Impedance study of giant dielectric permittivity in BaTi$_{0.4}$(Fe$_{0.5}$Nb$_{0.5}$)$_{0.6}$O$_3$ ceramic

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ABSTRACT

The BaTi$_{0.4}$(Fe$_{0.5}$Nb$_{0.5}$)$_{0.6}$O$_3$ ceramic is synthesized by a solid-state reaction technique. The X-ray diffraction of the sample at room temperature shows a cubic phase. The dielectric properties are investigated as a function of frequency ($20-10^6$ Hz) at different temperatures ($80-417$ K). A giant low frequency dielectric permittivity ($\varepsilon_r \sim 3 \times 10^5$) was obtained. Two dielectric relaxation peaks were observed on the curve of dielectric loss vs. temperature. The intrinsic dielectric permittivity calculated by impedance spectroscopy from the values of the obtained bulk capacitances were remarkably high $230 < \varepsilon_r < 330$. The extrinsic factors play an important role on their dielectric response giving rise to a giant dielectric permittivity at $T > 150$ K. The heterogeneities conduction in the grains, grain boundaries and interfacial layers are related to a Maxwell–Wagner relaxation.

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1. Introduction

The search for materials with a high dielectric permittivity has long been a field of interest, due to the important applications of such a property in many electric and electronic devices, such as capacitors [1,2]. Recently, a new perovskite-related material CaCu$_3$Ti$_4$O$_{12}$ (CCTO) has been developed with an unusually high dielectric permittivity, which is nearly independent of temperature in a wide temperature range [3–5]. It is considered that the origin of this large permittivity in CCTO could be due to the interfacial polarization mechanism, and no ferroelectric transition as in the high permittivity perovskites has been observed. A very high and nearly temperature-independent dielectric permittivity was observed also in (M and N)-doped NiO (M = Li, Na and K, and N = Ti, Al, Si and Ta) [6–8] and CCTO/(Li and Ti)–NiO composites; it often arises in a material consisting of grains separated by more insulating intergrain barriers [15,16]. In this context and in our last work we have doped the ferroelectric BaTiO$_3$ with Fe and Nb in B site leading to the composition BaTi$_{1-x}$(Fe$_{0.5}$Nb$_{0.5}$)$_x$O$_3$ where 5$^+$ Niobium and 3$^+$ Iron are equally balanced to comply with the 4$^+$ valence of the site [17]. With $x = 15\%$, a very high value of dielectric permittivity ($\varepsilon_r \sim 32000$ at 1 kHz) in a wide temperature interval ($200–450$ K) was observed [18]. The origin of the high value of dielectric permittivity was ascribed to grain boundary layer. In the present paper, we further increased the Fe and Nb content up to 40% leading to a still larger permittivity $\varepsilon_r \sim 3.10^5$. We show that this giant and extrinsic permittivity results from the superposition of grain, grain boundaries and electrode layer contributions.

2. Experimental procedure

BaTi$_{0.4}$(Fe$_{0.5}$Nb$_{0.5}$)$_{0.6}$O$_3$ ceramic composition was prepared by a conventional solid state reaction. Powders of BaCO$_3$, Fe$_2$O$_3$, TiO$_2$, and Nb$_2$O$_5$ of high purity were taken in stochiometric ratio and mixed in an agate mortar for 1 h. The mixture was pressed into pellets and calcined at 1100 °C in air for 15 h. After calcination, powder was mixed for 1 h and pressed under 100 MPa into 8 mm diameter and about 1 mm in thickness. Finally, the pressed pellet was sintered in oxygen atmosphere at 1350 °C for 3 h followed by furnace cooling.

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The X-ray powder diffraction pattern of the sample was recorded at room temperature using a Philips diffractometer of CuKα radiation (λ=1.5406 Å) in the angular range of, 5° ≤ 2θ ≤ 110° with 10 s counting time for each step of 0.02° in order to determine the structure of BaTi₀.₄(Fe₀.₅Nb₀.₅)₀.₆O₃ ceramic composition. The compactness value C (defined as the ratio between the experimental density \(d_{\text{exp}}\) and theoretical density \(d_{\text{theor}}\)) was systematically determined as \((\phi_{\text{init}}-\phi_{\text{fin}})/\phi_{\text{init}}\) (\(\phi_{\text{init}}\) and \(\phi_{\text{fin}}\) represent initial and final diameters, respectively). Their values were 94% and 0.168. Dielectric measurements were performed using a parallel plate capacitor arrangement. The main sample faces were electroded using gold sputtering deposition. The area of Au electrode and the distance between electrodes are 22.31 mm² and 0.82 mm, respectively. The real and the imaginary capacitances were measured in a frequency range from 20 to \(10^6\) Hz using a HP4284 impedance analyzer in the temperature range 80–417 K with a heating rate of 1 K min⁻¹ for temperature dependence and a step of 10 K for frequency dependence.

3. Results and discussion

3.1. X-ray diffraction analysis and microstructure

Fig. 1 shows the X-ray diffraction pattern of the sample taken at room temperature. All the reflection peaks of the X-ray profiles were indexed in cubic Pm₃m space group and lattice parameters were determined by a global profile-matching method with the software “FULLPROF”. Good agreement between the observed and calculated interplanar spacing (\(d\)-values) suggests that the compound has cubic structure at room temperature with \(a=4.0241\) Å. The X-ray diffraction study confirms that the specimen is single phase.

Microstructure studies were performed by scanning electron microscopy (SEM) (JEOL JED2300). Fig. 2 shows representative SEM micrograph of the surface of BaTi₀.₆(Fe₀.₅Nb₀.₅)₀.₄O₃ ceramic. The SEM micrographs show a few pores at grain boundaries, but cracks or micro-cracks were not detected. The average grain size of BaTi₀.₄(Fe₀.₅Nb₀.₅)₀.₆O₃ was around ~10 μm.

3.2. Electrical properties

The variation of dielectric permittivity and dielectric loss as a function of temperature is shown in Fig. 3a and b, respectively, for
various frequencies. A giant dielectric permittivity step \((-10^6)\) is observed over a broad temperature interval \((120–300\, \text{K})\), and drops quickly when the sample is cooled down through a critical temperature \((180\, \text{K} \text{ at } 100\, \text{Hz}, 235\, \text{K} \text{ at } 1\, \text{kHz} \text{ and } 370\, \text{K} \text{ at } 100\, \text{kHz})\). The critical temperature obviously increases with increasing frequency. In the higher temperature range, another giant dielectric step \((-10^5)\) is observed in a wide temperature \((240–417\, \text{K})\) are identified in the tan\(\delta\) curve (Fig. 3b). With decreasing frequency these peaks shift to a lower temperature, which is a hint of thermally excited relaxation process. At high temperature, the increase in tan\(\delta\)\(T)\) is mainly due to the conductivity contribution. As expected, the influence of the conductivity becomes apparent with increasing temperature and decreasing frequency \([2]\). The conductivity increase is probably caused by the presence of Fe\(^{2+}\) in sintered BaTi\(_{0.6}\)(Fe\(_{0.5}\)Nb\(_{0.5}\))\(_{0.6}\)O\(_3\) ceramic. The concentration of Fe\(^{2+}\) ions is known to be very sensitive to the sintering temperature, and it increases as temperature increases \([19]\). It is known that the co-existence of Fe\(^{2+}\) and Fe\(^{3+}\) ions on equivalent crystallographic sites can give rise to an electron-hopping conduction mechanism. This conduction mechanism tends to be more effective at lower frequencies.

Fig. 4 shows the frequency dependence of the dielectric permittivity and the dielectric loss of BaTi\(_{0.6}\)(Fe\(_{0.5}\)Nb\(_{0.5}\))\(_{0.6}\)O\(_3\) ceramic composition for various temperatures. As it can be observed, the high dielectric permittivity keeps a constant value for a certain temperature range for very low frequencies. In this region of frequencies and when temperature increases, the \(\varepsilon'\) value increases significantly. This behavior is consistent with that of common ferroelectrics. The higher values of \(\varepsilon'\) at lower frequencies are due to the presence of all different types of polarizations (i.e., interfacial, dipolar, atomic, ionic and electronic contribution) in the material. When frequency increases, \(\varepsilon'\) decreases gradually accompanied by a first broad peak in tan\(\delta\), then \(\varepsilon'\) maintains a constant value for a certain frequency range, and then decreases accompanied by a second broad peak in tan\(\delta\).

For both dielectric relaxations, we have investigated the corresponding \(f\) variation with temperature using the simple Cole–Cole relaxation equation \([20]\).

\[
\varepsilon' = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + (j\omega\tau)^{\alpha}}
\]

where \(\varepsilon_0\) is the static permittivity, \(\varepsilon_\infty\) is the permittivity at very high frequencies, \(\omega\) is the angular frequency, \(\tau\) is the mean relaxation time and \(\alpha\) represents the degree of the distribution of relaxation time \(\tau\). \(\varepsilon'\) can be further expressed as

\[
\varepsilon' = \varepsilon_\infty + \frac{(\varepsilon_0 - \varepsilon_\infty) [1 + (\omega\tau)^{1-\alpha}\sin((\omega\tau)\pi/2)]}{1 + 2(\omega\tau)^{1-\alpha}\sin((\omega\tau)\pi/2) + (\omega\tau)^{2-2\alpha}}
\]

Using Eq. (2), we can fit the two relaxation processes separately (Fig. 4a). Good agreement between experimental and calculated data is seen over a wide frequency range for both relaxation processes. The variation of the relaxation frequency obeys the thermally activated Arrhenius law, \(f = f_0 e^{-E_a/(kT)}\), where \(f_0\) is the pre-exponential term, \(E_a\) is the activation energy, and \(k\) is the Boltzmann constant. Activation energies are calculated from the line slope of log \(f\) vs. \(1/T\). The \(E_a\) values for the first (low frequency) and second (high frequency) relaxation processes are 0.25 and 0.19 eV, respectively.

The electrical properties of the BaTi\(_{0.6}\)(Fe\(_{0.5}\)Nb\(_{0.5}\))\(_{0.6}\)O\(_3\) ceramic composition were investigated using a complex impedance spectroscopy technique. In general, the values of resistance \(R\) and capacitance \(C\) of a perfect crystal can be analyzed by an equivalent circuit of one parallel resistance–capacitance \(\text{(RC)}\) element. This RC element gives rise to one semicircular arc on the complex plane, which intercepts the \(Z\) axis at zero and \(R\). The impedance complex plane plot of BaTi\(_{0.6}\)(Fe\(_{0.5}\)Nb\(_{0.5}\))\(_{0.6}\)O\(_3\) for some temperature are shown in Fig. 5. As it can be seen, for low temperatures \((T=158\, \text{K})\) it shows two arcs. The high frequency arc is assigned to the grains while the low frequency arc is assigned to the grain boundaries. This plot can be modeled with two RC elements connected in series. At intermediate temperatures \((T=257\, \text{K})\), a third semicircle appears, which is attributed to the interfacial layers. The best fits were obtained when modeling the impedance spectroscopy data on the basis of the equivalent circuit displayed in the inset of Fig. 5b. The capacitance was determined using \(C = 1/(\omega_{\text{max}}R)\), which is held approximately at the peak maximum of the semicircular arc. The order of magnitude of the capacitance associated with the low frequency arc \((\text{grain})\) is about \(\mu\text{F}\), typical of bulk response \([21]\), while the capacitance of the high frequency arc \((\text{grain boundary and interfacial layers})\) is about \(\text{nF}\), typical of extrinsic factors. In the high temperature range \((T > 397\, \text{K})\), the impedance complex plane plots show only two arcs, where the first arc does not intercepts the coordinates origin, so this means that at these temperatures and in the frequency range studied only the response due to extrinsic factors is observed. This plot can be modeled with two RC elements connected in series and one \(R\), the grain resistance base line. In this region, we do not have data to estimate the bulk capacitance, and we cannot obtain information about the intrinsic \(\varepsilon'\) value. In fact, the measured \(\varepsilon'\) vs. \(T\) (Fig. 3a), the \(\varepsilon'\) value is mainly intrinsic at the lowest temperatures \((T < 150\, \text{K})\). However, at
higher temperatures $T > 150 \text{K}$, there is a notable rise of the permittivity due to the influence of extrinsic factors. The intrinsic dielectric permittivity calculated from the values of the obtained bulk capacitances was in the range $230 < \varepsilon_r < 330$. These obtained values for our ceramic are remarkably higher compared with the other oxides in agreement with the intrinsic ferroelectric properties of the network [22]. The impedance plots (Fig. 5) are thus in perfect agreement with the dielectric data (Fig. 3) showing the superposition of the three contributions to the giant permittivity, the strongest being the interfacial layer one. Also, we note that the simultaneous observation of three arches in the impedance Nyquist plot at a single temperature (Fig. 5) is often quoted in textbooks for ionic conductors but rarely observed in ferroelectric ceramics.

We now show that the thermal activation of dielectric relaxations and resistivities is very similar. The resistances $R_g$, $R_{gb}$ and $R_{inter-lay}$ are plotted against $1/T$ in Fig. 6 and fitted to the Arrhenius law

$$R = R_0 \exp \left( \frac{E_a(\sigma)}{kT} \right)$$  \hspace{1cm} (3)

where $R_0$ is a constant and $E_a(\sigma)$ is the conduction activation energy. From the slopes of the fitted straight lines, we obtain activation energy of about 0.26 eV for interfacial layers, about 0.19 eV for grain boundary and about 0.06 eV for grain. These results indicate that the grain, grain boundary and interfacial layers have different electrical transport characteristics. The activation energies of the two relaxation processes observed at low and high frequency in our work agree well with the values of 0.25 and 0.19 eV determined previously. This implies that the first relaxation (low frequency) is attributed to interfacial layers and the second (high frequency) is attributed to the grain boundary. The high temperature increase of $\tan \delta$ at low frequencies (Fig. 3b) can also be fitted to Arrhenius law leading to activation energy of 0.12 eV. There is thus agreement between the high temperature conductivity on one hand and intermediate temperature interfacial layer and grain boundary resistances on the other hand. This clearly shows that the giant dielectric properties results from the conduction mechanism and not from bulk polarisability in agreement with Raevsky et al. [14].

The giant dielectric permittivity and its weak temperature dependence over a certain temperature in BaTi$_{0.4}$Fe$_{0.5}$Nb$_{0.5}$O$_3$ are of extrinsic origin. This behavior can be described by a Maxwell–Wagner relaxation mechanism. In fact, the similarity between our material and the so-called high-$k$ materials is explained by the fact that we have an important conductivity of grains and insulating of grain boundaries.
4. Conclusion

The giant dielectric material BaTi$_{0.4}$(Fe$_{0.5}$Nb$_{0.5}$)$_{0.6}$O$_3$ has been investigated by RX diffraction and impedance spectroscopy. This material crystallizes in cubic pervoskite structure at room temperature. The complex impedance analysis enables us to separate the contributions from grains, grain boundaries and interfacial layers of our material. The grain boundaries and interfacial layers effect (extrinsic dielectric) are responsible for giant dielectric permittivity of our material at $T > 150$ K. The intrinsic dielectric permittivities (grain) were $230 < \varepsilon'_r < 330$. These obtained values for our ceramic are remarkably higher compared with other oxides in agreement with the intrinsic ferroelectric properties of the network. The giant dielectric permittivity in BaTi$_{0.4}$(Fe$_{0.5}$Nb$_{0.5}$)$_{0.6}$O$_3$, which is of extrinsic origin, can be considered as a Maxwell–Wagner relaxation mechanism resulting from the coexistence of conductive grains separated by insulating grain boundaries (or insulating interfacial layers).

References