Ferroelectric, piezoelectric and Raman spectroscopy studies of BaTi$_{0.925}$(Nb$_{0.5}$Yb$_{0.5}$)$_{0.075}$O$_3$ ceramic

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Abstract

Lead-free BaTi$_{0.925}$(Nb$_{0.5}$Yb$_{0.5}$)$_{0.075}$O$_3$ ceramic was prepared by a solid-state reaction method. This ceramic was characterized by X-ray diffraction as well as dielectric permittivity, piezoelectric measurements and Raman spectroscopy. The existence of the morphotropic phase boundary (MPB) in our ceramic has been observed from BaTi$_1-x$(Nb$_{0.5}$Yb$_{0.5}$)$_x$O$_3$ phase diagram and confirmed by XRD measurement and Raman spectroscopy. The Rietveld refinement powder X-ray diffraction analyses showed that this ceramic has a mixture phase of rhombohedral and tetragonal phases. The tetragonal is the dominating phase with fraction close to 83%. The BaTi$_{0.925}$(Nb$_{0.5}$Yb$_{0.5}$)$_{0.075}$O$_3$ shows a typical nonlinear hysteresis loops at room temperature with a low value of $E_C$ ($E_C = 0.34$ kV/cm). The piezoelectric measurement reveals a piezoelectric coefficient $d_{31}$ about 94 pC/N at temperature near the $T_C = 320$ K.

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1. Introduction

Simple perovskite compounds have the chemical formula ABO$_3$. The most interesting materials were based on complex oxides with two different kinds of B atoms of the form A (B'B+)/O$_3$. Complex perovskite oxides with high dielectric and good piezoelectric properties play an important role in various technological applications such as wireless communication systems, microelectronics and global positioning systems.

Up to present, the dominant piezoelectric materials are lead-based, represented by Pb(Zr,Ti)O$_3$ (PZT) systems thanks to their excellent piezoelectric and electromechanical performances. On the other hand, much attention has been paid to the phase composition of ferroelectric ceramics with morphotropic phase boundaries (MPBs), such as Pb(Mg,Nb)O$_3$–PbTiO$_3$ (PMN–PT). The term “morphotropic” was coined by Jaffe et al. [1] and means literally the boundary between two forms. However, the use of lead-based ceramic may cause serious environmental problems because of the toxicity of lead oxide. Therefore, there is an increasing need for lead-free piezoelectric ceramics to reduce lead pollution [2,3]. The Ba-based complex perovskite is one of the main lead-free materials for piezoelectric devices and capacitor ceramics [4–8]. The lead-free BaTi$_{1-x}$(Nb$_{0.5}$Yb$_{0.5}$)$_x$O$_3$ (0.1 $\leq x < 0.2$) system displays a classical ferroelectric (0 $\leq x < 0.1$) and relaxor ferroelectric behaviour (0.1 $\leq x < 0.2$). From BaTi$_{1-x}$(Nb$_{0.5}$Yb$_{0.5}$)$_x$O$_3$ phase diagram, the morphotropic phase boundary was deduced, by the intersection of $T_{rhombo}$-ortho, $T_{ortho}$-tetrag and $T_C$ or $T_m$ versus $x$ which occurs at the sample with $x=0.075$ (Fig. 1). The composition with $x=0.075$ exhibits exceptional dielectric properties with a maximum of dielectric permittivity as high as 8500 (at 1 kHz) at $T_C=320$ K, which opens the way to possible use of it in capacitor applications.

Therefore, the aim of our work is to study the ferroelectric and piezoelectric properties of BaTi$_{0.925}$(Nb$_{0.5}$Yb$_{0.5}$)$_{0.075}$O$_3$ ($x=0.075$) ceramic. A discussion of the existence of the morphotropic phase boundary with XRD measurement and Raman spectroscopy was reported.

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goodness fitting was observed as a result of the superposition of two spectral contributions (P4mm–R3m) which indicate the MPB of our ceramic. To estimate the relative fraction of coexisting phases for BaTi0.925(Nb0.5Yb0.5)0.075O3, we used a multiple-peak separation method for peaks around $2\theta=45^\circ$ (inset in Fig. 2). According to Yoon et al. [10], the tetragonal fraction can be roughly estimated by the following equation:

$$\text{tetragonal fraction} = \frac{I_{\text{tetragonal}}}{I_{\text{tetragonal}} + I_{\text{rhombohedral}}} \times 100\%$$

The percentage of tetragonal phase is about $\sim 83\%$. Hence, we notice that the tetragonal is the dominating phase.

The cell parameters were determined using a global profile-matching method with the software “fullprof” [11]. The values of these parameters have been given in Table 2.

3.2. Dielectric properties

The evolution of a real part ($\varepsilon'$) of the dielectric permittivity and dielectric loss (tan$\delta$) as function of temperature at various frequencies ($110-2 \times 10^2$ Hz) of BaTi0.925(Nb0.5Yb0.5)0.075O3 sample are showed in Figs. 3 and 4 respectively. The temperature of Curie $T_C$ in this composition is detected at $T_C=320$ K. Here $T_C$ is lower than that of BaTiO3 ($T_C=420$ K), which is attributed to the replacement of Ti$^{4+}$ ion (0.56 Å) with the larger ionic radius cations Nb$^{5+}$ (0.62 Å) and Yb$^{3+}$ (1.008 Å). Replacement of smaller ionic radius cation with larger cations causes a smaller displacement of the first cation (Ti$^{4+}$ : B site) from its octahedral central position in the non-polar phase. The transition temperature is directly related to relative displacement of cations with respect to oxygen octahedra (i.e. $T_C$ ($K)=2 \times 10^4(\Delta z)^2 (\text{Å})$) [12], the Curie temperature of our composition must be lower than that of BaTiO3, which is in good agreement with experimental results. Furthermore, the sharp dielectric peak at $T_C$ ($\varepsilon'_\text{max}$) is dependent on the measuring frequency (left inset in Fig. 3). This
dispersion can be explained by the fact that the behaviour of our ceramic is between ferroelectric and relaxor. The dielectric loss $\tan \delta$ of this composition is relatively low ($0.05 < \tan \delta < 0.092$) in the ferroelectric phase ($T < T_C$). This result reveals a good dielectric property in our composition. However, in the paraelectric phase ($T > T_C$), $\tan \delta$ exhibits an increase included at high temperatures. This demonstrates, probably, the effect of conductivity at high temperatures. In BaTi$_{0.925}$(Nb$_{0.5}$Yb$_{0.5})_{0.075}$O$_3$, the thermal variation of $1/\varepsilon'_r$ is of Curie–Weiss type at $T > T_C$ (right inset in Fig. 3). Based on the theory of Landau, the transition is of the second order ($T_C \approx T_0$).

3.3. Hysteresis loop

Fig. 5 shows the $P$–$E$ hysteresis loop of BaTi$_{0.925}$(Nb$_{0.5}$Yb$_{0.5})_{0.075}$O$_3$ sample at room temperature. Development of saturated $P$–$E$ hysteresis loop confirms the ferroelectric nature of our sample. Here, the remnant polarization and coercive field were, respectively, about 0.63 mC/cm$^2$ and 0.34 kV/cm. Benabdallah et al. [13], have showed, by $P$–$E$ hysteresis loop, that BCTZ50 has a low coercive field $E_C$ which is about 1.61 kV cm$^{-1}$. They have deducted the high flexibility of polarization under electric field or stress in their sample. However, in our composition $E_C$ is smaller which can raise again the flexibility of polarization under electric field or stress.

3.4. Piezoelectric properties

We perform the piezoelectric measurements according to the temperature of the BaTi$_{0.925}$(Nb$_{0.5}$Yb$_{0.5})_{0.075}$O$_3$. The method of adopted measurement is that of electromechanical resonance by using an analyzer of impedance (model HP 4194A). The frequency used band extends from 380 to 500 kHz and that of the temperature extends from 205 to 480 K. BaTi$_{0.925}$(Nb$_{0.5}$Yb$_{0.5})_{0.075}$O$_3$ ceramic (with a diameter 6.81 mm and

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**Table 1**
The refinement results of X-ray pattern of BaTi$_{0.925}$(Nb$_{0.5}$Yb$_{0.5})_{0.075}$O$_3$ with different structure models (P4mm, R3m and P4mm–R3m).

<table>
<thead>
<tr>
<th></th>
<th>P4mm</th>
<th>R3m</th>
<th>P4mm–R3m</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_p$</td>
<td>8.31</td>
<td>8.59</td>
<td>7.49</td>
</tr>
<tr>
<td>$R_{opt}$</td>
<td>11.7</td>
<td>12.7</td>
<td>11.3</td>
</tr>
<tr>
<td>$R_{exp}$</td>
<td>9.95</td>
<td>9.98</td>
<td>9.95</td>
</tr>
<tr>
<td>$R_p$</td>
<td>1.39</td>
<td>1.63</td>
<td>1.3</td>
</tr>
</tbody>
</table>

**Table 2**
Cell parameters of BaTi$_{0.925}$(Nb$_{0.5}$Yb$_{0.5})_{0.075}$O$_3$ at room temperature.

<table>
<thead>
<tr>
<th>Space group</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>$\alpha$ (°)</th>
<th>$\beta$ (°)</th>
<th>$\gamma$ (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P4mm</td>
<td>4.0200</td>
<td>4.0200</td>
<td>4.0252</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>R3m</td>
<td>5.6903</td>
<td>5.6903</td>
<td>13.9253</td>
<td>90</td>
<td>90</td>
<td>120</td>
</tr>
</tbody>
</table>

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thickness 0.89 mm) is beforehand polarized under a continuous electric field of 786 V/mm between 320 and 200 K during a few minutes under atmosphere of helium. After polarization, the two electrodes were short-circuit during 10 min in order to eliminate the space charges.

For example Fig. 6 presents the variations of the frequency of the admittance (G) and the susceptance (B) of the ceramic BaTi0.925(Nb0.5Yb0.5)0.075O3 at 205 K (below TC) (Fig. 6-a) and T=330 K (above TC) (Fig. 6-b). We notice that the piezoelectric properties persist even in the paraelectric phase. This phenomenon can be demonstrated by the fact that the passage from the ferroelectric phase to the paraelectric phase is not done brutally. This can be explained by the following equation:

\[ d_{31} = k_{31} \sqrt{\epsilon_{33}^{f} S_{11}^{E}} \]

where \( \epsilon_{33}^{f} \) is the longitudinal permittivity component, \( S_{11}^{E} \) is the elastic compliance and \( k_{31} \) is the coupling factor for the electric field in direction 3 and longitudinal vibrations in direction 1. The value of the coefficient \( d_{31} \) reaches a maximum at temperature near the temperature of ferro-paraelectric transition \( (d_{31} = 94 \ pC/N) \). Since, for our ceramic, the tetragonal symmetry is the dominating phase, we can attribute the maximum of \( d_{31} \) to the minimum value of energy barrier \( E_B \) between \( T \) and \( C \) phases. In fact, \( E_B \) is given by the following equation:

\[ E_B = \frac{4\alpha_0^{3/2}}{27\sqrt{D}} \left( T_C + \frac{1}{2} T_0 - \frac{3}{2} T \right)^{3/2} \]

where \( \alpha_0 = 1/\epsilon_0 C \), \( \epsilon_0 \) is the Vacuum permittivity and \( D \) is a coefficient which appear in the expression of the free energy given by Landau–Devonshire theory [14,15]. The phase transition between \( T \) and \( C \) phases of this system is closed to a second order phase transition, so we get that \( T_C \approx T_0 \) (right inset in Fig. 3), then we get that

\[ E_B = \left( \frac{2\alpha_0^{3/2}}{27D} \right)^{1/2} \left( T_C - T \right)^{3/2} \]

In addition, from Fig. 7, \( K_p \) displays also a maximum at the ferroelectric transition temperatures, \( (K_p \approx 18.5\%) \) which is in agreement with the dielectric behavior. This behavior is expected in ferroelectric materials.

Furthermore, we note an amplification of the coefficient \( d_{31} \) in comparison with the case of BaTiO3 \( (d_{31} \approx 78 \ pC/N) \). The enhanced piezoelectric response in this composition can be due to the high flexible polarization vector under external stimuli such as electric field or stress [13]. Our results prove that our material is soft lead-free piezoceramics which exhibit a behavior between relaxors and ferroelectrics. Also, and compared to previous literature [16-19], the enhanced of the piezoelectric response can be related to the MPB of our ceramic.

3.5. Raman spectroscopy

Raman spectroscopy (RS) is a valuable technique for the study of ferroelectric materials. In fact, this technique correlates between the ferroelectricity and lattice dynamics. In our work, the Raman spectra were recorded for BaTi0.925(Nb0.5Yb0.5)0.075O3 ceramic with a spectrophotometer triple monochromator (Dilor Z 24), equipped with an argon ionized laser by using the

![Fig. 6. The frequency variation of the admittance (G) and the susceptance (B) of a ceramic BaTi0.925(Nb0.5Yb0.5)0.075O3. (a) before TC and (b) after TC.](image)

![Fig. 7. Thermal evolution of \( d_{31} \) and \( K_p \) for BaTi0.925(Nb0.5Yb0.5)0.075O3.](image)
intense bands associated with $A_1\,(TO_2)$ and $A_1\,(TO_3)$ optical features. The result of temperature-dependent Raman measurements was based on bibliographical data related to BaTiO$_3$ variations, in comparison with BaTiO$_3$, in intensity and green exiting line ($\lambda=514.5\,\text{nm}$). The spectral resolution is 3 cm$^{-1}$. The measurements were taken at different temperatures. The result of temperature-dependent Raman measurements on BaTi$_{0.925}$Nb$_{0.5}$Yb$_{0.5}$O$_{3.075}$, for a broad frequency band 50–1000 cm$^{-1}$, is shown in Fig. 8. The attribution of the bands was based on bibliographical data related to BaTiO$_3$ [20–23]. The spectrum shows two asymmetric, broad and intense bands associated with $A_1\,(TO_2)$ and $A_1\,(TO_3)$ optical modes, a sharp band [i.e., the “silent” mode $A_1+E\,(TO+LO)$ from cubic $F_{2g}$] and a weak band [$A_1\,(LO_3)$], peaking at 251, 517, 300, and 712 cm$^{-1}$, respectively. The broad band $A_1\,(TO_3)$ which is assigned to BO$_6$ bending vibrations appear at 251 cm$^{-1}$, however, for BaTiO$_3$ is observed at 275 cm$^{-1}$. The displacement of this band characterizes the weak substitution of Ti$^{4+}$ by Nb$^{5+}$ and Yb$^{3+}$. This substitution introduces some variations, in comparison with BaTiO$_3$, in intensity and frequency for all observed peaks. These variations characterize a new dipolar distribution of the nanoregion in our composition. This new distribution of the nanoregion appears to correspond probably to the weak dispersion observed on dielectric measurements (left inset in Fig. 3).

At low temperature ($T<T_C$), the presence of the sharp $A_1+E\,(TO+LO)$ and $A_1\,(LO_3)$ of BaTi$_{0.925}$Nb$_{0.5}$Yb$_{0.5}$O$_{3.075}$ is considered as a signature of the long-range ferroelectric tetragonal phase. To these has to be added the presence of anti-resonance effect at 172 cm$^{-1}$ as an interference feature, is attributed to a coupling between the sharp $A_1\,(TO_3)$ and broad $A_1\,(TO_2)$ modes, which also occurs in the ferroelectric tetragonal phase only.

According to Marco et al. [24], for BaTiO$_3$, the presence of sharp and intense modes in the low-wavenumber region between 100 and 200 cm$^{-1}$ identifies the rhombohedral phase at low temperature. Also, the appearance of a mode at 490 cm$^{-1}$ marks the transition to the lower-symmetry O phase. Whereas, for BaTi$_{0.925}$Nb$_{0.5}$Yb$_{0.5}$O$_{3.075}$, at low temperature ($T<T_C$), the same modes between 100 and 200 cm$^{-1}$ persist but not sharp and undergo damping. Also, in our case, we notice the nonappearance of the peak at 490 cm$^{-1}$. This is interpreted as the signature of the presence of the rhombohedral phase at low temperature ($T<T_C$). Nevertheless, for our composition, possibly multiple local symmetries (rhombohedral/tetragonal) may coexist over a wide temperature range below $T_C$ which confirms the MPB of our composition.

Moreover, as temperatures rise, the band intensity of the sharp $A_1+E\,(TO+LO)$ decreases with the disappearance of the interference dip at 172 cm$^{-1}$. The persistence of $A_1+E\,(TO+LO)$ with a low intensity for temperatures higher than $T_C$ suggests the coexistence of the tetragonal and cubic phases in the paraelectric phase. This is in agreement with the piezoelectric measurement when we reveals the presence of piezoelectric effect at $T>T_C$. The disappearance of this peak at temperatures much higher than $T_C$ indicates the existence of only one phase which is the cubic phase. At the same time, the two broad bands $A_1\,(TO_3)$ and $A_1\,(TO_3)$ persist into the cubic phase above $T_C$, which is attributed to intrinsic disorder in the cubic phase [25–27], and they become broad and weak with increasing temperature [28].

### 4. Conclusion

The lead-free BaTi$_{0.925}$Nb$_{0.5}$Yb$_{0.5}$O$_{3.075}$ ceramic was characterized by several techniques and a relationship between these characterizations was found. The XRD analyses shows that BaTi$_{0.925}$Nb$_{0.5}$Yb$_{0.5}$O$_{3.075}$ has a mixture phase of tetragonal and rhombohedral at room temperature which confirms the MPB of our ceramic. The mass fraction of tetragonal and rhombohedral was 83.0 and 17.0% respectively. The BaTi$_{0.925}$Nb$_{0.5}$Yb$_{0.5}$O$_{3.075}$ presents a typical nonlinear hysteresis loop with a low value of $E_C$. The low coercive field ($E_C=0.34\,\text{kV/cm}$) offers an indication about the high flexibility of polarization under electric field or stress. This result and the MPB of BaTi$_{0.925}$Nb$_{0.5}$Yb$_{0.5}$O$_{3.075}$ are shown to be the origin of the amplification of $d_{31}$ response compared to BaTiO$_3$. The Raman spectroscopy reveals the co-existence of rhombohedral and tetragonal which confirms again the MPB of our ceramic.

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