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X-ray diffraction, dielectric, pyroelectric, piezoelectric and Raman spectroscopy studies on $(Ba_{0.95}Ca_{0.05})_{0.8875}Bi_{0.075}TiO_3$ ceramic

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Abstract

The $(Ba_{0.95}Ca_{0.05})_{0.8875}Bi_{0.075}TiO_3$ ceramic composition was prepared using the conventional mixed-oxide technique. X-ray diffraction at room temperature and dielectric permittivity in the temperature range from 85 to 450 K and frequency range from 10^2 to 2×10^5 Hz, respectively, were studied. The X-ray spectra were investigated by profile refinement technique with the use of specialized software at room temperature, the $(Ba_{0.95}Ca_{0.05})_{0.8875}Bi_{0.075}TiO_3$ composition crystallizes in quadratic perovskite structure. The dielectric measurements show classical ferroelectric behavior. The pyroelectric and piezoelectric results confirm the dielectric measurements. The pyroelectric coefficient is about 69.2 nC/cm^2 K at the transition temperature ($T_C = 367$ K). The piezoelectric constant is $d_{31} = 31.1$ pC/N and the electromechanical coupling factor is $k_P = 0.14679$. Raman spectra of $(Ba_{0.95}Ca_{0.05})_{0.8875}Bi_{0.075}TiO_3$ ceramic were taken at various temperatures and measured over the wave number range from 50 to 1000 cm^{-1}. All the Raman bands were assigned as the transitional modes of Ba^{2+}, Ca^{2+}, Bi^{3+} and Ti^{4+} cations. The temperature evolution of Raman spectra across the transition shows an important evolution characterizing the disorder of the high temperature phase.

Keywords: Ferroelectric; Pyroelectric; Piezoelectric; Raman spectroscopy

1. Introduction

According to their behavior, ferroelectric materials with perovskite structure can be divided into different classes depending on whether they are classical ferroelectrics or relaxors [1]. Due to their technological applications, compounds exhibiting high piezoelectric and electromechanical coupling constants have attracted the interest of many material science researches in the past few years. Lead-based ferroelectric materials exhibit excellent dielectric, pyroelectric and piezoelectric properties [2,3]. However, lead is a toxic element and with increasing demands of the environment protection, lead-free materials are highly desirable. The ferroelectric ceramic $BaTiO_3$ is one of the most important ferroelectric materials which has been extensively studied in the electronic industry and used as passive components in capacitors [4–7]. However, the ferroelectric phase transition in this material is of displacive type with $T_C = 404$ K.

To make $BaTiO_3$ ceramics usable at room temperature, cations of Ca^{2+} and Bi^{3+} were substituted for Ba^{2+} cation. The system $(Ba_{1-x}Ca_x)_{1-3y/2}Bi_yTiO_3$ which is one of the Ba-based perovskite, was studied in our previous work [8]. The structure and dielectric properties of $(Ba_{1-x}Ca_x)_{1-3y/2}Bi_yTiO_3$ solid solution were reported. As a function of composition a classical or a relaxor behavior was observed. In fact, we have showed the effect of doping by Bi and Ca on ferroelectric properties and relaxor character in the $(Ba_{1-x}Ca_x)_{1-3y/2}Bi_yTiO_3$ solid solution. The relaxor character in Bi doped barium calcium titanate ceramics is related with the Bi^{3+} ions and the Ca^{2+} ions. The presence of relaxor character in this solid solution is attributed to the nature of substitution element and not to the heterogeneity introduced by any substitution. The composition with $x = 0.05$ and $y = 0.075$, which crystallizes in tetragonal perovskite structure, is of strong interest for applications.

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In the present work, the $(Ba_{0.95}Ca_{0.05})_{0.8875}Bi_{0.075}TiO_3$ (BCBT-7.5%) composition ceramic was firstly investigated by X-ray analysis and dielectric study. Secondly, we are interested to ferroelectric properties of BCBT-7.5% using pyroelectric and piezoelectric measurements. Finally, we have related the macroscopic behavior to microscopic properties around the ferroelectric–paraelectric phase transition using Raman spectroscopy as a function of temperature.

2. Sample preparation

The composition BCBT-7.5%, was prepared by solid-state synthesis. The starting materials powders of $BaCO_3$, $CaCO_3$, Bi_2O_3 and TiO_2 were of high-purity (99.9%). The mixture was ball-milled, dried and then calcined at 850 °C for 12 h. The calcined pellets were reground and pressed. Ceramics with disk shape were sintered at 1250 °C for 2 h under air atmosphere.

3. X-ray diffraction study

Room temperature XRD pattern for BCBT-7.5% ceramic was fully indexed in the tetragonal symmetry. This demonstrates that the ceramics is in the single-phase state. The values of lattice and profile parameters were determined by using a global profile-mashing method with the fullprof software [9]. The observed, calculated and the difference of the X-ray diffraction patterns is given in Fig. 1. The structure and lattice parameters for BCBT-7.5% are listed in Table 1.

4. Dielectric study

From Fig. 2, we can deduce that the BCBT-7.5% ceramic, was already shown to display classical ferroelectric behavior with a slightly peak of ε'_r characteristic of ferroelectric–paraelectric phase transition and the value of T_C was not dependent on frequency. The value of $\varepsilon'_{r\max}$ is about 2864 at $T_C = 367$ K. In spite of the small amount of substitution of Ba by Bi and Ca in $BaTiO_3$, the dielectric permittivity presents an important decrease. However, the phase transition temperature presents a decreasing and tends near room temperature.

Table 1
Structure and lattice parameters of the composition $(Ba_{0.95}Ca_{0.05})_{0.8875}Bi_{0.075}TiO_3$.

Structure	*a* (Å)	*c* (Å)	*c*/*a*
Tetragonal	4.0087(3)	3.9872(6)	0.9946

5. Pyroelectric study

The ceramic sample BCBT-7.5%, was poled using a dc electric field of 0.7 kV mm^{-1} from 380 to 293 K in a dry helium atmosphere. The two electrodes were then short-circuited for 30 min in order to eliminate any residual space charge. The pyroelectric depolarization current was measured on heating from 293 to 380 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: $p = i/(sb)$, where s is the area of an electrode. The spontaneous polarization P_s was computed by integration of the value of p versus T ($p = dP_s/dT$) curve. The results are plotted in Fig. 3. From this figure, it can be seen that the pyroelectric current, p, shows a broad peak at a temperature lower than T_C which is characteristic of the ferroelectric–paraelectric phase transition, and then decreases to reach zero around 400 K. The pyroelectric coefficient, p is of about 69.2 nC/cm^2 K at T_C. An increase in the temperature leads to a decrease in the spontaneous polarization, P_s, which falls progressively to zero above T_C.

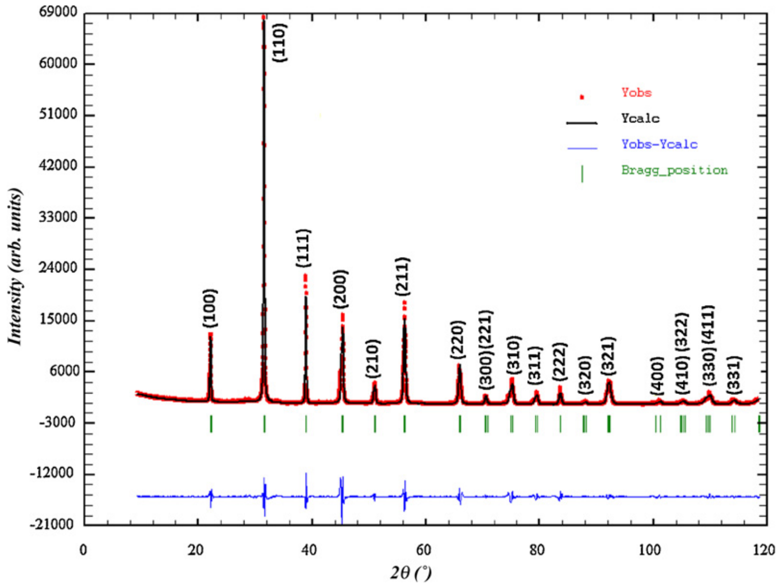

Fig. 1. X-ray diffraction pattern of a tetragonal sample with composition $(Ba_{0.95}Ca_{0.05})_{0.8875}Bi_{0.075}TiO_3$.

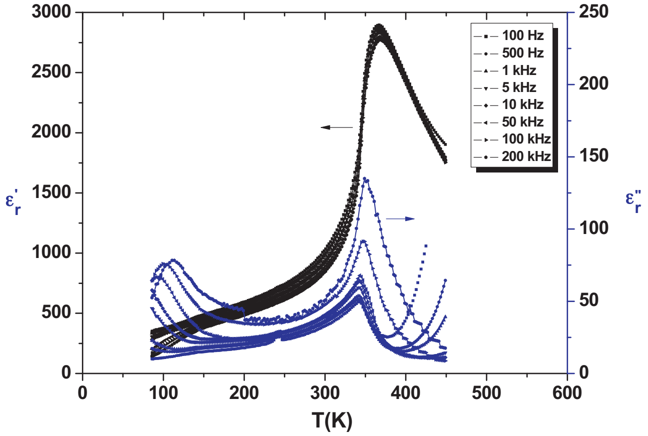

Fig. 2. Temperature dependence on ε'_r and ε''_r for $(Ba_{0.95}Ca_{0.05})_{0.8875}Bi_{0.075}TiO_3$ ceramic.

6. Piezoelectric investigation

Piezoelectric resonance measurements were undertaken on BCBT-7.5% ceramic composition prepared in disc shapes using an HP4194A impedance analyzer and were performed at 300 K. The sample was firstly poled using a DC electric field of 0.7 kV mm^{-1} at 300 K for 20 min and then short-circuited for 10 min at the same temperature in order to eliminate any residual space charge. The evolution of admittance and susceptance versus frequency in the range 400–600 kHz is plotted in Fig. 4. The determination of the piezoelectric parameters is 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 piezoelectric parameters were computed using the IEEE International Standards [10]. For a disk vibrating along a diameter, the value of the planar coupling coefficient (K_p) follows the relation:

$$\frac{K_p^2}{1-K_p^2} = 2.51\,\frac{f_a - f_r}{f_r}$$

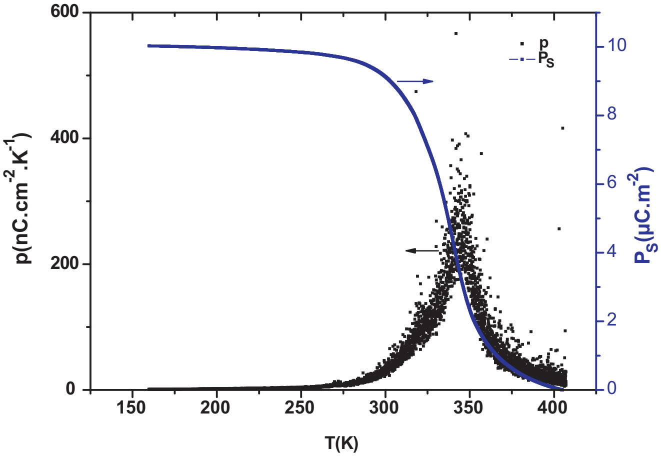

Fig. 3. Thermal evolution of pyroelectric coefficient p and spontaneous polarization P_s for the ceramic $(Ba_{0.95}Ca_{0.05})_{0.8875}Bi_{0.075}TiO_3$.

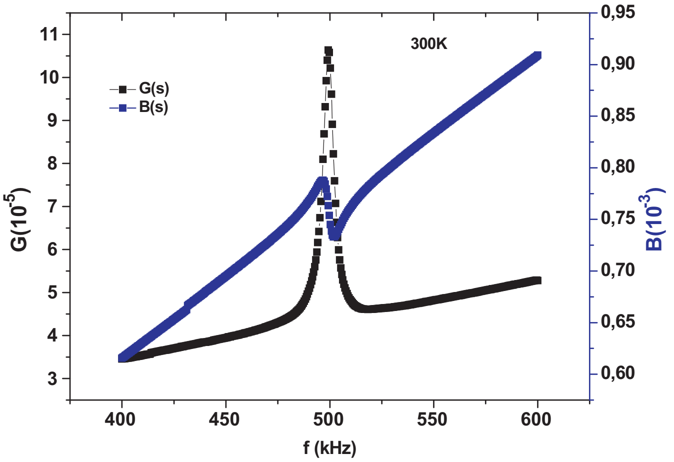

Fig. 4. Admittance G and susceptance B vs. frequency for $(Ba_{0.95}Ca_{0.05})_{0.8875}Bi_{0.075}TiO_3$ ceramic around the main radial piezoelectric resonance.

Table 2
Piezoelectric characteristics of $(Ba_{0.95}Ca_{0.05})_{0.8875}Bi_{0.075}TiO_3$ ceramic at 300 K.

Radial resonance frequency, f_r (kHz)	496.741
Young's modulus, $1/s_{11}$ (Nm^{-2})	6.72×10^{10}
Antiresonance frequency, f_a (kHz)	502.255
Planar coupling factor, k_p	0.14679
Piezoelectric coefficient, d_{31} (pCN^{-1})	31.1

where f_r is the resonance frequency and f_a is the antiresonance frequency. The d_{31} transverse piezoelectric coefficient is defined as:

$$d_{31} = k_{31}\sqrt{\varepsilon_{33}^T s_{11}^E}$$

where ε_{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.

The piezoelectric coefficients d_{31} and K_p were calculated from IRE standards [11]. The results are reported in Table 2. The value obtained for the d_{31} transverse piezoelectric coefficient is 31.1 pCN^{-1}. This piezoelectric coefficient is comparable to the values obtained in some ceramic such as $Na_{0.5}Bi_{0.5}TiO_3$ (d_{31} = 14) [12]. The d_{31} value can make BCBT-7.5% ceramic of interest for many applications.

In $BaTiO_3$, the d_{31} coefficient is about 78 pC/cm^2 at 300 K; then the introduction of Ca and Bi into the lattice of $BaTiO_3$ induces not only a decrease in the T_C value but also a sharp decrease in d_{31}.

7. Raman spectroscopy measurements

Raman scattering experiments were performed using a micro Raman spectrometer (LABRANHR-800), working in a back-scattering configuration, equipped with a He^+ ion (λ = 633 nm) laser. The spectral resolution of the system was 3 cm^{-1}.

Fig. 5, shows the temperature dependence of the Raman spectra of BCBT-7.5% ceramic close to the ferroelectric–paraelectric phase transition in the frequency range 50–1000 cm^{-1}. The Raman spectra of the BCBT-7.5% ceramic

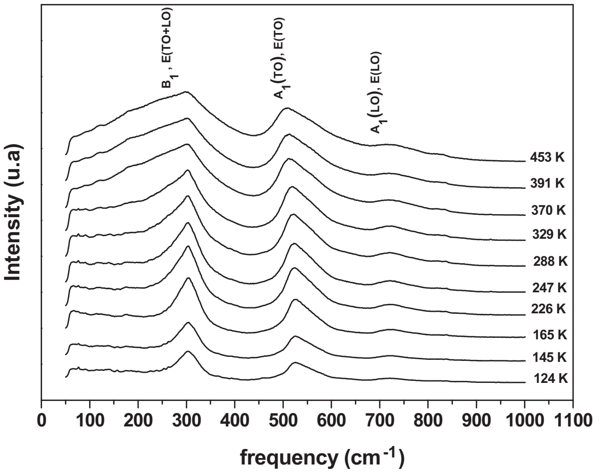

Fig. 5. Raman spectra of $(Ba_{0.95}Ca_{0.05})_{0.8875}Bi_{0.075}TiO_3$ in different temperature ranges from 50 to 1000 cm^{-1}.

showed the same $BaTiO_3$ bands [13]. At high temperature, $BaTiO_3$ has cubic phase with $Pm3m$ symmetry and possesses four triply degenerate optical vibrations, namely, $3F_{1u} + F_{2u}$. In the ferroelectric tetragonal phase at 25 °C, each mode splits into two modes, the $A_1 + E$ irreducible representation of P4 mm symmetry. Each of the A_1 and E modes splits further into TO and LO modes due to the presence of long-range electrostatic forces. Both A_1 and E modes are Raman and infrared active. In our material, we observe three bands denoted B_1, E(TO + LO); A_1(TO), E(TO); A_1(LO), E(LO). In fact, the B_1, E(TO + LO) phonon Raman spectrum observed at 309 cm^{-1} for $BaTiO_3$ is observed at 304.161 cm^{-1} for our material. However, the peak A_1(TO), E(TO) which observed at 519 cm^{-1} for $BaTiO_3$ is observed in this composition at 522.013 cm^{-1}. This increase in frequency is probably linked to the electrostatic forces introduced by the lattice disorder resulting from the substitutions in the Ba site. In Fig. 5, we observe a broadening of all the Raman bands as the temperature increases and a remarkable decrease in intensity especially after $T_C = 376$ K. This behavior characterizes the important disorder introduced at high temperature [14,15]. In the high frequency region there is an overlapping wide band which is similar to that observed in $BaTiO_3$ and which can be generalized for all the Raman spectra of perovskite structure involving relaxor and/or classical ferroelectric ceramics.

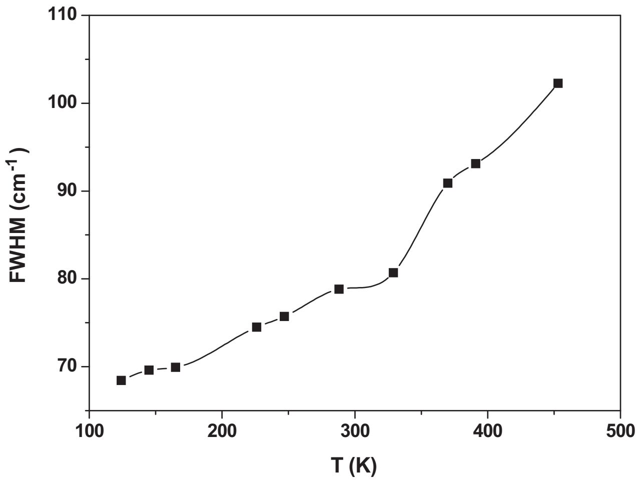

Fig. 6. Variation of the Raman FWHM (full width at half maximum) against the temperature for the band (at 500 cm^{-1}) in $(Ba_{0.95}Ca_{0.05})_{0.8875}Bi_{0.075}TiO_3$.

As that observed in former work [16], it can be found that the bands at 304.161 cm^{-1} and 720.755 cm^{-1} were independent of the formation of Ca_{Ba} and Ca_{Ti}. Moreover, the Ba–O bonds are closely related to the formation of 522.013 and 720.755 cm^{-1} bands, and Ti–O bands are closely related to the formation of 304.161 cm^{-1} band. Raman spectra show also the development of the new weak Raman band at 836.369 cm^{-1} for our material. From these observations, we confirm the interpretation of last works [16], that this Raman band can be a result of the formation of Ca_{Ti} defects formed by Ca^{2+} ions substitution for B-site Ti^{4+} ions and O^{2-} vacancies formed to compensate the charge imbalance.

The variation of the bandwidth for [A_1(TO), E(TO)] modes at 522.013 cm^{-1} of the composition BCBT-7.5% is presented in Fig. 6. It can be noted that the full width at half maximum (FWHM) increases as temperature increases. An abrupt increasing of the width at half maximum (FWHM) was observed around T_C. This evolution characterizes the phase transition from ferroelectric to paraelectric phase. In this state, vibration modes are affected by the fluctuations caused by the phase transition. This evolution characterizes the elongation of the cell in polarization direction which induces the transformation from cubic to tetragonal phase.

8. Conclusions

BCBT-7.5% ceramic with perovskite structure was prepared by a conventional ceramic fabrication technique. It has been investigated by several physical experiments. The X-ray diffraction study shows that this compound exists in a single phase at room temperature with a tetragonal symmetry. The pyroelectric and piezoelectric properties of BCBT-7.5% ceramic were studied. From the pyroelectric measurements, the pyroelectric coefficient evolution characterizes the ferroelectric–paraelectric phase transition. Then, we deduce that when the temperature increases from low temperature, the spontaneous polarization shows a slow evolution and then a drastic decrease when approaching T_C, meanwhile we notice the disappearance of the ferroelectric state. The evolution of the piezoelectric parameters shows that this composition is ferroelectric from low temperature to T_C that was determined by dielectric measurements. Raman spectra of our composition taken at various temperatures confirm our structural and dielectric results.

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