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Physical Properties of New, Lead Free $\text{BaTi}_{1-x}(\text{Nb}_{0.5}\text{Yb}_{0.5})_x\text{O}_3$ Ceramics

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New lead free ceramics derived from the ferroelectric material BaTiO_3 by substituting Ti^{4+} by Nb^{5+} and Yb^{3+} . The dielectric and ferroelectric properties were studied. The compositions $\text{BaTi}_{1-x}(\text{Nb}_{0.5}\text{Yb}_{0.5})_x\text{O}_3$ display a classical ferroelectric ($0 \leq x < 0.1$) and relaxor ferroelectric behaviour ($0.1 \leq x \leq 0.2$). $\text{BaTi}_{0.9}(\text{Nb}_{0.5}\text{Yb}_{0.5})_{0.1}\text{O}_3$ specimen present a relaxor behaviour at a temperature close to room with high permittivity ($\epsilon'_r = 9500$ at 1 kHz), which opens the way for possible use of it for capacitor applications. The polarisation hysteresis loops were observed of relaxor $\text{BaTi}_{0.875}(\text{Nb}_{0.5}\text{Yb}_{0.5})_{0.125}\text{O}_3$ specimen. The ceramic $\text{BaTi}_{0.9}(\text{Yb}_{0.5}\text{Nb}_{0.5})_{0.1}\text{O}_3$ provides a piezoelectric constant d_{31} of about 11.17 pC/N near room temperature.

Keywords Dielectric properties; ferroelectric; ytterbium; relaxor; Piezoelectric

1. Introduction

Ferroelectric materials with perovskite structure can be divided into two different classes according to their behaviour: depending on whether they are classical ferroelectrics or relaxor [1]. The relaxor behaviour in perovskites was studied predominantly in Pb containing ternary compounds (PMN, PZN, PST) and solid solutions (PLZT, PMN PT) [2]. Various models, such as the inhomogeneous microregion [3], the superparaelectric [4], the dipolar glass, the order disorder [5] and the local electric field [6] models have been proposed to explain the relaxor behaviour. During the past years, some lead free BaTiO_3 derived from solid solution compositions attracted much attention as environmentally benign relaxor materials [7–11]. However, up to now the obtained values of the dielectric permittivity maximum temperature, T_m , in the BaTiO_3 -based relaxors were too low for potential applications [12]. The aim of the present paper is to study the ferroelectrics properties of $\text{BaTi}_{1-x}(\text{Nb}_{0.5}\text{Yb}_{0.5})_x\text{O}_3$ solid solution forming a new family of lead free materials.

2. Experiment

The various compositions of $\text{BaTi}_{1-x}(\text{Nb}_{0.5}\text{Yb}_{0.5})_x\text{O}_3$ were obtained from BaCO_3 , TiO_2 , Nb_2O_5 and Yb_2O_3 after calcinations at 1100°C for 15 h under oxygen. Disk shaped ceramics

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were sintered at 1300°C–1400°C, depending on the composition, for 4 h under oxygen atmosphere.

Room temperature powder X-ray diffraction (XRD) was performed on a Philips diffractometer using Cu-K α radiation ($\lambda = 1.5418 \text{ \AA}$). The diameter shrinkage was systematically determined as $\Delta\Phi/\Phi = (\Phi_{\text{init}} - \Phi_{\text{final}}/\Phi_{\text{init}})$ of the ceramics are in the range 14–17%. The densities of the sintered samples were 93–95% of the theoretical values. From room temperature X-ray scattering, we checked that the purity phase of the ceramics was limited to $x = 0.2$ composition.

Dielectric measurements were performed on ceramic discs after deposition of gold electrodes on the circular faces by dc sputtering. The real and imaginary parts of the permittivity ϵ'_r and ϵ''_r were measured under helium as a function of both temperature (85–500 K) and frequency (10^2 – 2×10^5 Hz) using a Wayne-Kerr 6425 component analyzer.

The ferroelectric hysteresis loop parameters such as remanent polarization (P_r) and coercive field (E_c) were estimated from the hysteresis loop observed on the screen of a 515A JEKT Ronicks oscilloscope with the aid of a homebuilt 'Sawyer–Tower' circuit.

Piezoelectric resonance measurements were undertaken with an HP4194A impedance analyzer of the samples prepared in disc shapes. The sample was poled using a DC electric field of 1.6 kVmm^{-1} at 270 K for some minutes and then short circuited for 10 min in order to eliminate any residual space charge. Piezoelectric measurements were performed at 280 K.

3. Results and Discussion

3.1. Phase Identification

The structural type was kept as a perovskite. When $0 \leq x < 0.1$, room temperature XRD patterns were fully indexed on the tetragonal symmetry, while for $0.1 \leq x \leq 0.2$, they were fully indexed in cubic symmetry. The observed, calculated and the difference of the X-ray diffraction patterns for ceramics with compositions $x = 0.1$ is given as an example in Figure 1.

3.2. Dielectric Properties

For x varying from 0 to 0.075, the ceramics showed classical ferroelectric behaviour with a slightly peak of ϵ'_r characteristic of ferroelectric-paraelectric transition (see Figure 2 as an example) and the value of T_C was not dependent on frequency. For these compositions, the temperature dependence of $1/\epsilon'_r$ at 10^3 Hz showed that the Curie Weiss law $\epsilon'_r = C/(T-T_0)$ is followed for $T > T_C$ (inset in Figure 2). The transition which was of first order for BaTiO₃ moved to second order for $0 < x \leq 0.075$.

In composition range $0.1 \leq x \leq 0.2$, the peak of ϵ'_r becomes very broad with strong frequency dispersion of ϵ'_r and ϵ''_r and shift of T_m . Figure 3 shows, for example, the dielectric behaviour for $x = 0.15$. The maximum value of ϵ'_r decreased and the temperature T_m associated to $\epsilon'_{r\text{max}}$ shifted to higher values as the frequencies increased. The temperature T_m of ϵ''_r was shifted to higher values at greater frequencies, but opposite to the evolution of ϵ'_r , ϵ''_r increased when the frequency increased (Figure 4). Moreover, there was a deviation from the Curie Weiss law (inset in Figure 3). The value of the Curie Weiss temperature T_0 was greater than that of T_m . As x increased, the value of T_{dev} T_m increased. A strong dielectric dispersion is evidenced leading to Vogel Fulcher behaviour. The latter was computed using the equation $f = f_0 \exp(E_a/k_B(T_m - T_{VF}))$ where f_0 is the high temperature extrapolation

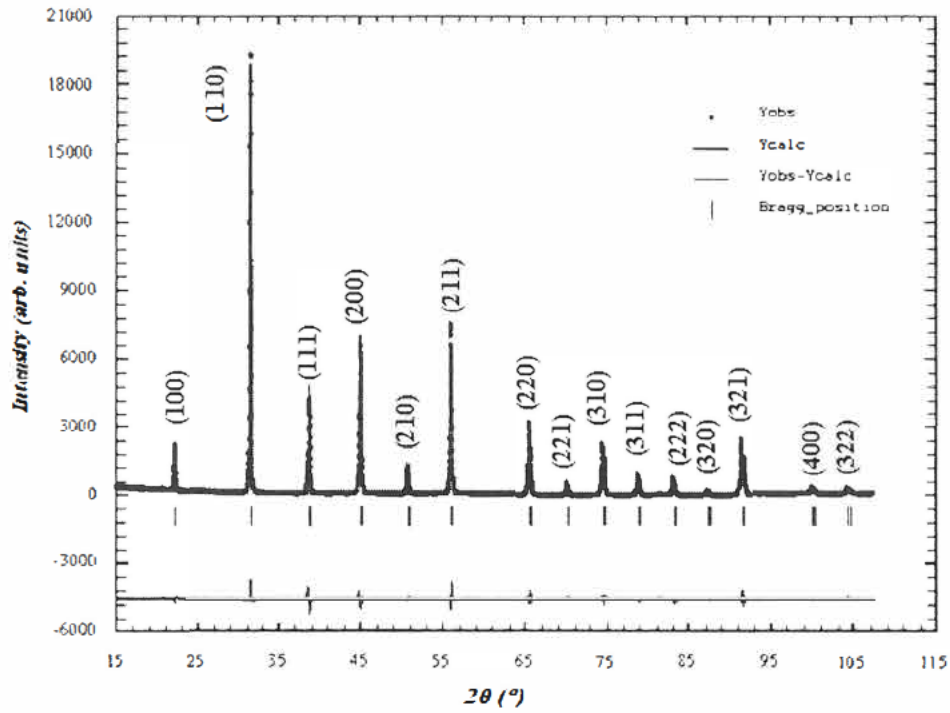


Figure 1. X ray diffraction pattern of a cubic sample with composition $\text{BaTi}_{0.9}(\text{Nb}_{0.5}\text{Yb}_{0.5})_{0.1}\text{O}_3$.

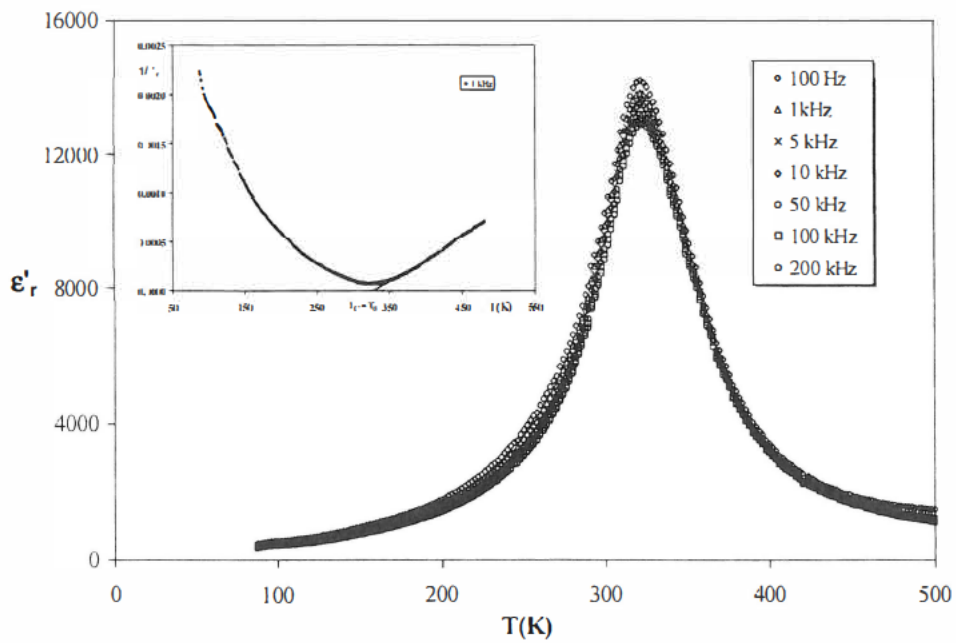


Figure 2. Temperature and frequency dependence on ϵ'_r , the real part of the permittivity, and the temperature dependence of $1/\epsilon'_r$ at 10^3 Hz, for a ceramic with composition $\text{BaTi}_{0.925}(\text{Nb}_{0.5}\text{Yb}_{0.5})_{0.075}\text{O}_3$.

Properties of $BaTi_{1-x}(Nb_{0.5}Yb_{0.5})_xO_3$

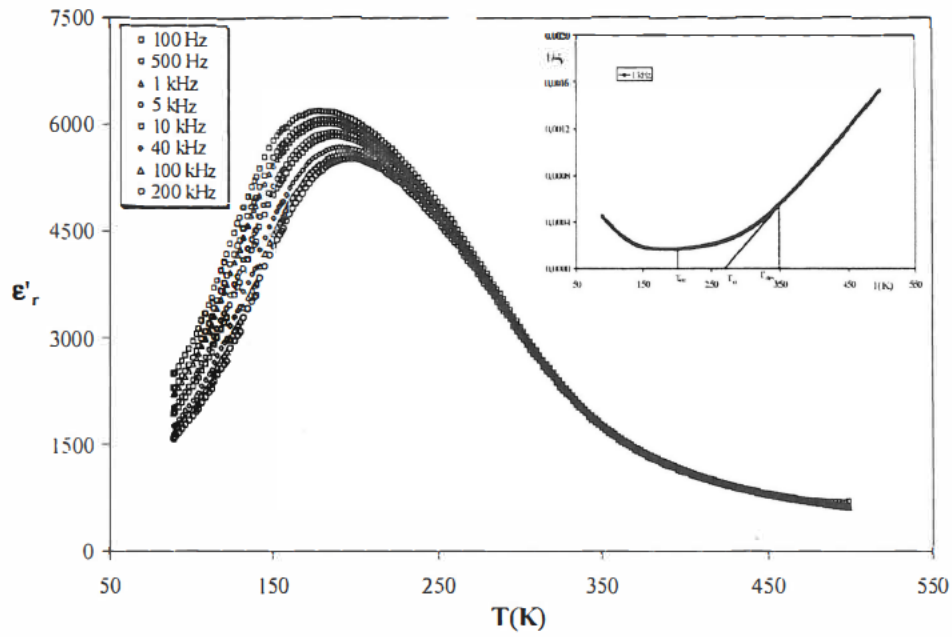


Figure 3. Temperature and frequency dependence on ϵ'_r , the real part of the permittivity, and the temperature dependence on $1/\epsilon'_r$ at 10^3 Hz, for a ceramic with composition $BaTi_{0.85}(Nb_{0.5}Yb_{0.5})_{0.15}O_3$.

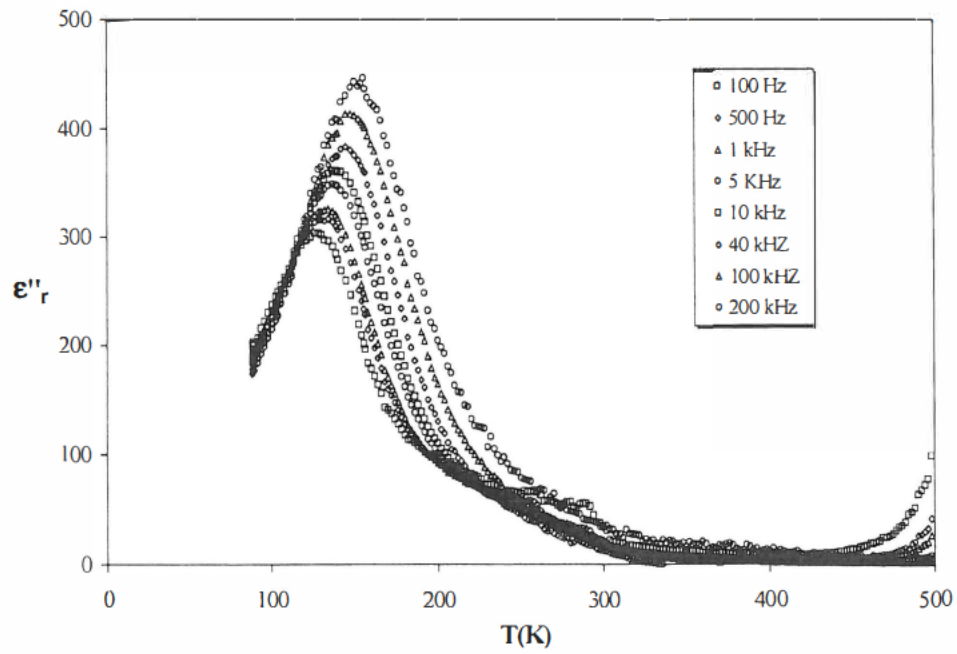


Figure 4. Temperature and frequency dependence of ϵ''_r , the imaginary part of the permittivity, for a ceramic with composition $BaTi_{0.85}(Nb_{0.5}Yb_{0.5})_{0.15}O_3$.

Table 1

Physical properties for BaTi_{1-x}(Nb_{0.5}Yb_{0.5})_xO₃ ceramics. $\Delta T_m = T_m(10^5 \text{ Hz}) - T_m(10^2 \text{ Hz})$ and $\Delta \varepsilon'_r / \varepsilon'_r = \varepsilon'_r(10^2 \text{ Hz}) - \varepsilon'_r(10^5 \text{ Hz}) / \varepsilon'_r(10^2 \text{ Hz})$ at T_C (or T_m)-40 K

Composition	T _C (K)	T _m (K) at 1 kHz	$\varepsilon'_{\text{max}}$ at 1 kHz	ΔT_m (K)	$\Delta \varepsilon'_r / \varepsilon'_r$
0.000	400		8652		0.06
0.050	358		11420		0.07
0.075	324		13800		0.08
0.100		284	9517	6	0.21
0.125		242	6772	10	0.25
0.150		184	6027	18	0.31
0.175		158	5276	20	0.34
0.200		146	2331	22	0.35

of the attempt frequency, E_a the activation energy, k_B the Boltzmann constant and T_{VF} the static freezing temperature [13]. For example, for $x = 0.15$ the parameters of Vogel–Fulcher relation were $E_a = 0.042$ eV, $f_0 = 7 \times 10^9$ Hz and $T_{VF} = 151$ K. All these characteristics are typical of relaxor behaviour.

All dielectric data for BaTi_{1-x}(Nb_{0.5}Yb_{0.5})_xO₃ ceramics are summarised in Table 1. We noted that the temperature T_C (or T_m) decreases with the increase of Nb⁵⁺ and Yb³⁺ were substituted for Ti⁴⁺. This variation is related to the sizes of Nb⁵⁺ and Yb³⁺ which are larger than that of Ti⁴⁺ ($r_{\text{Nb}^{5+}} = 0.64$ Å, $r_{\text{Yb}^{3+}} = 0.868$ Å and $r_{\text{Ti}^{4+}} = 0.605$ Å for six coordinations [14]). This limits the shift (Δz) of the tetravalent cation from the octahedron centre, leading to a decrease of T_C, according to the empirical relation [15], where T_C and $(\Delta z)^2$ are directly correlated. In addition, we remark that in classical ferroelectric phase, substituting of Ti⁴⁺ by Nb⁵⁺ and Yb³⁺ induces not only a decrease in T_C but also an increase of $\varepsilon'_{\text{max}}$, which reaches 13800 at 324 K for $x = 0.075$ composition.

For a Nb⁵⁺ and Yb³⁺ for Ti⁴⁺ substitution rate ($x \geq 0.1$) the relaxor phase appears. The main dielectric relaxor characteristics (ΔT_m and $\Delta \varepsilon'_r$, Table 1) increases as x increases. This is due of course to the strong composition heterogeneity that exacerbates the relaxor effect. This was typically the case in the lead perovskite relaxor Pb(Mg_{1/3}Nb_{2/3})O₃ where a local 1:1 order between niobium and magnesium atoms generated ordered regions surrounded by rich niobium polar regions. The heterogeneity thus created induced the relaxor effect commonly correlated with nanoscale spontaneous [2]. The present result is of great interest for obtained relaxor compositions at temperature close to 295 K for use as lead capacitor dielectrics or actuators. As an example, the composition $x = 0.1$, presents a relaxor behaviour at $T_m = 284$ K with an important value of ε'_r of about 9500 at 1 kHz (Table 1). The room temperature values of ε'_r and $\tan \delta$ are 8990 and 0.01 respectively.

3.3. Ferroelectric Behaviour

The polarisation hysteresis loops of BaTi_{0.875}(Nb_{0.5}Yb_{0.5})_{0.125}O₃ measured at different temperatures are shown in Figure 5. At temperature far below $T_{\varepsilon'_{\text{rm}}}$ near-square $P - E$ loops are observed, with remanent polarization (P_r) of $4.725 \mu\text{C}/\text{cm}^2$ and coercive field (E_C) of 3.61 kV/cm at 110 K. With increasing temperature, P_r and E_C decrease simultaneously (Figure 6). However, at $T_{\varepsilon'_{\text{rm}}}$ and above, P_r is not zero, a nonlinear P-E behaviour is present, typical ferroelectric relaxor characteristic [4].

Properties of $\text{BaTi}_{1-x}(\text{Nb}_{0.5}\text{Yb}_{0.5})_x\text{O}_3$

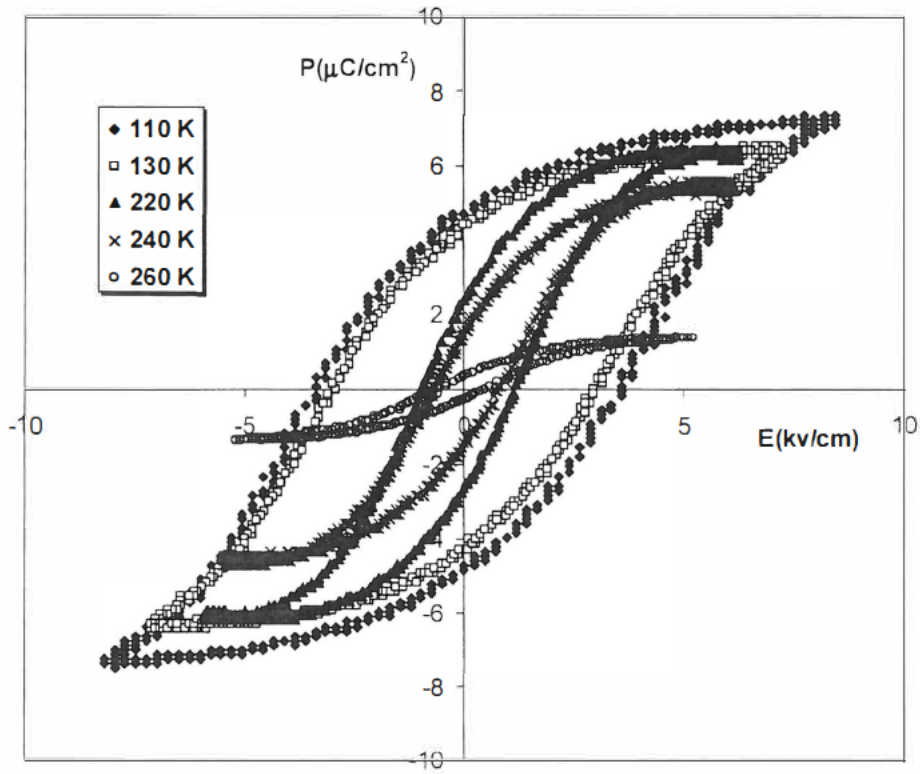


Figure 5. P - E hysteresis loops of $\text{BaTi}_{0.875}(\text{Nb}_{0.5}\text{Yb}_{0.5})_{0.125}\text{O}_3$ ceramic recorded at different temperature.

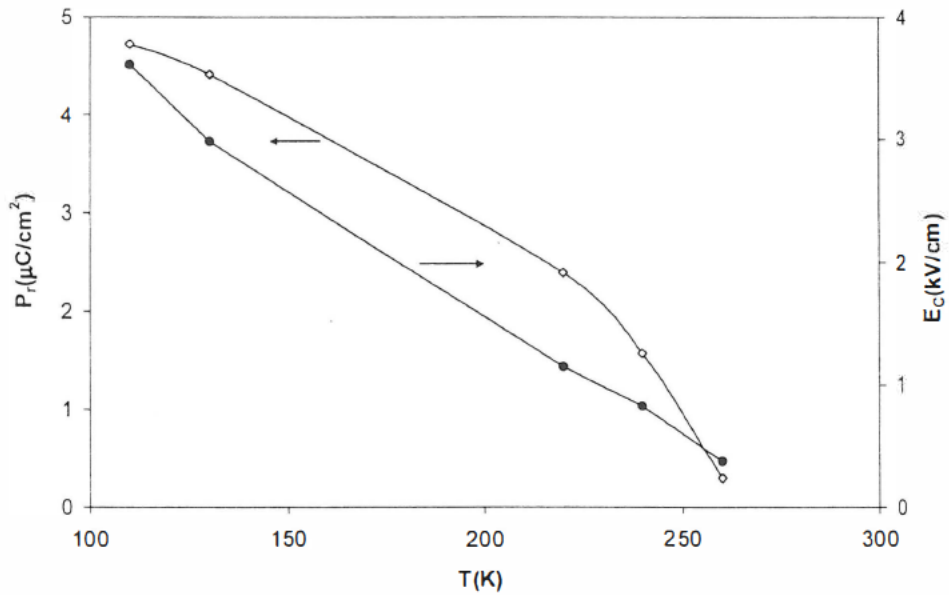


Figure 6. Remanent polarisation (P_r) and coercive field (E_c) as a function of temperature for $\text{BaTi}_{0.875}(\text{Nb}_{0.5}\text{Yb}_{0.5})_{0.125}\text{O}_3$ ceramic.