X-ray diffraction, dielectric and Raman spectroscopy studies of Ba$_{1-x}$Nd$_{2x/3}$(Ti$_{0.9}$Zr$_{0.1}$)O$_3$ ceramics

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Abstract

Polycrystalline samples of Ba$_{1-x}$Nd$_{2x/3}$(Ti$_{0.9}$Zr$_{0.1}$)O$_3$ (0 $\leq$ x $\leq$ 0.125) have been synthesized by high-temperature solid-state reaction technique. These ceramics were characterized by X-ray diffraction as well as dielectric permittivity measurements and Raman spectroscopy. The ceramic samples crystallize in the tetragonal perovskite structure for $x$ = 0 and in cubic for 0.025 $\leq$ x $\leq$ 0.125. Dielectric measurements showed that prepared compositions exhibit an evolution from a classical ferroelectric to a relaxor ferroelectric with rising substitution rate $x$. $T_c$ or $T_m$ decreases when neodymium (Nd) is introduced in the lattice of Ba(Ti$_{0.9}$Zr$_{0.1}$)O$_3$. A relaxor character with $\Delta T_m$ = 12 K and $\varepsilon'_r$ about 11.650 at 1 kHz with $T_m$ = 212 K was found for Ba$_{0.9}$Nd$_{0.06}$(Ti$_{0.9}$Zr$_{0.1}$)O$_3$ composition. The evolution of the Raman spectra was studied as a function of compositions and temperatures. The results of the Raman spectroscopy studies confirm our dielectric measurements.

Keywords: C. Dielectric properties; Ceramics; Solid-state reaction; X-ray diffraction

1. Introduction

BaZr$_x$Ti$_{1-x}$O$_3$ (BZT) ceramics are interesting materials for being used as dielectrics in commercial capacitor applications. They present high dielectric permittivity, high voltage resistance, and composition dependent Curie temperature and exhibit better temperature stability in the paraelectric state than Ba$_{1-x}$Sr$_x$TiO$_3$ [1–4]. Relaxors are characterized by their broad dielectric transition, known as diffuse phase transition with frequency dispersion [5,6]. These materials have great interest for applications, such as tunable ceramic capacitors and tunable microwave devices. The relaxor materials usually used are lead-based ceramics, for example PbMg$_{2/3}$Nb$_{2/3}$O$_3$ (PMN) and derived compounds. However, these materials have a drawback due to the volatility and the toxicity of PbO. At the present time current research is oriented to environmentally-friendly applications using lead-free materials.

Recently, several researchers have reported that homovalent and heterovalent substitution improves the dielectric properties of Ba$_{1-x}$A$_x$(Ti$_{0.7}$Zr$_{0.3}$)O$_3$ (A=Ca, Sr) [7] and Ba$_{1-x}$A'$_{2x/3}$ (Ti$_{1-y}$Zr$_y$)$_x$O$_3$ (A' = Y, La, Bi, ... and y=0.2, 0.3) Ba$_{1-x}$Ln$_x$Zr$_{1-y}$Ti$_y$O$_3$ ceramics [7,8]. For instance, the temperature of phase transition is drastically decreased by the addition of rare-earth ions and a relaxor-type behavior is induced [8]. Hence, the BZT system provides a wide set of properties as well as interesting characteristics in their dielectric response [9–11].

The purpose of our study is to investigate the effect of the substitution in A site cation in perovskite related materials on the dielectric properties in order to elaborate lead-free ceramics with relaxor behavior at room temperature. So we tried here to
prepare a series of compounds with general formula Ba$_{1-x}$Nd$_{2x/3}$ (Ti$_{0.9}$Zr$_{0.1}$)O$_3$. The influence of Nd$^{3+}$ content on structural and dielectric properties of the Ba$_{1-x}$Nd$_{2x/3}$ (Ti$_{0.9}$Zr$_{0.1}$)O$_3$ ceramics with ($0 \leq x \leq 0.125$) were examined and discussed. The evolution of the Raman spectra was studied as a function of various compositions at room temperature and at different temperatures for the ceramic with $x=0.075$ composition.

2. Experimental

The polycrystalline ceramic samples of Ba$_{1-x}$Nd$_{2x/3}$ (Ti$_{0.9}$Zr$_{0.1}$)O$_3$ with $x=0$, 0.025, 0.05, 0.075, 0.1 and 0.125 were prepared by solid-state synthesis using the following chemical reaction:

$$(1-x)\text{BaCO}_3+x/3\text{Nd}_2\text{O}_3+0.9\text{TiO}_2+0.1\text{ZrO}_2 \rightarrow \text{Ba}_{1-x}\text{Nd}_{2x/3}(\text{Ti}_{0.9}\text{Zr}_{0.1})\text{O}_3+(1-x)\text{CO}_2$$

The starting materials are highly-pure (99.9%) powders of BaCO$_3$, Nd$_2$O$_3$, ZrO$_2$ and TiO$_2$.

All these materials were dried at 200 °C for 2 h, weighed, mixed for 1 h and calcined at 1100 °C for 12 h. After calcination, powders were mixed for 2 h and pressed under 100 MPa into 8 mm diameter and about 1 mm thick. Finally, the pellets were sintered in oxygen atmosphere at 1420 °C for 2 h followed by furnace cooling. The compactness value, C (defined as the ratio between the experimental density $d_{exp}$ and theoretical density $d_{theor}$) obtained for sintered specimens were in the range 92–96%. The diameter shrinkages of ceramics disks $\Delta d$ the specimens is tetragonal for $x\leq0.025$ and becomes cubic for $x=0.1$.

Room temperature powder X-ray diffraction patterns were recorded on a Philips diffractometer using CuK$_{\alpha}$ radiation ($\lambda=1.5406$ Å) in the angle range $10^\circ \leq \theta \leq 100^\circ$ with 10 s counting time for each step of 0.02° in order to determine the structure for all prepared ceramic compositions.

The dielectric measurements were performed on ceramic discs after deposition of gold electrodes on the circular faces by cathodic sputtering. The dielectric permittivity of the ceramics disks was determined by measuring the capacitance between the electrodes at different frequencies and temperatures.

3. Results and discussion

3.1. X-ray diffraction study

The X-ray diffraction (XRD) patterns were analyzed to confirm the symmetry and to calculate the lattice parameters for Ba$_{1-x}$Nd$_{2x/3}$ (Ti$_{0.9}$Zr$_{0.1}$)O$_3$ samples with $x=0$–0.125. A profile matching of the XRD spectra was made using the “Fullprof” software [12]. The analysis was carried out at room temperature according to the $\theta$–2$\theta$ mode between 10° and 100° in steps of 0.02°. The X-ray diffraction patterns of Ba$_x$Ti$_{0.9}$Zr$_{0.1}$O$_3$ and Ba$_x$Nd$_{0.066}$Ti$_{0.9}$Zr$_{0.1}$O$_3$ ceramics were shown in Fig. 1(a) and (b) respectively as examples.

A perovskite phase was certified for the powders and no secondary phase can be found within the sensitivity of XRD. The analysis of the XRD pattern reveals that the symmetry of the specimens is tetragonal for $x=0$ and becomes cubic for $0.025 \leq x \leq 0.125$. Fig. 2 shows the variations of the lattice parameters and cell volume versus composition at room temperature.

The cell parameters decrease as $x$ increases. The ionic radii of the Ba$^{2+}$ and Nd$^{3+}$ ions in eight coordination are 1.43 Å and 1.27 Å respectively [13]. Therefore, replacement of Ba by Nd introduces a smaller A site ions and causes a decrease in space between network of TiO$_6$ octahedra and consequently in the unit cell volume. These results can strongly influence the dielectric properties and ferroelectricity in these materials.

3.2. Dielectric study

The evolution of real part ($\varepsilon'$) of the dielectric permittivity as a function of temperature at various frequencies ($10^3$–$10^6$ KHz)
of \( Ba_{1-x}Nd_{2/3}(Ti_{0.9}Zr_{0.1})O_3 \) (0 \( \leq x \leq 0.125 \)) samples has shown two types of different behaviors depending essentially on the rate of substitution of the cation \( Ba^{2+} \) by \( Nd^{3+} \). Classical ferroelectric behavior of the compound \( Ba(Ti_{0.9}Zr_{0.1})O_3 \) is conserved for substitution rate \( x \leq 0.05 \). In fact, the paraelectric ferroelectric transition temperature \( T_C \) and the associated maximum are independent of frequency. Moreover, compared to the ceramic \( Ba(Ti_{0.9}Zr_{0.1})O_3 \), the variation of the permittivity as a function of temperature and composition \( Ba_{0.975}Nd_{0.025}(Ti_{0.9}Zr_{0.1})O_3 \) \( (x=0.025) \) shows a single relatively broad peak with a where \( \varepsilon'_{\text{max}} \) is about 4000 at \( T_C=325 \) K (Fig. 3a).

The inverse of the dielectric permittivity shows that \( \varepsilon' \) follows in paraelectric phase the Curie–Weiss law.

\[
\varepsilon' = \frac{C}{T-T_0}
\]

Fig. 4a shows as example the temperature dependence of \( 1/\varepsilon' \) for the ceramic with composition \( x=0.025 \). In this case, the phase transition is of second order type \( (T_C \neq T_0, \text{ where } T_0 \text{ is the Curie–Weiss temperature}) \). All these dielectric results are in agreement with a classical ferroelectric behavior for compositions in the range \( 0 \leq x \leq 0.05 \).

For compositions in the range \( x \geq 0.075 \), a relaxor behavior was detected. In fact, changes in the real part of permittivity for compositions \( x=0.075, x=0.1 \) and \( x=0.125 \), show broad peaks over a temperature range due to the diffuse nature of the transition (Fig. 3b). Furthermore, the temperature of the real permittivity maximum, \( T_m \), moves towards higher temperatures and the values \( \varepsilon'_r \) decrease progressively as the frequency increases. This behavior is more pronounced for the composition \( x=0.1 \). Thus, the effect of the substitution of \( Ba^{2+} \) by \( Nd^{3+} \) on the dielectric properties in the material is to lower the transition temperature and to promote the relaxor behavior of materials with high values.

The relaxor characteristics for some compositions are reported in Table 1 as the \( T_m \) shift, \( \Delta T_m = T_m-(10^6 \text{ Hz})-T_{m_{0}} \) and the relative frequency dispersion \( \Delta \varepsilon'/\varepsilon'=(\varepsilon'_f/(10^3 \text{ Hz})-\varepsilon'_r/(10^6 \text{ Hz}) \), \( \Delta \varepsilon'/\varepsilon' \). A relaxor character with \( \Delta T_m = 12 \) K, \( \Delta \varepsilon'/\varepsilon' = 0.182 \) at 212 K and \( \varepsilon'_{rm} \) about 11.650 at 1 kHz was found for \( Ba_{0.9}Nd_{0.06}(Ti_{0.9}Zr_{0.1})O_3 \) composition.

In recent years, the relaxor phenomenon has been explored in relaxor perovskite structure such as \( Ba_{1-x}Bi_{2/3}TiO_3 \) \( [14] \), \( (Pb_{1-x}La_{x})(Mg_{1/3}Nb_{2/3})O_3 \) \( [15] \), \( Pb_{1-x}La_{x}TiO_3 \) \( [16] \) and \( (Pb_{1-x}La_{x})(Zr_{1-x}Ti_{x})O_3 \) \( [17] \). The relaxor behavior can be induced by the presence of a microscopic domain into macro polar region, or coupling of the order parameter and local disorder mode through the local strain \( [18–21] \).

The relaxor behavior in our solid solution \( Ba_{1-x}Nd_{2/3}(Ti_{0.9}Zr_{0.1})O_3 \) can be attributed to the strong heterogeneity introduced in A site. In fact, the local fluctuation of composition in A site following the partial substitution of \( Ba^{2+} \) by \( Nd^{3+} \) perturbs the Coulomb interactions at long distance and exhibits the formation of the ferroelectric nano-domains. Therefore, the order becomes at short distances and every nano-domain transits at a given temperature which explains the diffuse character of the transition but not the dielectric relaxation observed at temperatures below \( T_m \). The dielectric dispersion is explained by the dynamics of these nano-domains.

For ceramic composition \( x=0.1 \), the Curie–Weiss behavior is observed only in the region where \( T > T_{dev} \), when \( T < T_{dev} \), the values of \( T_0 \) are higher than \( T_m \) (Fig. 4b). This is another parameter that shows that in this case the transition is diffuse and of relaxor-type. Thus, we cannot deduce the order of the transition.

In comparison with the work of C. Ostos et al. \( [22] \) of the system \( Ba_{1-x}La_{2/3}(Ti_{0.9}Zr_{0.1})O_3 \), for \( x=0.1 \), maximum permittivity is about 6870 at \( T=180 \) K while for our ceramic...
Fig. 4. The inverse of the permittivity $\varepsilon_r$ as a function of temperature of the solid solution $\text{Ba}_{1-x}\text{Nd}_{2x/3}(\text{Ti}_{0.9}\text{Zr}_{0.1})\text{O}_3$ at frequency 100 kHz for the composition: (a) $x=0.025$ and (b) $x=0.1$.

Table 1

<table>
<thead>
<tr>
<th>$x$</th>
<th>$T_m$ (K at 100 kHz)</th>
<th>$\Delta T_m$ (K)</th>
<th>$\gamma$</th>
<th>$\Delta \varepsilon_r/\varepsilon_r$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.075</td>
<td>255</td>
<td>6</td>
<td>1.78</td>
<td>0.140</td>
</tr>
<tr>
<td>0.100</td>
<td>218</td>
<td>12</td>
<td>1.83</td>
<td>0.182</td>
</tr>
<tr>
<td>0.125</td>
<td>188</td>
<td>14</td>
<td>1.90</td>
<td>0.155</td>
</tr>
</tbody>
</table>

$\text{Ba}_{1-x}\text{Nd}_{2x/3}(\text{Ti}_{0.9}\text{Zr}_{0.1})\text{O}_3$ ($x=0.1$) the maximum is 11650 at $T=212$ K. This comparison shows that Nd induces better dielectric properties than La on ferroelectric relaxor compounds.

The degree of disorder in the $\text{Ba}_{1-x}\text{Nd}_{2x/3}(\text{Ti}_{0.9}\text{Zr}_{0.1})\text{O}_3$ was evaluated using an empirical formula developed by Uchino and Nomura [23]

$$\frac{1}{\varepsilon_r} - \frac{1}{\varepsilon_{r,m}} = \frac{(T - T_m)^{\gamma}}{K}$$

Where $K$ is a constant and $\gamma$ is the measure of diffuseness of the phase transition, which varied from 1 to 2. For ideal relaxors (completely disordered), $\gamma$ should amount to 2, and for classic ferroelectrics $\gamma$ equals 1. The higher the $\gamma$ value is, the more relaxor behavior the material displays [24]. The logarithmic plots related to this equation for all doped compositions $x=0.075$–0.125 are shown in Fig. 5. The slope of the curve gives the value of $\gamma$ at 100 kHz. These parameters are $\gamma=1.78$ to 1.9 as $x$ increases from 0.075 to 0.125 respectively.

Materials of relaxor ferroelectric type are generally subject to the Vogel–Fulcher relation [25] which has the form $f=f_0 \exp[-E_a/(T_m - T_f)]$, where $f$, $E_a$, $T_f$ and $f_0$ are the applied frequency, the activation energy, the freezing temperature and the attempt frequency, respectively. In our case, the compositions with $x=0.075$, 0.1 and 0.125 are also subject to this relation. In Fig. 6, we present the variation of the In $f$ as a function of $1/T_m$ for $x=0.075$, 0.1 and 0.125. The parameters of Vogel–Fulcher relation for $x=0.075$ were $E_a=0.040$ eV, $f_0=5.834 \times 10^{14}$ Hz and $T_f=234$ K, for $x=0.1$ were $E_a=0.037$ eV, $f_0=9.314 \times 10^{11}$ Hz and $T_f=191$ K and when $x=0.125$, $E_a=0.015$ eV, $f_0=5.84 \times 10^8$ Hz and $T_f=168$ K. It can be noted that as $x$ increases $E_a$ and $f_0$ decrease reflecting a higher barrier between two wells and an enlargement in potential well respectively [26].

The variation of the phase transition temperatures $T_C$ or $T_m$ as a function of composition $x$ at 1 kHz is shown in Fig. 7. $T_C$ or $T_m$ decreases strongly and linearly as $x$ increases. A similar behavior was observed in $\text{Ba}_{1-x}\text{Nd}_x\text{TiO}_3$ solid solution [27].

In addition, Gaussian diffuseness ($\delta_g$) in neodymium-substituted BZT ceramics was calculated using the relation $\ln(\varepsilon_{r,\text{max}}/\varepsilon_r) = (T - T_m)^{\delta_g}$ as shown in Fig. 8. [28]. This relation is valid within the limit $1 \leq \varepsilon_{r,\text{max}}/\varepsilon_r \leq 1.5$. As $\varepsilon_{r,\text{max}}/\varepsilon_r$, the only physically meaningful limit of $\delta_g$ is $\varepsilon_{r,\text{max}}/\varepsilon_r \leq 1.5$. The value of $\delta_g$, which is related to the broadening of the $\varepsilon_r$ ($T$) curve, can be used to determine the degree of compositional fluctuations in the material. This diffuseness parameter $\delta_g$ depends upon not only the chemical composition of the material but also on the frequency. The values of $\delta_g$ for $x=0$ and 0.1 are 24.59 K and 59.35 K at 10 kHz and 24.15 K and 56.05 K at 1 MHz respectively.
3.3. Raman spectroscopy

Room temperature depolarized Raman spectra of all Ba$_{1-x}$Nd$_{2x/3}$(Ti$_{0.9}$Zr$_{0.1}$)O$_3$ compositions are presented in Fig. 9. The Raman spectra of the pure Ba(Ti$_{0.9}$Zr$_{0.1}$)O$_3$ ($x=0$) ceramic show the same BaTiO$_3$ bands [20,27] in tetragonal phase. This spectrum is the starting point for any interpretation of Raman activity in Ba$_{1-x}$Nd$_{2x/3}$(Ti$_{0.9}$Zr$_{0.1}$)O$_3$ solid solutions. The low wavenumber band was assigned to vibration within the A site of the perovskite, whereas the higher wavenumber bands can probably be assigned to vibrations of the TiO$_6$ octahedra. So, the Raman spectrum of the tetragonal Ba(Ti$_{0.9}$Zr$_{0.1}$)O$_3$ showed the commonly-reported $A_1$(TO$_1$), $A_1$(TO$_2$), $B_1$+E (TO+LO), $A_1$(TO$_3$), and $A_1$(LO$_2$)+E (LO$_3$) optical modes, peaking at approximately 180, 240, 305, 510, and 714 cm$^{-1}$, respectively. The presence of the $E$+$B_1$ mode at 305 cm$^{-1}$ is considered a sign of the long range ferroelectric tetragonal phase. As Nd substitution content increases, the silent mode at 305 cm$^{-1}$ decreases in intensity and disappears from a doping rate $x=0.025$ which confirms the tetragonal – cubic structural transition observed by analysis of X-ray diffraction. The cubic paraelectric phase is characterized by three very broad lines at $E_{2}$ 240, 510, 714.

It should be pointed out that normal modes are not Raman active in the paraelectric phase and the origin of their activation should be found in a strong disorder. It can be noted also that when $x$ content increases all the bands show significant broadening, a weaker intensity and shifted to the high frequency. This would be undoubtedly connected with the disorder created on the A site of Ba(Ti$_{0.9}$Zr$_{0.1}$)O$_3$ as a consequence of Nd substitution. All these results confirm that increasing Nd$^{3+}$ content produces a crossover from ferroelectric long-range order toward a relaxor (short-range order) state as previously indicated by the dielectric experiments.

In addition, from the Raman spectra, a new peak at about 830 cm$^{-1}$ appeared with as Nd-doping level increases. Kchi-kech and Maglione [29] first reported the band at 840 cm$^{-1}$ in La-doped BaTiO$_3$, with an intensity increasing linearly with Nd content. Hence, the difference of cation ionic radii between...
Ba\(^2^+\), Ti\(^{4+}\), Zr\(^{4+}\) and Nd\(^{3+}\) can lead to the changes of the volumes of cell parameter in perovskites by XRD results indicative of the internal deformation/distortion of TiO\(_6\) octahedron which can be responsible for the band at 350 cm\(^{-1}\). The presence of the broad peak around 240 cm\(^{-1}\) in both compositions, J. Appl. Phys. 67 (1990) 1453.

The evolution of the Raman spectra studied as a function of Nd concentration and this up to the composition \(x = 0.125\). The characterization of dielectric behavior with empirical parameters \(T_{\text{relax}}\) and \(\gamma\) indicates that the relaxor degree increases as Nd contents increase. This new lead-free relaxor, Ba\(_{1-x}\)Nd\(_{2/3}\)(Ti\(_{0.9}\)Zr\(_{0.1}\))O\(_3\) with a higher value of permittivity attracts attention from the view point of environmental preservation. The Raman measurements show changes as a function of \(x\).

### References


[8] K. Alouane, A. Guehria-Laidoudi, A. Simon, J. Ravez, Study of new relaxor materials in Ba\(_{2/3}\)TiO\(_3\)-BaZr\(_{0.5}\)La\(_{0.5}\)TiO\(_3\) system, Solid State Sci. 7 (2005) 1324.


[18] F. Bousjilien, F. Bahri, C. Boudaya, A. Maalej, H. Khemakhem, A. Simon, M. Maglione, Effect of Ni doped BaTiO\(_3\) on the dielectric properties in the Ba(Ni\(_{0.5}\)Nb\(_{2/3}\))\(_{4-x}\)Ti\(_{4-x}\)O\(_{12}\) solid solution, J. Alloys Compd. 481 (2009) 559.


and Raman studies in Na_{0.925}Bi_{0.075}Nb_{0.925}Mn_{0.075}O_3 ceramic, J. Appl. Phys. 111 (2012) 044101.


G. Fulcher, Analysis of recent measurements of the viscosity of glasses, J. Am. Ceram. Soc. 8 (1925) 339.


