Ferroelectric, piezoelectric, pyroelectric studies on BaTi$_{0.95}$(Ni$_{1/3}$Nb$_{2/3}$)$_{0.05}$O$_3$ ceramic

This content has been downloaded from IOPscience. Please scroll down to see the full text.

(http://iopscience.iop.org/1757-899X/13/1/012003)

View the table of contents for this issue, or go to the journal homepage for more

Download details:

IP Address: 115.145.186.11
This content was downloaded on 14/02/2016 at 13:17

Please note that terms and conditions apply.
Ferroelectric, piezoelectric, pyroelectric studies on BaTi$_{0.95}$(Ni$_{1/3}$Nb$_{2/3}$)$_{0.05}$O$_3$ ceramic

F. Boujelben$^{1,1}$, H. Bouzid$^1$, F. Bahri$^1$, A. Maalej$^1$, H. Khemakhem$^1$, A. Simon$^2$ and M. Maglione$^2$
$^1$Laboratoire des Matériaux Ferroélectriques, Faculté des Sciences de Sfax, Route Soukra Km 3.5; B.P.1171,3000 Sfax, Tunisie
$^2$CNRS, Université Bordeaux, ICMCB, 87, avenue du Docteur A. Schweitzer, 33608 Pessac France
E-mail: faizaboujelben@yahoo.fr

Abstract. The main objective of this paper is to study dielectric, ferroelectric, pyroelectric and piezoelectric proprieties of BaTi$_{0.95}$(Ni$_{1/3}$Nb$_{2/3}$)$_{0.05}$O$_3$. From dielectric experiments, a single ferroelectric transition temperature of about 300K was found. The ferroelectric hysteresis loops were recorded versus temperature evidencing a saturation polarisation of about $4 \mu$C/cm$^2$ and a coercive field of 0.97kV/cm at the lowest temperature. The most promising result for BaTi$_{0.95}$(Ni$_{1/3}$Nb$_{2/3}$)$_{0.05}$O$_3$ is its effective piezoelectric coefficient $d_{31}$ which reaches 55pCN$^{-1}$ at room temperature.

1.Introduction
Since the discovery of the high-permittivity of the ferroelectric ceramic BaTiO$_3$ in 1943, BaTiO$_3$-based ceramics have been studied widely in the electronics industry and used as passive components in capacitors [1-4]. However, BaTiO$_3$ has still several drawbacks which are high dielectric losses and strong sensitivity of the dielectric properties versus temperature because of the proximity of the ferroelectric transition temperature. BaTiO$_3$ has a characteristically anomalous in the dielectric constant near the ferroelectric–paraelectric phase transition temperature (400 K) [5-7]. To make BaTiO$_3$ ceramics usable at room temperature the cations of nickel and niobium were substituted for the titanium cation. The present work concerns the preparation, dielectric, ferroelectric pyroelectric and piezoelectric characterisations of the lead-free ceramic composition BaTi$_{0.95}$(Ni$_{1/3}$Nb$_{2/3}$)$_{0.05}$O$_3$. This composition, which crystallizes in cubic perovskite structure, is of strong interest because it was already shown to display exceptional dielectric properties with a maximum of dielectric permittivity as high as 9700 (at 1 kHz) at $T_{max} = 298$ K and with little dielectric loss. In the present report, we want to check whether this peculiar composition BaTi$_{0.95}$(Ni$_{1/3}$Nb$_{2/3}$)$_{0.05}$O$_3$ also displays improved piezoelectric performances. We checked the thermal evolution of the ferroelectric properties of BaTi$_{0.95}$(Ni$_{1/3}$Nb$_{2/3}$)$_{0.05}$O$_3$ using hysteresis, piezoelectric and pyroelectric measurements. The saturated ferroelectric polarisation is about $4 \mu$C/cm$^2$ while the transverse piezoelectric coefficient was found to be 54pC/m at room temperature, a value which is of interest even being smaller than the one reported in literature [8-10].

$^1$ To whom any correspondence should be addressed.
2. Elaboration and ceramic processing
The lead-free piezoelectric ceramic BaTi$_{0.95}$(Ni$_{1/3}$Nb$_{2/3}$)$_{0.05}$O$_3$ was prepared by solid-state synthesis using the following chemical reaction:

$$\text{BaCO}_3 + 0.05/3\text{NiO} + 0.05/3\text{Nb}_2\text{O}_5 + 0.95\text{TiO}_2 \rightarrow \text{BaTi}_{0.95}(\text{Ni}_{1/3}\text{Nb}_{2/3})_{0.05}\text{O}_3 + \text{CO}_2$$

The starting materials were high-purity (99.9%) powders of BaCO$_3$, NiO, Nb$_2$O$_5$ and TiO$_2$. All these materials were dried at 200 °C for 3 h, weighed, mixed for 1 h and calcined at 900 °C for 12 h. After calcination, powders were mixed for 1 h and pressed under 100MPa into pellets of 8mm diameter and about 1.5mm thickness. Finally, the pellets were sintered in oxygen atmosphere at 1350 °C for 2 h followed by furnace cooling. The compactness value, $C$ (defined as the ratio between the experimental density $d_{\text{exp}}$ and theoretical density $d_{\text{theor}}$) obtained for sintered specimens was 96%. The diameter shrinkages of ceramics disks $\Delta \Phi/\Phi$ were systematically determined as $(\Phi_{\text{init}}-\Phi_{\text{fin}})/\Phi_{\text{init}}$ ($\Phi_{\text{init}}$ and $\Phi_{\text{fin}}$ represent initial and final diameter, respectively). The value for BaTi$_{0.95}$(Ni$_{1/3}$Nb$_{2/3}$)$_{0.05}$O$_3$ is 0.16. At room temperature powder X-ray diffraction patterns were recorded on a Philips diffractometer using Cu K$_\alpha$ radiation ($\lambda = 1.5406$ Å) in the angle range 8.02$\leq 2\theta \leq 110^\circ$ with 10 s counting time for each step of 0.02$^\circ$ in order to determine the structure of this ceramic. 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 sample was measured under helium atmosphere as a function of both temperature (80–500 K) and frequency (100–2×10$^5$ Hz). Piezoelectric properties were measured by the resonance–antiresonance method based on of IRE Standards [11] using an impedance analyser (HP 4194A). These piezoelectric experiments were conducted versus temperature after a poling step.

3. Results and discussion
3.1. X-ray diffraction analysis
The X-ray diffraction profiles of all samples reveal that they are free from any parasitic phase. The lattice parameters were determined using a global profile-matching method with the software “fullprof” [12]. The observed, calculated and the difference of the X-ray diffraction patterns for the complex BaTi$_{0.95}$(Ni$_{1/3}$Nb$_{2/3}$)$_{0.05}$O$_3$ ceramics is given in Fig.1. All the reflection peaks of the X-ray profiles were indexed. Good agreement between the observed and calculated inter planer spacing suggests that this composition has a cubic structure at room temperature.

![Figure 1. X-Ray diffraction pattern of a BaTi$_{0.95}$(Ni$_{1/3}$Nb$_{2/3}$)$_{0.05}$O$_3$ ceramic](image-url)
3.2. Dielectric studies

The evolution of real part ($\varepsilon_r$) of the dielectric permittivity and dielectric loss (tan $\delta$) as a function of temperature at various frequencies ($100–2\times10^5$ Hz) of BaTi$_{0.95}$(Ni$_{1/3}$Nb$_{2/3}$)$_{0.05}$O$_3$ ceramic is shown in Figs. 2 and 3. The dielectric peak at about 298K signs the ferroelectric transition, in agreement with the XRD data suggesting a room temperature cubic phase.

Fig. 4 depicts the variation of $1/\varepsilon_r'$ against temperature at $10^3$ Hz. The Curie-Weiss relation, $\varepsilon_r' = C/(T-T_0)$, holds at $T \geq 312$ K where C is the Curie constant and $T_0$ is the Curie temperature. $T_0$ of 383 K and C of $1.56\times10^5$ K have been obtained for a pure BaTiO$_3$ crystal [13]. For BaTi$_{0.95}$(Ni$_{1/3}$Nb$_{2/3}$)$_{0.05}$O$_3$, the $\varepsilon_r'$ was fitted to the Curie-Weiss law. The fitting parameters are $C = 1.05\times10^5$K and $T_0 = 298$K nearly equal to $T_C$ at 1 kHz. In Landau's theory of phase transition [14], a first-order transition takes place when $T_C > T_0$, and a second order in the case of $T_C = T_0$. Therefore, for the composition BaTi$_{0.95}$(Ni$_{1/3}$Nb$_{2/3}$)$_{0.05}$O$_3$, the second order ferroelectric paraelectric transition occurs as well as for BaTi$_{1-x}$Zr$_x$O$_3$ for $x$<0.2 in which the composition is very close to BaTiO$_3$ [14-15].

All these physical properties show that BaTi$_{0.95}$(Ni$_{1/3}$Nb$_{2/3}$)$_{0.05}$O$_3$ compound is a classical ferroelectric.
In addition, comparing dielectric properties of BaTiO$_3$ which is characterized by $\varepsilon'_\text{rm} \approx 9000$ and $T_C \approx 400$ K [16] to our specimen BaTi$_{0.95}$(Ni$_{1/3}$Nb$_{2/3}$)$_{0.05}$O$_3$ (Fig. 2), we note that substituting Ti by Ni and Nb, the Curie temperature $T_C$ decreases to room temperature ($T_C=298$K at 1 kHz) and $\varepsilon'_\text{rm}$ increases to 9500. This is an important result in ferroelectric perovskite materials.

### 3.3. Temperature dependence of hysteresis loops

The P(E)-hysteresis were recorded as a function of temperature using a Sawyer–Tower circuit [17] to determine the saturation and remnant polarization and coercive field. Figure 5 shows the P(E) hysteresis curves measured at different temperatures for BaTi$_{0.95}$(Ni$_{1/3}$Nb$_{2/3}$)$_{0.05}$O$_3$ ceramic.

We note at temperature below $T_{\text{max}}$ a nonlinear P–E loops are observed that confirms the ferroelectric behaviour of this material. The temperature dependence of the remnant polarization ($P_r$) and the coercive field ($E_c$) derived from the P–E hysteresis loops of BaTi$_{0.95}$(Ni$_{1/3}$Nb$_{2/3}$)$_{0.05}$O$_3$ ceramic are plotted on Fig. 6. We note that the two parameters $E_c$ and $P_r$ decrease with increasing temperature especially above $T_{\text{max}}$. The remnant polarization $P_r$ is about 2.05 $\mu$C/cm$^2$ at 272 K with a coercive electric field $E_c \approx 2.19$ kV/cm. On the other hand, at 305K $P_r$ and $E_c$ are about 0.57 $\mu$C/cm$^2$ and 0.56 kV/cm, respectively. The value different from zero of $P_r$ shown in Fig. 6 by a slight P–E loop implies that residual domains are persisting even above $T_{\text{max}}$. This shows that this transition is of second order.
The almost vertical lines of the loop indicate sharp switching of macrodomains like “PSN-0.425PT” single crystal [18]. The polarization and coercive electric field values show that BaTi_{0.95}(Ni_{1/3}Nb_{2/3})_{0.05}O_3 have polarization smaller than that of pure BaTiO_3 (saturation Ps=4\mu C/cm^2 instead of Ps=25\mu C/cm^2). We will now discuss the piezoelectric performances of this new composition.

![Figure 6](image-url)

**Figure 6.** Temperature dependence of the remanent polarization and the coercive field.

### 3.4. Piezoelectric study

Piezoelectric resonance measurements were undertaken using an HP4194A impedance analyzer on samples prepared in disc shapes. The sample was set in a home-made cell and poled using a DC electric field of 1.4 kV mm\(^{-1}\) for 20 min between 350 and 100 K and then short-circuited for 10 min in order to eliminate any residual space charge. Piezoelectric measurements were performed on the poled samples at different temperatures. The determinations of the piezoelectric parameters are based on the measurements of the real G(f) and imaginary B(f) parts of the admittance 1/Z* in a frequency range in the vicinity of the resonance of the sample. The evolution of admittance and susceptance versus frequency is plotted in Fig.7. The value of the characteristic elements of the equivalent circuit of the piezoelectric sample is obtained by fitting the admittance circle B = f(G) and the curves G(f) and B(f) [19]. We are here interested only in the transverse mode, implying radial oscillations of the disc, which lies in the range 450 to 600 kHz. The piezoelectric parameters were computed using home-made software following the IEEE specifications [20]. The admittance circle recorded at 140 K is shown in Fig. 8 as an example.

For a disk vibrating along a diameter, the value of the planar coupling coefficient (K_p) follows the relation:

\[ k_p^2/(1-k_p^2) = 2.51(f_a - f_r)/f_r \]  

where \( f_r \) is the resonance frequency and \( f_a \) is the anti-resonance frequency.

The transverse piezoelectric constant \( d_{31} \), is computed using the following equation:

\[ d_{31} = k_{31}(\varepsilon_{33}^T s_{11}^E) \]  

where \( \varepsilon_{33}^T \) 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.
Figure 7. Admittance G and susceptance B versus frequency for BaTi$_{0.95}$(Ni$_{1/3}$Nb$_{2/3}$)$_{0.05}$O$_3$ ceramic around the main radial piezoelectric resonance.

Figure 8. Piezoelectric admittance circle for a BaTi$_{0.95}$(Ni$_{1/3}$Nb$_{2/3}$)$_{0.05}$O$_3$ ceramic at 140 K. The open circles are the experimental results and the solid line is the fitted result.

Fig 9 and fig 10 show the piezoelectric properties of BaTi$_{0.95}$(Ni$_{1/3}$Nb$_{2/3}$)$_{0.05}$O$_3$ as a function of temperature. The planar electromechanical coupling factor $k_p$ and the piezoelectric coefficient $d_{31}$ increase in the ferroelectric range, then also reach a maximum at $T = T_{\text{max}}$. Just below the ferroelectric–paraelectric phase transition, these two parameters drastically decrease which can be linked to the disappearance of the remnant polarization. In addition, the temperature profile of $d_{31}$ constant is quite similar to the temperature profile of the real part $\varepsilon'$ of the dielectric permittivity. A similar behaviour was observed by Hemphill et al. [21] in Pb(Sc0.5Nb0.5)O$_3$. The $d_{31}$ reaches its maximum of 52pC/N at 298 K. This piezoelectric coefficient is comparable to the values obtained in some ceramic such as KTa$_{0.6}$Nb$_{0.4}$O$_3$ ($d_{31} = 18$) [22] and Na$_{0.5}$Bi$_{0.5}$TiO$_3$ ($d_{31} = 14$) [23]. These results show that BaTi$_{0.95}$(Ni$_{1/3}$Nb$_{2/3}$)$_{0.05}$ is among the best lead-free piezoelectric materials. Pyroelectric experiment was then undertaken in order to trace the possible origin of this piezoelectric efficiency.
3.5. Pyroelectric study
A BaTi$_{0.95}$(Ni$_{1/3}$Nb$_{2/3}$)$_{0.05}$O$_3$ ceramic was first submitted to a DC field of about 1.4 kV mm$^{-1}$ from 350 to 75 K during 15 min in a dry helium atmosphere. The two electrodes were then short-circuited for 30 min in order to eliminate any residual space charge. After this initial poling step, the pyroelectric depolarization current was measured on heating at a rate of about 2 K min$^{-1}$ from 75 to 350 K. The temperature dependence of the pyroelectric coefficient (p) was calculated from the rate of variation of the temperature b and pyroelectric current i following the relation $p = i / s b$, where $s$ is the area of an electrode. The spontaneous polarization $P_s$ was computed by integration of the $p$ vs. $T$ ($p = dP_s / dT$) curve. The results are plotted on Fig. 11. From this figure, it can be seen that the pyroelectric current has a broad maximum in the vicinity of $T_{\text{max}}$ and then decreases to reach zero around 270 K. The pyroelectric coefficient $p$ is of about 119 $\mu$C cm$^{-2}$ at $T_{\text{max}}$. The spontaneous polarization presents a slow variation at low temperature and then decreases progressively to reach zero at $T > T_{\text{max}}$, which confirms the hysteresis measurements.
4. Conclusion

BaTi$_{0.95}$(Ni$_{1/3}$Nb$_{2/3}$)$_{0.05}$O$_3$ ceramic with perovskite structure was prepared by a conventional ceramic fabrication technique. These dielectric, ferroelectric, piezoelectric and pyroelectric properties were investigated. Dielectric permittivity was measured in the temperature and frequency range, respectively, 80-500K and 0.1-200 kHz. Substituting Ti by Ni and Nb induce a decrease of T$_c$ to room temperature and increase of $\varepsilon'_r$. A $P_r$ of 0.72 µC/cm$^2$ and $E_c$ of 0.97kV/cm were obtained at T= 298 K. The most promising result was the high room temperature piezoelectric coefficient $d_{31}=54pC/N$ that we have recorded.

References

  Cross L E 1994 Ferroelectrics 151 305


