

Full Length Research Paper

Dielectric study of calcium doped barium titanate $Ba_{1-x}Ca_xTiO_3$ ceramics

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Calcium doping effect on the ferroelectric properties of $Ba_{1-x}Ca_xTiO_3$: BCTx ($x = 0.01, 0.05, 0.1$) ceramic material prepared via the sol-gel process was studied. X-ray diffraction (XRD) showed that the powders of calcined BCTx at $900^\circ C$ crystallize in a pure phase of perovskite type without secondary phases. Microstructural morphology was analyzed by Scanning Electronic Microscopy (SEM). Dielectric measurements were carried out by an analyzer of impedance in an active temperature range from ambient to $400^\circ C$ for various frequencies (0.1 kHz – 1 MHz). The modeling of the permittivity shows a thermal behavior controlled by the traditional Curie-Weiss law and the transition remains of first order for all the concentrations studied similar to that of the $BaTiO_3$ sample.

Key words: BCT, Sol-Gel, Ferroelectric, SEM, Curie point.

INTRODUCTION

Because of its excellent ferroelectric properties, to which is added the very good stability of its chemical and mechanical perovskite structure, barium titanate $BaTiO_3$ remains the preferred material for many applications such as: dielectric capacitors (Hung et al., 2003), ceramics with Positive Temperature Coefficient of Resistance: PTCR (Hreniak et al., 2006).

$BaTiO_3$ is known for its transition or Curie temperature, T_C of $120^\circ C$ (Haertling, 1999) which delimits the two dielectric states: ferroelectric state for $T < T_C$ in which the material crystallizes in the quadratic system and paraelectric state for $T > T_C$ where the structure becomes cubic system.

Several doping elements can be added to $BaTiO_3$ for

adapting some particular properties to specific applications: Sr^{2+} would decrease its transition temperature T_C , Pb^{2+} would increase T_C and Co^{2+} would attenuate the losses for intense electric fields without affecting its piezoelectric constant (Haertling, 1999). Barium calcium titanate crystals show promising applications in advanced laser systems, optical interconnects and electronic or optical storage devices (Veenhuis et al., 2000).

Considerable efforts have been devoted to elucidate the effect of Ca doping on the dielectric properties of $BaTiO_3$ in the solid solution of $Ba_{1-x}Ca_xTiO_3$ (BCT). In fact, calcium acts as a reduction inhibitor in $BaTiO_3$ and reduces the possibility of formation of the unwanted

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hexagonal phase (Victor et al., 2003). However some properties still remain source of many controversies such its effect on the variation in the BaTiO₃ temperature transition and on the change of the nature of the ferro-to-paraelectric transition: brutal transition or diffuse phase transition (DPT). Indeed, Berlincourt and Kulesar (1952) deferred that Ca doping of BaTiO₃ out of calcium leads to a negligible change of the Curie transition T_c. Later Mitsui and Westphal (1961) showed that the permittivity of BaTiO₃ modified with Ca²⁺ presents diffuse character of peak transition. Zhuang et al. (1987) found that the addition of an even small quantity in the Ti⁴⁺octahedral site led to a DPT transition and T_c dropped significantly. Subsequently, and contrary to Zhuang et al. (1987), Tiwari et al. (1989) reported that the Ba²⁺substitution by Ca²⁺ in the tetrahedral site of BaTiO₃ causes a significant increase in T_c and induces a diffuse type transition. Very recently Varatharajan et al. (2000) observed an increase in the transition temperature, T_c according to Ca²⁺ which depends on the site of occupation and possibly on the preparation method. Having adopted the recent sol-gel method as preparation procedure owing to its many advantages: very low crystallization temperature, stoichiometry, purity and smoothness of the grains and moderate cost (Xing et al., 2004; Zhu et al., 2006), we aimed, through this work, to study the behavior of the transition temperature as a function of Ca doping in the solid solution Ba_{1-x}Ca_xTiO₃ (BCT_x x= 0.00, 0.01, 0.05 and 0.10). In the present work for x=0.00, 0.01, 0.05 and 0.10, we have used BT, BCT0.01, BCT0.05, BCT0.1 notations. X-ray Diffraction (XRD), Scanning Electronic Microscopy (SEM) and Impedance-Spectroscopy Analysis (ISA) measurements are used for physical-chemical characterization.

EXPERIMENTAL PROCEDURE

The preparation route can be summarized as follows and it is similar to that deferred in Kadira et al. (2003). The titanium sol was prepared, starting from titanium alkoxide (titanium tetraisopropoxide Ti[OCH(CH₃)₂]₄, 97% min Assay Johnson Matthey GmbH) peptized with the lactic acid (CH₃CH(OH)COOH, ACS, 85.0-90.0% (Assay)). Ba²⁺ and Ca²⁺ solutions were prepared respectively by dissolution of barium acetate dihydrate (Ba(CH₃COO)₂·3H₂O, ACS reagent, 99%, 243671 SIGMA-ALDRICH) and CaCO₃ (Assay 100.1%, Fisher Scientific International Compagny) in an acetic acid (ACS reagent, ≥99.7%, SIGMA-ALDRICH) solution (1M). Then the various solutions are mixed with stoichiometric quantities according to the chemical formulation Ba_{1-x}Ca_xTiO₃ (x= 0.00, 0.01, 0.05 and 0.1). Drying with the drying oven leads to transparent xerogels which after crushing give raw powders of BCT. These powders were calcined at 900°C (4 h) for the formation of the crystalline phase. XRD Analysis is carried out on a XPERT-PRO diffractometer with a CuK-α radiation (λ=1.54056 Å) and was controlled by a PC. A continuous sweeping was adopted with a step of 0.017° and 1.905 s time per step. The angular range of selected measurement was of 10 to 75°. All the various pastilles were sintered at 1300°C for 4 h in air. Scanning Electronic Microscopy Analysis was carried out on a JEOL JSM5500 apparatus. Metallization was carried out with carbon by cathodic evaporation by means of a metal sprayer of the

type SPI carbon Coater and dielectric measurements were collected by an LCZ3330 impedance analyzer controlled in temperature and computer assisted in both the heating and cooling phases.

RESULTS AND DISCUSSION

Figure 1 shows XRD diagrams of BCT_x samples calcined at 900°C (4 h). All preparations crystallized in the pure perovskite phase without presence of secondary phases.

Figure 2 represents the microstructure of BCT0.1 sintered at 1300°C (4 h). It shows that the material has less porosity and that the distribution of the grains is rather uniform with an average diameter of 5 μm approximately. The perovskite phase of BCT ceramic remains very thermally stable after the sintering process, as indicated by the XRD diffractogram performed on a pulverized BCT0.1 pellet (Figure 3).

The chemical analysis of the iso-valent modified BT sample (BCT0.1 sample sintered at 1300°C (4h)) synthesized by Sol-Gel route was achieved by energy dispersive X-ray spectroscopy (EDX), using an EDX spectrometer attached to the same SEM unit. Figure 4 shows the EDX results of BCT0.1 sample. Table 1 corresponding to Figure 4, confirms the stoichiometry of BCT0.1 sample. EDX results are in good agreement with those calculated from the chemical formula.

Figure 5a and b present the thermal variation of the permittivity, ε_r and of the dielectric losses, tgδ of BCT0.1 material, respectively for various frequencies. When the temperature increases from the ambient one, ε_r first increases in the ferroelectric state, passes through a maximum at 136.25°C then decreases (paraelectric state) up to 250°C and increases again. The Curie point shows a dispersive behavior according to the frequency. The dielectric losses remain lower than 0.1% in the vicinity of the transition. The temperature region higher than 250°C is marked by an important dispersion of ε_r associated considerable dielectric losses which are of the order 2.3%. This indicates that the increase in the permittivity in this region is due to the mobility of space charges (ionic conductivity). The thermal hysteresis of this sample is about 23°C as illustrated in Figure 6. It indicates that the transition is of the first order.

Table 2 gives the values of the temperature of transition, T_c and the maximum of the permittivity, ε_{r,max} for the various calcium concentrations. It illustrated also Curie-Weiss temperature (T₀) and Curie-Weiss constant (C) values versus calcium concentration. The effect of calcium on T_c is illustrated in Figure 7. T_c increases in a significant way between 0 and 5% of Ca²⁺, then it undergoes a very light reduction beyond.

Probably, there exists a critical concentration between 5 and 10% for which T_c presents a maximum. In fact Mitsui and Westphal (1961) have found that this critical concentration is around 8%. For the concentrations studied in this work, BCT0.01 sample presents the lower

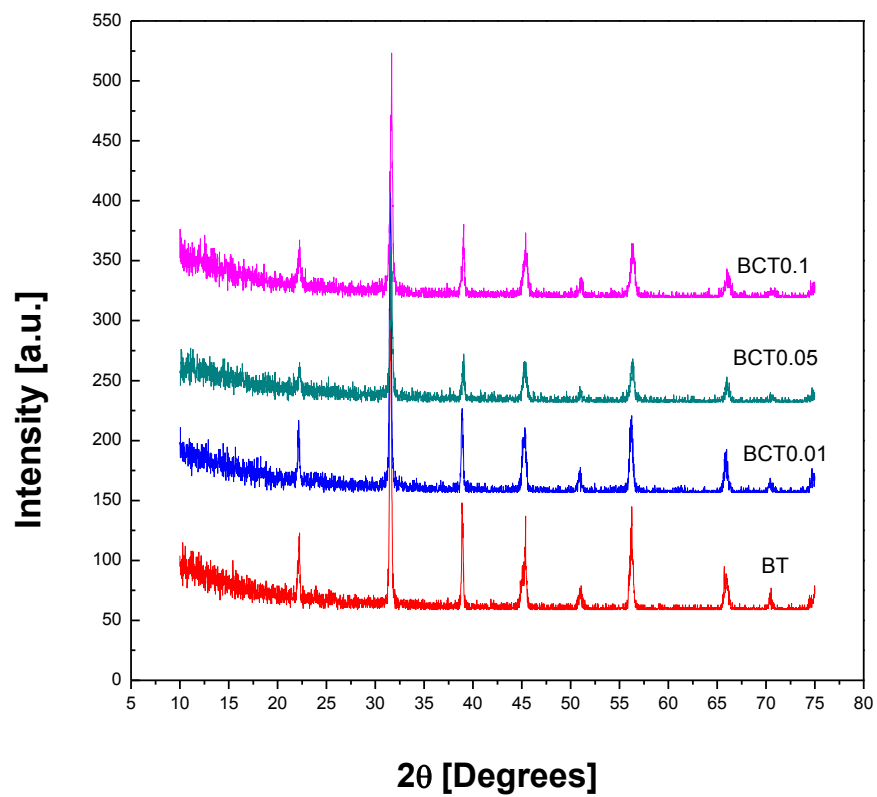


Figure 1. XRD patterns of BCT samples calcined at 900°C .

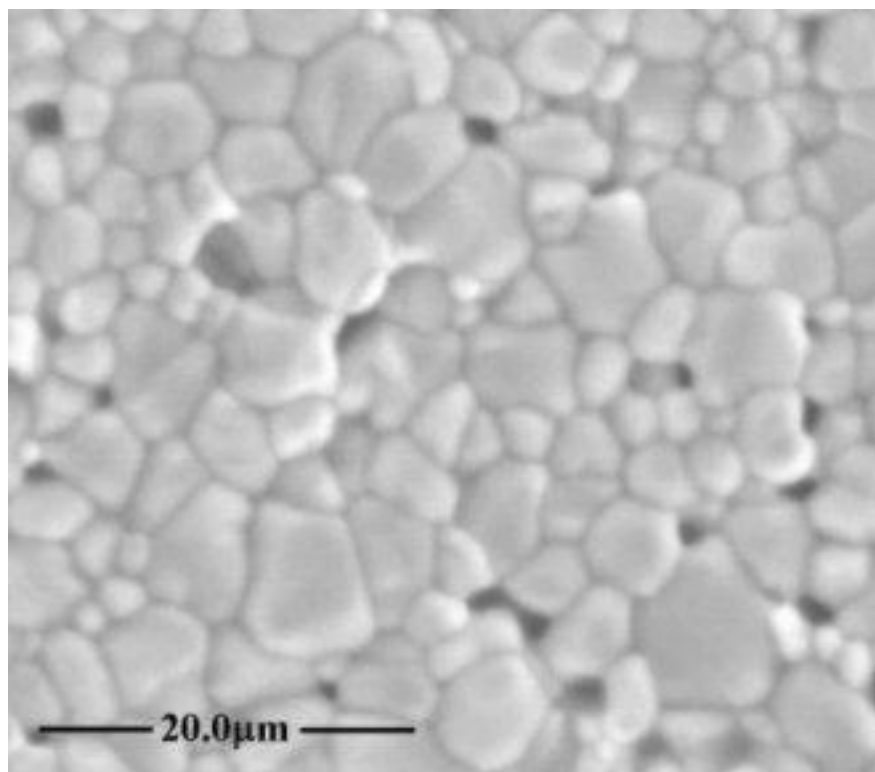


Figure 2. SEM micrograph of sintered BCT0.1 sample.

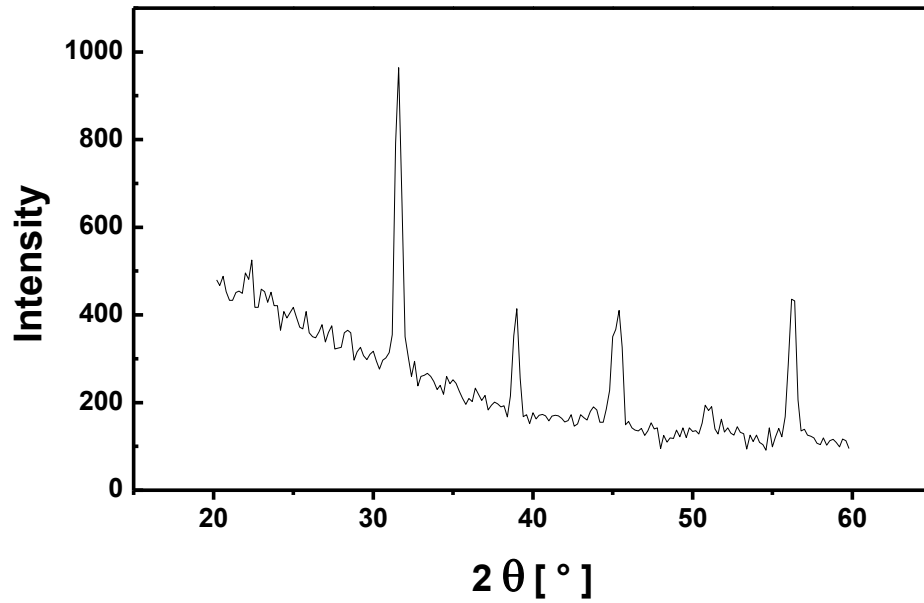


Figure 3. XRD pattern of BCT0.1 sintered at 1300°C (4 h).

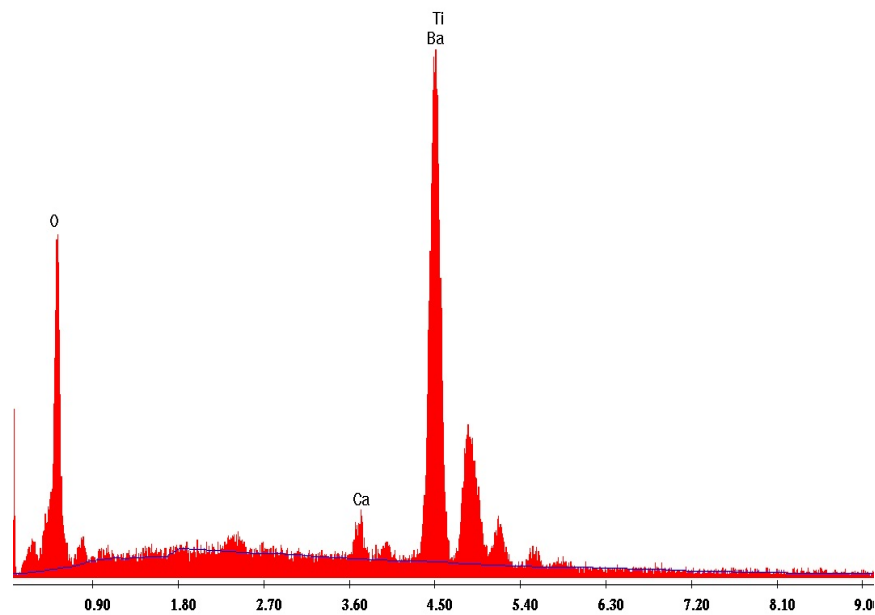


Figure 4. EDX of BCT0.1 sample sintered at 1300°C (4 h).

Table 1. EDX BCT0.1 sample sintered at 1300°C (4 h).

Element	% theo.	% Exper.	Differ.
MBa	55.18	50.98	4.200
MCa	1.79	1.96	0.170
MTi	21.60	25.48	3.880
MO	21.43	21.58	0.150

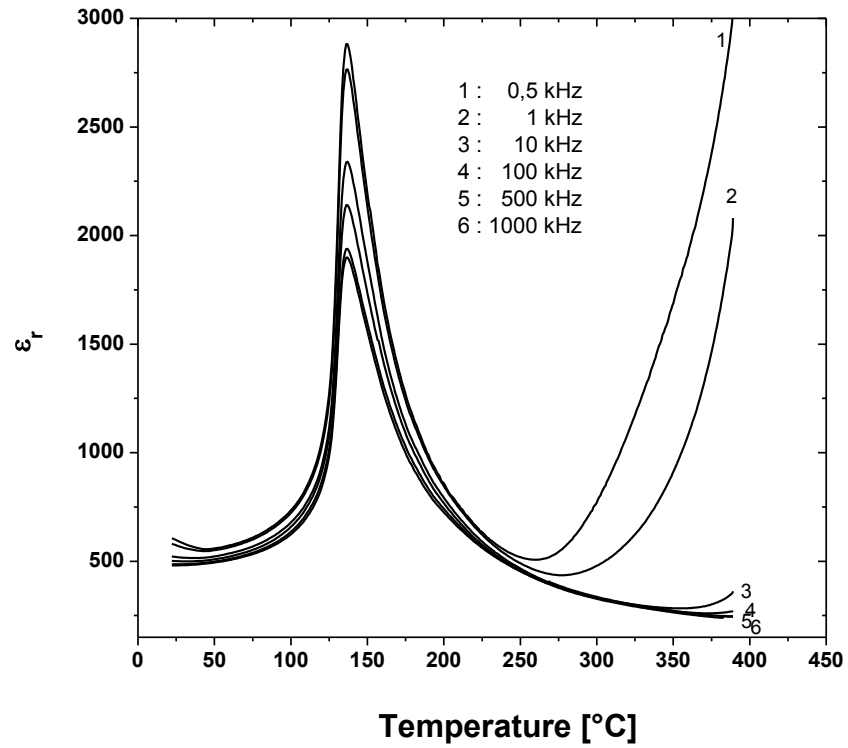


Figure 5a. Thermal variation of ϵ_r of BCT0.1 for various frequencies.

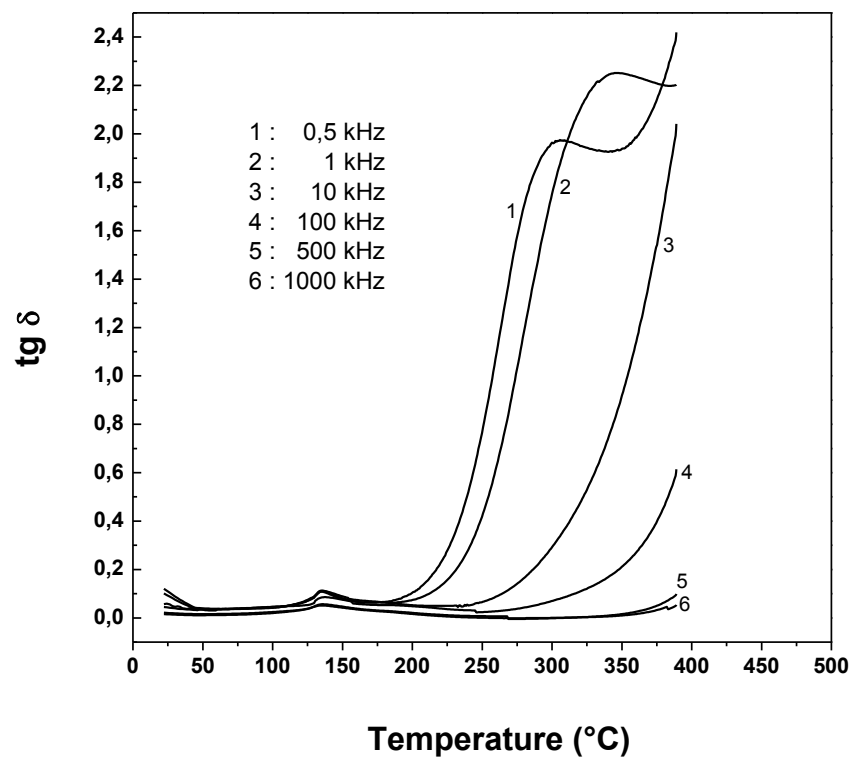


Figure 5b. Thermal variation of $\text{tg } \delta$ measurements of BCT0.1 for various frequencies.

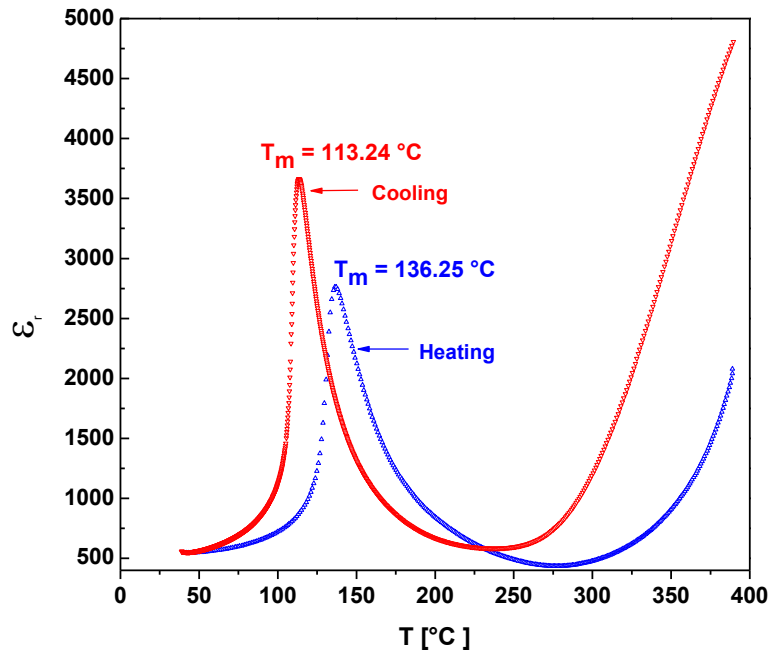


Figure 6. Thermal hysteresis for BCT0.1 sample (4 h).

Table 2. Dielectric results obtained for BCT samples.

Ca ²⁺ (%)	ε _{rmax}	T _c	T ₀	C	T _c -T ₀
0	2508.77	130.00	91.76	10.08 10 ⁺⁴	38.24
1	3229.79	131.26	107.46	8.46 10 ⁺⁴	23.80
5	2889.43	136.41	107.32	7.11 10 ⁺⁴	29.09
10	2764.55	136.25	115.69	6.41 10 ⁺⁴	20.56

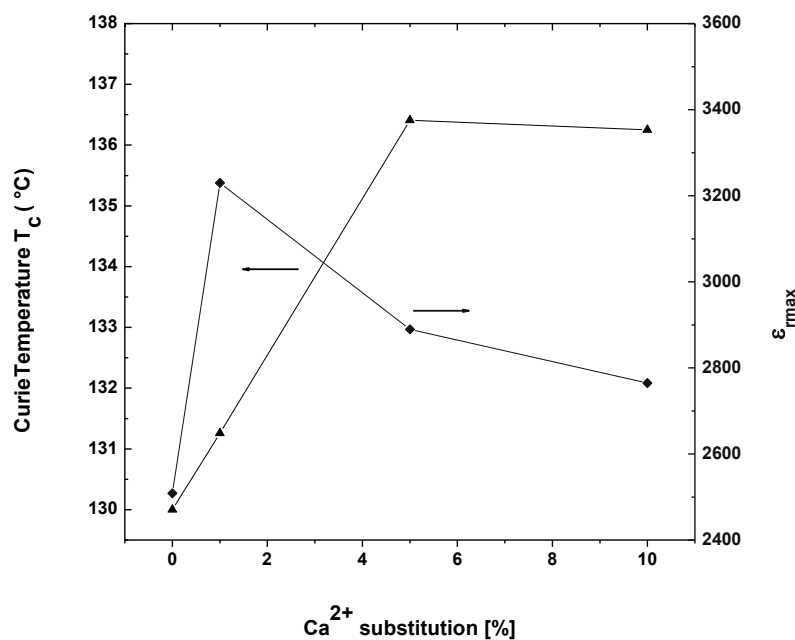


Figure 7. T_c and ε_{rmax} versus calcium concentration.

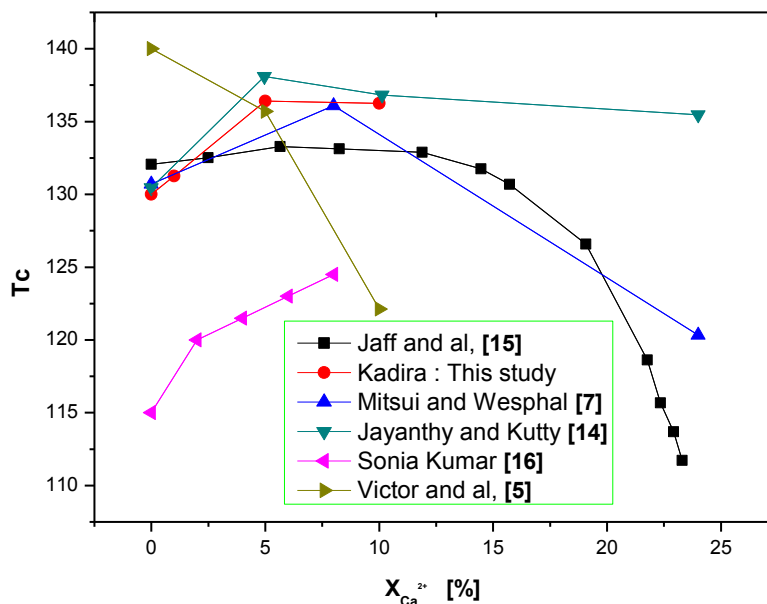


Figure 8. Literature comparative study of T_c versus $[Ca^{2+}]$.

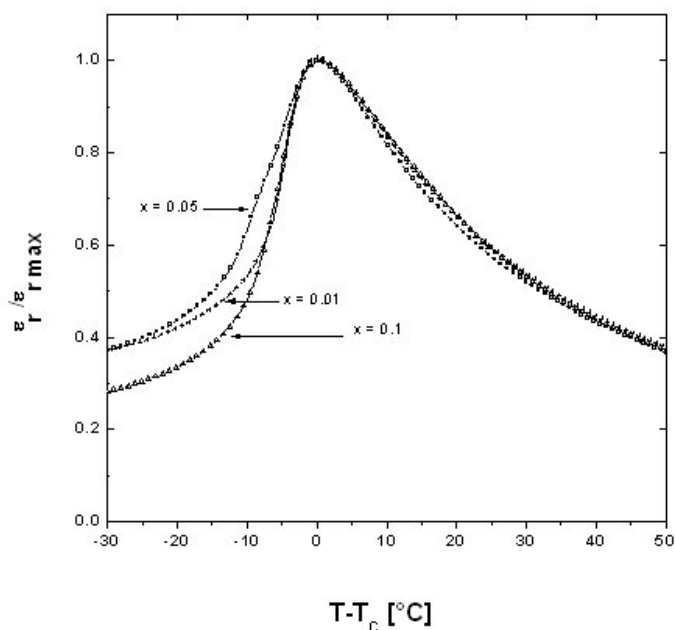


Figure 9. Diffuse character of Curie transition vs. calcium doping.

maximum permittivity ϵ_{rmax} value as shown in Figure 7.

Ca^{2+} doping in perovskite A site was conducted in several literature works: wet chemical route by Jayanthi and Kutty (2004), solid route by Mitsui and Westphal (1961), Jeffe et al. (1971) and Victor et al. (2003), modified Solid State Reaction and Microwave Sintering Routes by Kumar (2011) and sol-gel method in this study. However, sintering conditions are so different. In

Figure 8, we compare the results of these works to that of the present study; T_c variation as a function of x we found is in perfect agreement with the literature.

To highlight the influence of Ca^{2+} on the diffuse behavior of the transition, we indicated in Figure 9 the evolution of $\epsilon_r/\epsilon_{rmax}$ according to $T-T_c$ for the various concentrations of BCT. According to this figure, one notice that $BaTiO_3$ modified at 5% on calcium presents

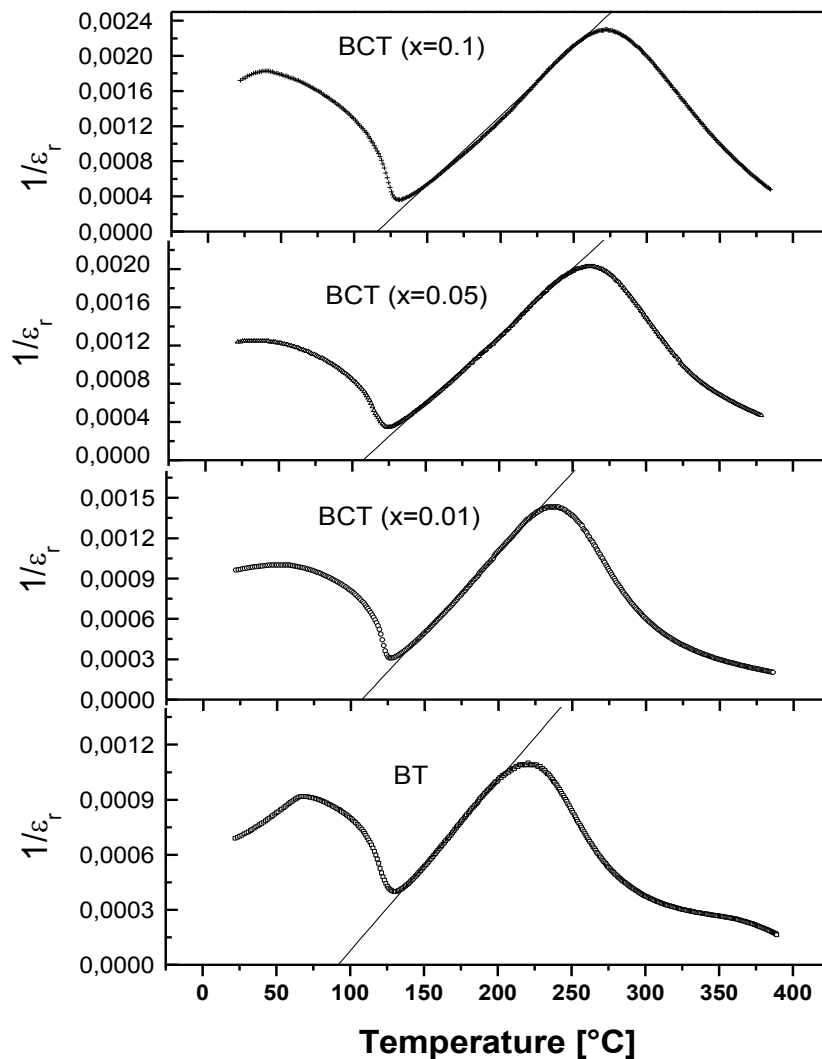


Figure 10. Paraelectric behavior modeling of BCT samples versus temperature.

the most diffuse phase transition. The spreading out of the Curie peak decreases for doping with 0.01 out of Ca^{2+} , then an increase for the fraction of 0.05 undergoes. The sample relating to 10 at % of Ca^{2+} appreciably presents the same degree of spreading out as that of the sample doped at 1%.

The modeling of the thermal paraelectric behavior of the various samples is given in Figure 10. The behavior of the various concentrations was described by the standard Curie-Weiss law: $\epsilon_r = C/T - T_0$, where T_0 and C are respectively the temperature and the constant of Curie-Weiss respectively. The temperature T_0 remains, in all cases, lower than T_C (Figure 11), which indicates that the nature of the transition is of the first order. The value of constant C decreases as Ca^{2+} doping increases (Figure 11) showing, thus, that the transition evolves gradually from the displacive type to the order-disorder one.

Conclusion

We have given in this work the study of the influence of calcium doping on the dielectric properties of BaTiO_3 . The samples were prepared by the recent sol-gel route. The structural characterization of the various concentrations of BCT by XRD reveals a complete crystallization in the pure perovskite structure. The dielectric study of BCT_x compounds doped up to $x=10$ at % of calcium shows that the later gave rises to an increase of the transition temperature for $x < 0.07$. Concerning the diffuse character of the transition, it was found that the concentration of $\text{BCT}_x=0.05$ shows the most diffuse transition. The thermal paraelectric behavior of the various samples was shown to follow the traditional Curie-Weiss law and the transition remains of first order for all the concentrations.

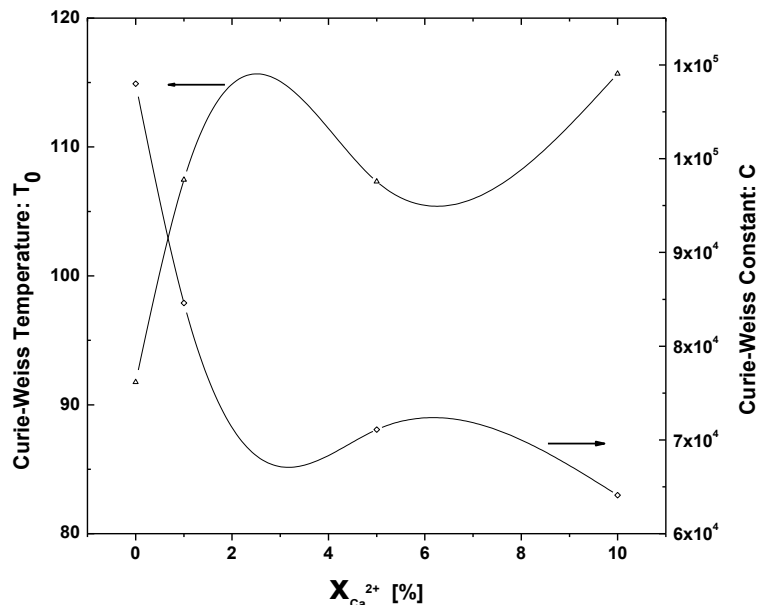


Figure 11. Curie-Weiss temperature, T_0 and Curie-Weiss constant, C versus calcium concentration.

Conflict of Interests

The authors have not declared any conflict of interests.

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