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Study of the dielectric relaxation mechanisms in $KNbO_3$-based electro-ceramics

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Abstract. Electro-ceramics based on the $KNbO_3$ ferroelectric system were synthesized from the solid-state reaction sintering method. In particular, the electrical properties have been investigated at room temperature in the $(1–x)KNbO_3–xBaNi_{1/2}Nb_{1/2}O_{3–\delta}$ (KBNN) solid-solution. The dielectric relaxation mechanisms have been analyzed as a function of the oxygen vacancy (δ) concentration and the frequency dispersion of the complex dielectric permittivity was analyzed in a wide frequency range. The obtained results were discussed within the framework of the current models reported in the literature for the dielectric relaxation processes.

1. Introduction

Ferroelectric materials have been widely studied during the last decades due to their excellent physical properties, which make them excellent candidates for several technological applications in the electro-electronic industry [1].

In particular, in view of the new environmental protection rules imposed, e.g., by the European Union (EU), and the worldwide efforts for using clean energy sources, eco-friendly (heavy metals-free) compounds appear as an alternative to substitute materials containing hazardous and high toxicity elements [2]. Over the last 10 years, a large amount of both single-phase and composite solid-solutions made from low-cost and non-toxic elements have been investigated [3]. In this way, special attention has been recently paid to $KNbO_3$-based ferroelectric systems because of their very interesting physical properties [4–6], together with an enhanced photovoltaic effect [7, 8], which make them multifunctional materials with potential for application in photovoltaic devices [6–8].

In this context, the present work aims the study of the electrical properties of $KNbO_3$-$BaNi_{1/2}Nb_{1/2}O_{(3-\delta)}$ electro-ceramics, considering different oxygen vacancy concentrations (δ = 0.025, 0.05 and 0.15). The dielectric response has been investigated in a wide frequency interval, and the influence of the vacancy defects has been analyzed.

2. Experimental procedure

Perovskite ceramic samples were obtained via the solid-state reaction method considering different oxygen vacancies concentrations [$(A^{'}A^{''})(B^{'}B^{''})O_{3-\delta}$, with $\delta = 0.025$, 0.05 and 0.15], according to the following chemical formulas: $(K_{0.9}Ba_{0.1})(Nb_{0.95}Ni_{0.05})O_{3-0.025}$, $(K_{0.9}Ba_{0.1})(Nb_{0.95}Ni_{0.025})$ $O_{3-0.05}$ and $(K_{0.9}Ba_{0.1})(Nb_{0.90}Ni_{0.05})$ $O_{3-0.15}$ (for the KBNN1, KBNN2 and KBNN3 samples, respectively). High purity starting reagents of K_2CO_3 (98%), Nb_2O_5 (99.9%), $BaCO_3$ (99%) and NiO (99.8%) were used as chemical precursors. The powders were mixed by planetary ball-milling, uniaxial pressed at 20 MPa, and then calcined at 850 ºC for 2 h in an air atmosphere. Next, the mixed oxides were ball-milled again, dried, and then isostatically pressed at 150 MPa. Finally, the samples were sintered in an air atmosphere at 1150 ºC for 2h [9]. Figure 1 depicts a schematic diagram showing the steps for the samples' preparation.

The dielectric properties were collected at room temperature by using an Impedance Analyzer (HP4194A) in the frequency range of 100 Hz–1 MHz. The samples were identified as KBNN1, KBNN2 and KBNN3 for $\delta = 0.025$, 0.05 and 0.15, respectively.

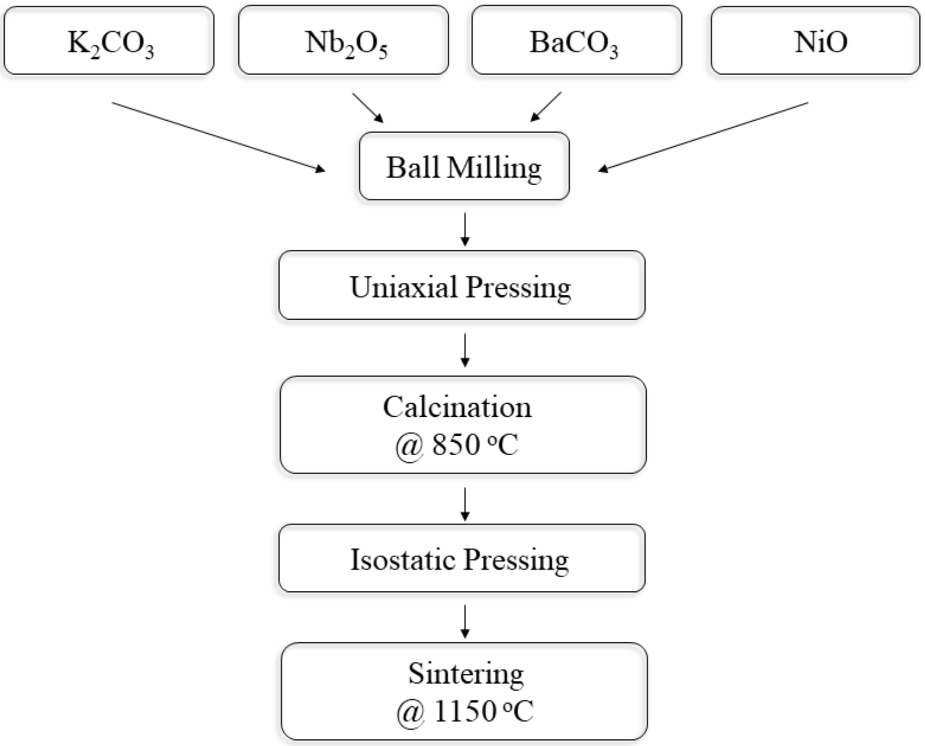

Figure 1. Schematic diagram for the KBNN samples preparation.

3. Results and discussion

Figure 2 shows the frequency dependence of the real and imaginary components of the dielectric permittivity (ε' and ε'', respectively) for the studied KBNN1, KBNN2 and KBNN3 compositions. It can be seen that the dielectric dispersions show a decrease of both ε' and ε'' with increasing number of oxygen vacancies. From the fundamental point of view, it is known that in ferroelectrics, structural defects (such as oxygen vacancies) promote the well-known domain wall pinning effect, where the suppression of the domain-wall motion could be caused by dipolar defects that involve cations-oxygen vacancy pairs. These defect mechanisms promote a shrinkage in some physical properties such as dielectric permittivity, dielectric losses and electromechanical response [10, 11]. Similar behavior has been reported by Hoshina *et al.* [12], revealing a decrease of the intrinsic dielectric permittivity in the presence of oxygen vacancies, which has been ascribed to the hardening of the Slater-type phonons in perovskite structure materials.

The obtained result in figure 2 confirms the strong influence of the structural defects on the dielectric response of the studied materials, which might affect the real dipolar mechanism by promoting unexpected conduction processes [13]. Since lattice defects induce additional space-charge polarization, such effect can be associated with the charge distribution of hopping carriers on defects [14].

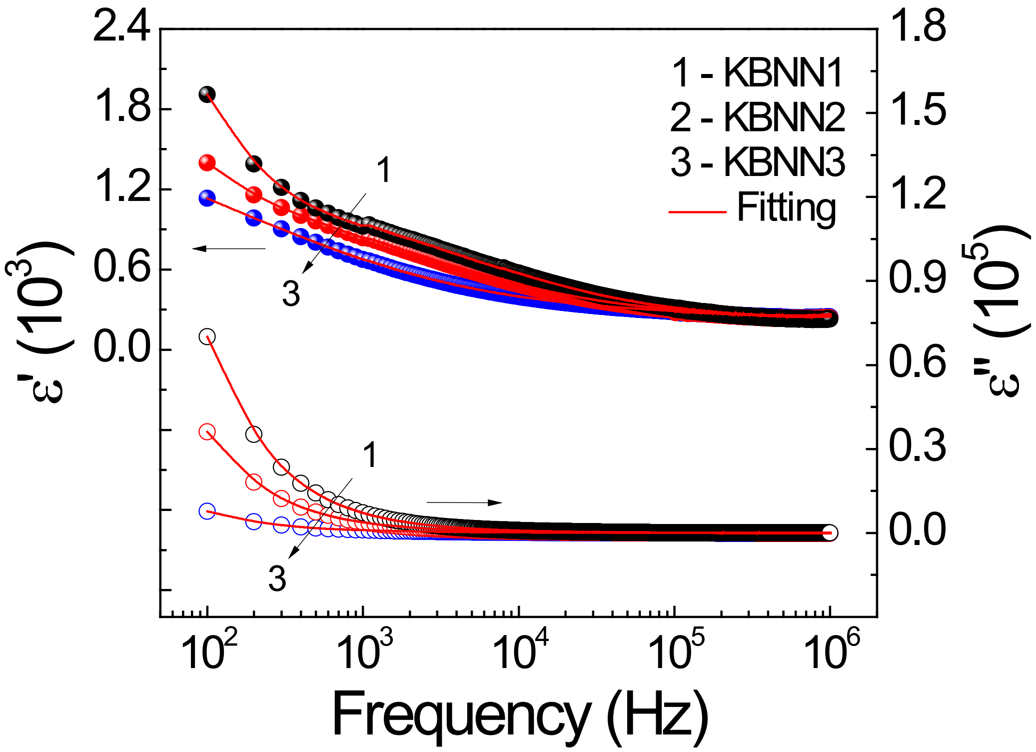

Figure 2. Frequency dependence of the real (ε’) and imaginary (ε’’) dielectric permittivity, obtained at room temperature, for the studied compositions.

In order to better investigate the dielectric relaxation as well as the influence of the vacancy defects, the experimental results were fitted by considering the semi-empirical Cole–Cole equation [15], expressed by equation (1), which takes into account a distribution function for the relaxation time of the relaxation process in the frequency dependence of the complex dielectric permittivity ($\varepsilon^* = \varepsilon' - j\varepsilon''$). The ε_o and ε_∞ parameters represent, respectively, the low (static) and high-frequency dielectric permittivity, ω is the angular frequency ($\omega=2\pi f$, where f is the measurement frequency), τ represents the mean relaxation time for the relaxation process and α is the exponent parameter, which is related to the relaxation time distribution function and describes the spectrum shape.

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{(\varepsilon_o - \varepsilon_\infty)}{1+(j\omega\tau)^{1-\alpha}} \tag{1}$$

As can be seen in the same figure 2, a good agreement between the experimental data (symbols) and the theoretical fitting (solid-lines) was observed for all the analyzed compositions. Table 1 shows the parameters obtained by fitting the experimental data to Cole–Cole equation at room temperature.

Table 1. Fitting parameters obtained at room temperature from the Cole-Cole's Eq. (1).

Sample	ε_o	ε_∞	α	τ (10^{-4} s)
KBNN1	2643	235	0.61	1.33
KBNN2	1744	257	0.53	1.93
KBNN3	1367	261	0.42	2.57

The obtained values for α were found to be in the range of around 0.4–0.6, which reveals the deviation from the ideal Debye's dielectric relaxation [16, 17]. Results also revealed very low dielectric losses at high frequencies (~ 0.001), which is a fundamental characteristic for applications in electronic devices, as well as a higher ε_o value for the KBNN1 composition.

4. Conclusions

The electrical properties have been investigated in KBNN lead-free ceramics as a function of the vacancy defects. Results obtained from the dielectric measurements confirm the strong influence of the structural defects in the involved polarization mechanisms, promoting additional conduction processes. Results revealed that the oxygen vacancies concentration has an important contribution on the dielectric response of these materials, and could be the main responsible mechanism for the dielectric relaxation processes observed for temperatures below the ferroelectric-paraelectric transition temperature in most of the studied ferroelectric systems.

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