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Structural, dielectric, piezoelectric, ferroelectric and electro-caloric properties of $Ba_{1-x}Ca_xTi_{0.975}(Nb_{0.5}Yb_{0.5})_{0.025}O_3$ lead-free ceramics

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ABSTRACT

Polycrystalline samples of $Ba_{1-x}Ca_xTi_{0.975}(Nb_{0.5}Yb_{0.5})_{0.025}O_3$ (where x = 0.15, 0.2 and 0.3, abbreviated as BCTYN) were prepared by the conventional solid state reaction method. The effect of calcium (Ca) substitution in $BaTi_{0.975}(Nb_{0.5}Yb_{0.5})_{0.025}O_3$ (abbreviated as BTYN25) on the structural, dielectric, piezoelectric and ferroelectric properties and electro-caloric effects (ECE) was investigated. X-ray diffraction (XRD) results at room temperature showed that the BCTYN samples in the composition $x < 0.3$ exhibited a pure tetragonal perovskite structure. Dielectric measurements showed a classical ferroelectric behavior for all samples. With the increase of the Ca content, the Curie temperature (T_C) was still maintained with a small shift towards low temperature. The evolution of the Raman spectra was studied as a function of compositions and temperatures. The Raman bands confirmed the structure and the phase transition of the BCTYN ceramics. By adding Ca, the piezoelectric properties and the remanent polarization (P_r) are relatively maintained for the compositions x = 0.15 and x = 0.2. A piezoelectric coefficient of d_{33} = 130 pC/N and a planar electromechanical coupling factor of k_p = 28% were obtained for these compositions. Two different methods were used to calculate the electro-caloric coefficients of the BCTYN ceramics. The incorporation of Ca was found to enhance the electro-caloric strength ($\xi = \Delta T/\Delta E$) within a broad temperature range with a best value of ξ = 0.2 Kmm/kV for x = 0.2.

1. Introduction

Ferroelectric materials have been applied to many electronic devices where their excellent dielectric and piezoelectric properties were utilized. The $BaTiO_3$ and the isovalent-substituted-$BaTiO_3$ are especially promising candidates and have been actively studied.

Among them, calcium-doped $BaTiO_3$ ($Ba_{1-x}Ca_xTiO_3$) compositions are considered to be one of the foremost potential candidates for the lead-free memory devices [1]. It has been pointed out that the Ca^{2+} ions in (Ba,Ca)TiO_3 caused a compensation polarization due to their off centering nature [2], which makes maintain the good piezoelectric and ferroelectric properties of the target materials. Based on the literature, the substitution of Ba^{2+} by Ca^{2+} in the $BaTiO_3$-based ceramics ameliorates the electro-caloric effect (ECE) of these materials and the best results are obtained after the incorporation of 15% and 20% of Ca [3–6].

In addition, it has been reported in some studies that better dielectric, piezoelectric, ferroelectric and electro-caloric properties of the $BaTiO_3$-based ceramics have been obtained by substituting Ti^{4+} by Nb^{5+} and Yb^{3+} [7–10].

According to the foregoing and in order to work out materials with good properties, the composition $BaTi_{0.975}(Nb_{0.5}Yb_{0.5})_{0.025}O_3$ (BTYN25) has been chosen as a targeted material and the substitute ions Ca^{2+} in the A-site have been selected with an amount of 15%, 20% and 30%. In this work, the effects of Ca^{2+} substitution on the structural, dielectric, piezoelectric, ferroelectric and electro-caloric properties of $Ba_{1-x}Ca_xTi_{0.975}(Nb_{0.5}Yb_{0.5})_{0.025}O_3$ (BCTYN) ceramics are investigated.

2. Experimental procedure

$Ba_{1-x}Ca_xTi_{0.975}(Nb_{0.5}Yb_{0.5})_{0.025}O_3$ (x = 0.15, 0.2 and 0.3) (BCTYN) powders were prepared by the conventional solid-state reaction method. The starting materials are high-pure (99.9%, Sigma-Aldrich) powders of $BaCO_3$, $CaCO_3$, TiO_2, Yb_2O_3 and Nb_2O_5. All these materials were dried at 150 °C for 2 h, weighed according to the composite formula $Ba_{1-x}Ca_xTi_{0.975}(Nb_{0.5}Yb_{0.5})_{0.025}O_3$, and mixed in an alcoholic medium for 1 h. The mixtures were calcined at 1150 °C for 12 h in air. The obtained powders, to which a 5 wt% polyvinyl alcohol (PVA) binder was added, were mixed for 1 h and pressed under 100 MPa into 8 mm diameter and about 1 mm thick pellets. Finally, the pellets were

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sintered at 1400 °C for 4 h with a speed of 250 °C/h followed by furnace cooling. Room temperature powder X-ray diffraction (XRD) patterns were recorded on a Philips diffractometer using CuKα$_1$ and CuKα$_2$ radiation (λ_1 = 1.540598 Å, λ_2 = 1.544426 Å) in the range $10° < 2\theta < 80°$ with a step of 0.02° and a counting time of 10 s per step in order to determine the structure for all the prepared ceramic compositions. The dielectric measurements were performed on the ceramic discs after deposition of silver electrodes on the circular faces. The dielectric permittivity of the sample was measured with a Solartron Impedance analyzer SI-1255 as a function of both temperature (0–120 °C) and frequency (10^2–10^5 Hz). The piezoelectric constant (d_{33}) was measured using a YE2730A d_{33} meter at room temperature. The electromechanical coupling factor (k_p) was calculated by the resonance–antiresonance method using the HP4194A impedance analyzer. Ferroelectric (*P-E*) loops were determined for different temperatures and different electric fields remanent polarization (P_r) and coercive field (E_c) were estimated from the hysteresis loops. The ceramic sample was immersed in a thermostatic oil bath. The current and the electric field were recorded while applying cyclic electric fields (current amplifier Keithley 428 and high voltage amplifier TREK Model 20/20C). The working frequency was fixed to 1 Hz. Raman scattering data was collected in the frequency range 50–1000 cm^{-1} using a Raman spectrometer (Horiba HR 800, JobinYvon). The heat-flow measurement was carried out using a modified Differential Scanning Calorimetry (MHTC96 Setaram, France) when the sample was subjected to an electric field under isothermal conditions in the temperature range 70–120 °C. The electric field ranging from 1 to 2.5 kV/mm was applied for 300 s over two thin wires reaching the heart of the apparatus.

3. Results and discussion

3.1. X-ray diffraction study

The XRD patterns of the $Ba_{1-x}Ca_xTi_{0.975}(Nb_{0.5}Yb_{0.5})_{0.025}O_3$ (x = 0.15, 0.2 and 0.3) (BCTYN) ceramics with different compositions are shown in Fig. 1. It should be noted that two very low intensity peaks are observed around the 2θ values of 28° and 34° as those observed in the target ceramic x = 0 (BTYN25) [10]. They may be associated with the Ba-deficient phase $Ba_6Ti_{17}O_{40}$ which does not affect the physical properties of ceramics [10].

The perovskite structure which is observed for the samples (x < 0.3) suggests that Ca diffuses into the target ceramic x = 0 (BTYN25) lattice forming a homogeneous solid solution. For the sample at x = 0.3, a secondary phase is observed and marked "*" representing the orthorhombic $CaTiO_3$ phase. So the limit of solubility of the calcium in the solid solution BCTYN is around 20%, which is similar to the $CaTiO_3$-$BaTiO_3$ system [11,12].

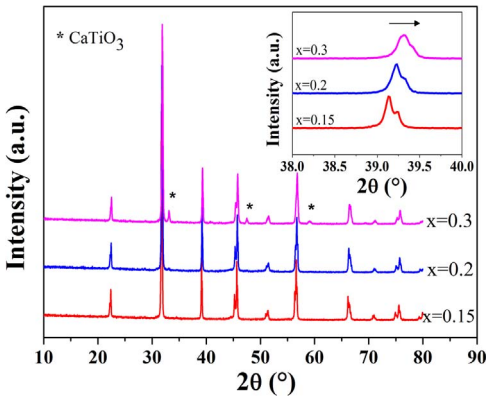

Fig. 1. Room temperature XRD patterns of BCTYN compounds. The inset illustrates the XRD patterns for the peak within the 2θ range of 38–40°.

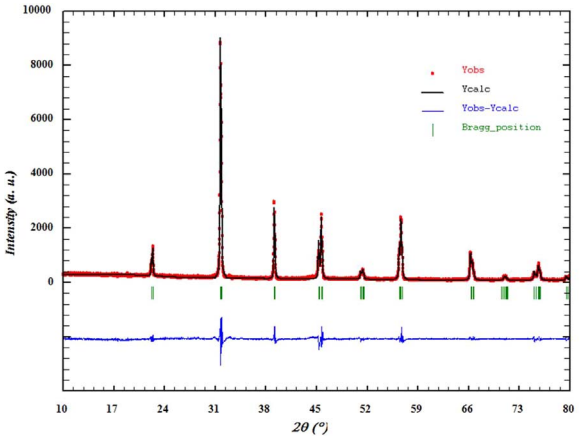

Fig. 2. Refined X-ray diffraction pattern of the BCTYN (x = 0.2) ceramic.

Moreover, as x increases, the diffraction peaks of the BCTYN ceramics shift to a larger 2θ (See the shift of the peak within the 2θ range of 38–40° presented inset Fig. 1 as an example), showing that the lattice parameters decrease with the addition of Ca. Because the ionic radius of Ba^{2+} (1.61 Å, 12 coordinate) is larger than that of Ca^{2+} (1.34 Å, 12 coordinate) [13], the substitution of Ba^{2+} by Ca^{2+} leads to the decrease of the lattice parameters [11,14,15].

The refinements of the XRD patterns are obtained with the tetragonal symmetry (with P4mm space group) in all ceramics. The refined XRD pattern of the BCTYN (x = 0.2) ceramics was shown in Fig. 2 as an example. The lattice parameters and the unit cell volume are calculated using a global profile matching method with the FullProf software [16]. The cell-parameters refinements for all compounds are shown in Table 1. By fitting, it is definitely confirmed that with increasing Ca content, the lattice parameters decrease, leading to a decrease in cell volumes. In addition, it is verified that the cell-volumes of the BCTYN ceramics are smaller than those of the x = 0 (BTYN25) undoped ceramic [10].

3.2. Dielectric properties

The evolution of the real parts of the permittivity as a function of temperature at 1 kHz of the target ceramic x = 0 (BTYN25) [10] and the BCTYN (x = 0.15, 0.2 and 0.3) ceramics are shown in Fig. 3.

When Ba^{2+} is substituted by Ca^{2+} in the BTYN25 ceramic, only one anomaly is observed, which is related to the tetragonal-cubic (T-C) phase transition. The orthorhombic-tetragonal (O-T) phase transition is not observed in these compositions. In fact, the substitution of Ba^{2+} by Ca^{2+} shifts this transition (O-T) to lower temperatures with the increase of the Ca content [17].

Moreover, it can be observed that this substitution causes a negligible change in the Curie temperature (T_C). It decreases from 100 °C for x = 0–91 °C for x = 0.3. As already explained by other authors [18], the lesser decrease in the Curie temperature T_C of the BCTYN ceramics was explained by the following Eq. (1):

$$T_C = (K_L - K_S)/B, \quad (1)$$

Table 1
Crystallographic data of BCTYN compounds.

Parameters	Compositions		
	x = 0.15	x = 0.2	x = 0.3
a (Å)	3971(7)	3970(3)	3969(7)
c (Å)	4002(2)	4002(1)	3998(0)
V (Å^3)	63,132(3)	63,086(2)	63,002(5)