the conductive processes. For $y = 0.03$ and 0.05 titanium concentration the loops have similar behavior and, above 160°C approximately, conductive processes appear, while slim-loops are seen above the transition temperature in all the samples.

Equation 1 characterizes the type of ferroelectric-paraelectric transition [12]:

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

where A is a constant and γ is an empirical variable that takes values between 1 and 2. When $\gamma = 1$, the ferroelectric material presents a normal transition, whereas for $\gamma = 2$ the ferroelectric material presents a diffuse phase transition, and the permittivity satisfies the Kirillov-Isupov relation [3, 19]:

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

Here, δ stands for the degree of cation disorder, that is, δ represents the diffuseness degree of the system. An increase in the diffuseness is obtained with increasing titanium content (see Fig. 2(c)), due to the higher cationic disorder in the structure. This fact can also be noticed from Fig. 1(a), that is, the permittivity curves become broader in the transition region. For lower titanium content ($y = 0.01$), the diffuseness coefficient is small (28°C), whereas for $y = 0.07$ the diffusivity coefficient is 53°C. The value of δ for $y = 0.07$ is higher than those obtained in the previously reported LSBN [12] and SBN 50/50 [3] systems, being 42°C in both cases. In the SBN system, the character of the transition depends on the cationic occupation ratio in the A sites (Sr/Ba ratio), allowing for the DPT characteristic of this system [20]. In our case, the increase in diffuseness with titanium content indicates that titanium is responsible for the diffuseness of the phase transition, and then, the diffuseness should be ascribed to the high occupancy disorder in the B sites (ferroactive cation site in the TTB structure), resulting in the decrease of the long-range ferroelectric order.

Conclusions

The electrical properties of the monophasic $Sr_{0.3}Ba_{0.7}Nb_{2-y}Ti_yO_{6-y/2}$ ceramic system with different concentration of titanium cation were studied. The permittivity curves show broad phase transitions, typical of ferroelectrics with diffuse phase transition. The transition temperature decreases linearly with increasing titanium content. The remanent polarization increases at room temperature with the increase of titanium content, in accordance with the rise in the room temperature permittivity. At high temperatures (around the transition temperature) two processes (a conductive and ferroelectric one) overlap. An increase in the diffuseness coefficient is obtained by increasing the titanium content, due possible to the higher cationic disorder in the structure, resulting in the decrease of the long-range ferroelectric order.

Acknowledgments

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