

## Effect of B<sub>2</sub>O<sub>3</sub> addition on the Sintering of BaTiO<sub>3</sub>-CaTiO<sub>3</sub> Composite Materials

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The effects of B<sub>2</sub>O<sub>3</sub> addition on the sintering behaviour of BaTiO<sub>3</sub>-CaTiO<sub>3</sub> (BCT) materials were investigated. (1-x) BaTiO<sub>3</sub>-x CaTiO<sub>3</sub>-y B<sub>2</sub>O<sub>3</sub> (where x is 3 or 7 % mol. and 0 ≤ y ≤ 3 mol.% respectively). Pellets were prepared from BaTiO<sub>3</sub> (BT) and CaTiO<sub>3</sub> (CT) powders mixture and sintered at 1,200, 1,250, 1,300 and 1,350 °C, gradually in air for 3 h. The relative density of BCT samples with 1 mol. % B<sub>2</sub>O<sub>3</sub> sintered at 1,200 °C were as good as those of undoped BCT sintered at 1,350 °C. When > 2 mol. % B<sub>2</sub>O<sub>3</sub> was added to BCT, the over doped B<sub>2</sub>O<sub>3</sub> did not form a liquid phase or volatilize, it remained in the samples and formed a secondary phase that lowered the sintering behaviour of the BCT. The X-Ray diffraction analysis carried out on both kind of pellets (x = 0.3 and x = 0.7) revealed the presence of BT and CT solutions together in an unidentified secondary phase.

**Key words:** BaTiO<sub>3</sub>, CaTiO<sub>3</sub>, B<sub>2</sub>O<sub>3</sub>, Sintering, Relative density, X-Rays diffraction.

### Introduction

The nonlinear properties of ferroelectrics materials have, recently, become the subject of intense research activity both in the fundamental and practical domains. These materials, are currently used in manufacturing of various microwave devices, such as voltage-controlled oscillators (VCO), tunable filters, phase shifters and varactors [1-3]. For such application, the basic requirements are; high dielectric tenability defined as the mean variation of the relative permittivity with field intensity, low dielectric loss tan δ, appropriate level of dielectric constant and a feeble temperature dependence of permittivity. In general, Strontium Titanate (ST) based materials are used for devices operation at low temperature while (Ba, Sr) TiO<sub>3</sub> (BST) based materials are used for devices operating at room temperature [4, 5]. Ferroelectric based materials present two major inconvenient, relatively high dielectric loss and larger temperature dependence of their relative permittivity. An efficient way is to dope oxides that have low dielectric loss into the ferroelectric materials. Additionally, the introduction of oxides would also be able to modulate the dielectric properties of these materials for specific applications. CaTiO<sub>3</sub> is a typical depressor in BaTiO<sub>3</sub> ceramics, which conduces to a significant decrease both in dielectric loss and in temperature coefficient of dielectric constant. Furthermore, CaTiO<sub>3</sub> introduces only slight change of Curie point when Ca<sup>2+</sup> substitute Ba<sup>2+</sup> in the A sites [6] but causes an important shift to lower temperature when

Ca<sup>2+</sup> substitute Ti<sup>4+</sup> in B sites [7]. In this latter case, it would be possible to obtain like diffuse phase structure conferring good dielectric and relaxer properties to these materials. Consequently, (Ba, Ca) TiO<sub>3</sub> systems are expected to be alternative candidates for tunable microwave dielectric materials with low dielectric loss and small temperature dependence [8].

BT or BCT ceramics usually require sintering temperature of > 1,300 °C. Such temperatures are, unfortunately, too high for industrial manufacturing. The principal objective of the present investigation was to decrease the sintering temperature of BCT based materials by introducing B<sub>2</sub>O<sub>3</sub> with different proportion in the initial powder mixture. B<sub>2</sub>O<sub>3</sub> is well known as a compound with low melting point, that would react with CaO and BaO to form glass phase, which enhance the liquid sintering process and consequently increase the densification of the sintered materials.

### Experimental

The BaTiO<sub>3</sub> (BT) powder used in this investigation was reagent commercial type manufactured by FLUKA while the used CaTiO<sub>3</sub> (CT) powder was prepared in laboratory following the conventional procedure of milling and calcination. The starting raw materials used for CT preparation were high purity commercial anatase TiO<sub>2</sub> powder (also made by FLUKA) and local CaCO<sub>3</sub> powder (extracted out from Khroub locality in Algeria). The starting powders were weighed and mixed in a stoichiometric proportion. The mixtures were then ball-milled for 6h using alumina balls in methanol alcohol. The obtained slurry was dried at 70 °C in electrical furnace and calcined in air at 1,100 °C for 8 h. XRD analysis was carried out on calcined powders to control

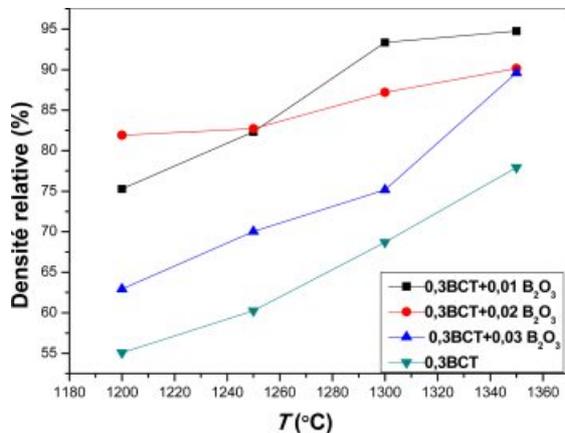
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the formation of CT phase.  $(1-x) \text{BaTiO}_3$ - $x \text{CaTiO}_3$ - $y \text{B}_2\text{O}_3$  (where  $x$  is 3 or 7% mol. respectively and  $0 \leq y \leq 3$  mol.%) mixtures pellets were prepared from  $\text{BaTiO}_3$  (BT),  $\text{CaTiO}_3$  (CT) and  $\text{B}_2\text{O}_3$  powders and re-milled by the same route. 1 mm high and 13 mm diameter pellets were obtained by uniaxial cold pressing under 70 MPa. The pellets were then sintered at 1,200-1,350 °C temperature range. The sintered samples were characterised in terms of apparent density by direct measure of mass and volume. X-Ray diffraction analysis was carried out on different sintered samples to follow the microstructure evolution.

## Results and Discussion

### Study of sample containing 70% of BT

The relative densities of samples sintered for 3 h at different temperatures are reported in Fig. 1. The obtained curves reveal identical evolution of the relative density as a function of the sintering temperature for all considered  $\text{B}_2\text{O}_3$  proportion in the initial mixture. We noticed as well that the increase in the relative density



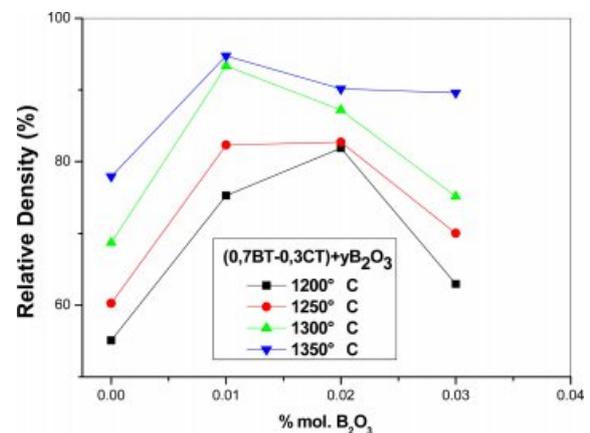
**Fig. 1.** Relative density of different  $((1-y)0.7 \text{BaTiO}_3 + 0.3 \text{CaTiO}_3) + y\text{B}_2\text{O}_3$  pellets as function of sintering temperature.

is, in all cases, about 17 to 20% per 150 °C. This result, probably, reveals identical densification mechanisms of pellets in this range of temperature.

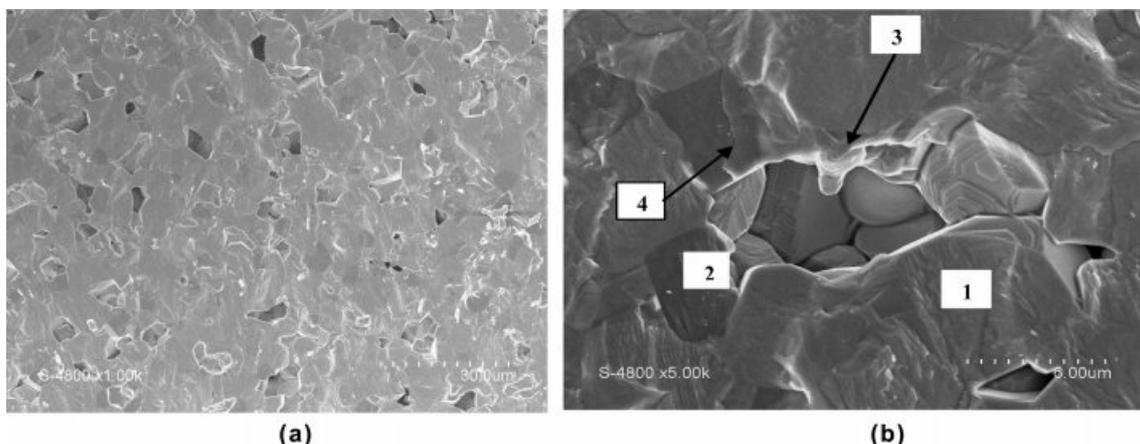
On the other hand, the obtained findings show (Fig. 2) an important increase in the relative density as a function of  $\text{B}_2\text{O}_3$  additions up to 1% mol. At the opposite, the relative density of pellets decreases beyond such a percentage. Moreover, It can be noticed that the decrease in the relative density is the more important that the sintering temperature is lower. This evolution is probably due to the formation of liquid phase, which enhances the densification for moderate proportion of  $\text{B}_2\text{O}_3$  by developing liquid sintering process. When the proportion of liquid phase became so important (for Higher  $\text{B}_2\text{O}_3$  proportion), the apparition of secondary porosity (Fig. 2) inhibits the sintering, consequently the pellet density decreases.

Higher  $\text{B}_2\text{O}_3$  proportion), the apparition of secondary porosity (Fig. 3(a)) inhibits the sintering, consequently the pellet density decreases.

The formation of liquid phase is probably the consequence of the reaction between BT, CT and  $\text{B}_2\text{O}_3$  at



**Fig. 2.** Relative density of different  $((1-y)0.7 \text{BaTiO}_3 + 0.3 \text{CaTiO}_3) + y\text{B}_2\text{O}_3$  pellets as function of proportion of added  $\text{B}_2\text{O}_3$ .



**Fig. 3.** (a) MEB micrograph of BT-0.3 CT + 3%  $\text{B}_2\text{O}_3$  pellet sintered at 1250 °C for 3 h and (b) SEM micrograph of 0.7BT-0.3 CT + 3%  $\text{B}_2\text{O}_3$  pellet sintered at 1,250 °C for 3 h.

lower temperature. X-Ray diffraction spectra recorded from different pellets effectively put in evidence the formation of BT and CT solution together an unidentified secondary phase for all considered sintering temperatures (Fig. 4). Furthermore, the obtained results reveal a decrease in proportions of BT and CT solutions respectively as function of added  $B_2O_3$ , while, the proportion of the unidentified phase increases. Consequently, the unidentified phase probably corresponds to liquid phase formed before than 1,200 °C.

Fig. 3(b) reveals the presence of 3 phases; the BT solid solution major phase (1), a minor dark phase (2) corresponding to CT solid solution and a glass-ceramics phase (3) designated by an arrow. Furthermore, it can be seen that the melting phase wraps a great area of a CT grain in zone (4) and is neighbored by secondary porosity which probably appears because of the shrinkage of the liquid phase during pellet cooling. Hence it must be concluded that the formation of secondary liquid phase enhances the densification of pellets for moderate proportion of  $B_2O_3$  by developing liquid sintering process. Contrariwise, when liquid phase content increases, the proportion of the secondary porosity, induced by the liquid phase shrinkage, increases too and leads to a diminution of pellets density.

#### Study of sample containing 70% of CT

The relative densities of samples containing 70% mol. of CT and sintered during 3 h at different temperatures are reported in Fig. 5.

As it can be observed, the evolution of the relative density is quiet different from that obtained in the case of sample containing 30% mol. of CT. Hence, the relative density increases between 1,200 and 1,300 °C and reaches a maximum of about 90% at 1,350 °C for all considered  $B_2O_3$  percentages. At the same time, the precedent curves reveal an important effect of  $B_2O_3$  addition on the relative density. This fact is more

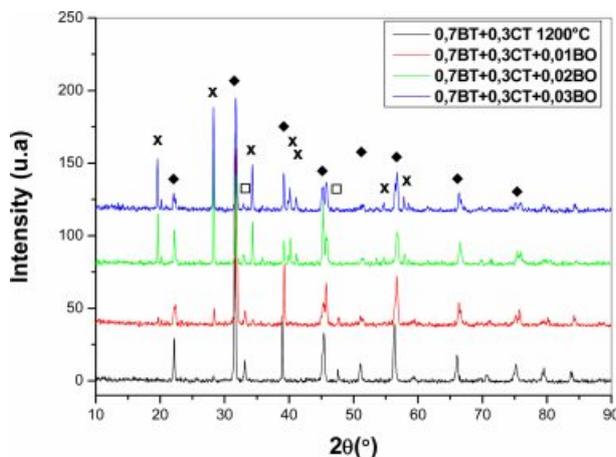


Fig. 4. X-Ray diffraction spectra recorded from different  $((1 - y)(0.7 BaTiO_3 + 0.3 CaTiO_3) + yB_2O_3)$  pellets sintered at 1,200 °C from 3 h; BT, CT, X unidentified phase.

apparent as we report the evolution of the relative density as a function of added  $B_2O_3$  percentage. In the case of pellets sintered at 1,200 or 1,250 °C, the obtained curves (Fig. 6) firstly reveal an important increase in the relative density with added percentage of  $B_2O_3$  up to 2% mol. For example, the relative density in pellets sintered at 1,200 °C pass from 42.3% in undoped sample to 82.3% in sample containing 2 mol.% of  $B_2O_3$ .

This corresponds to an augmentation of 100 per 100 in the relative density. Over 2% mol of added  $B_2O_3$ , the relative density decreases again probably owing to the formation of an important liquid phase proportion leading to the apparition of secondary porosity (Fig. 7) which restrain the densification in this range of temperature.

As in the case of pellets containing 30% of CT, the liquid phase probably corresponds to the unidentified phase revealed by X-Ray diffraction spectra recorded from different samples (Fig. 8). The spectra put in evidence the presence of BT solid solution, CT solid solution and unidentified phase whose proportion

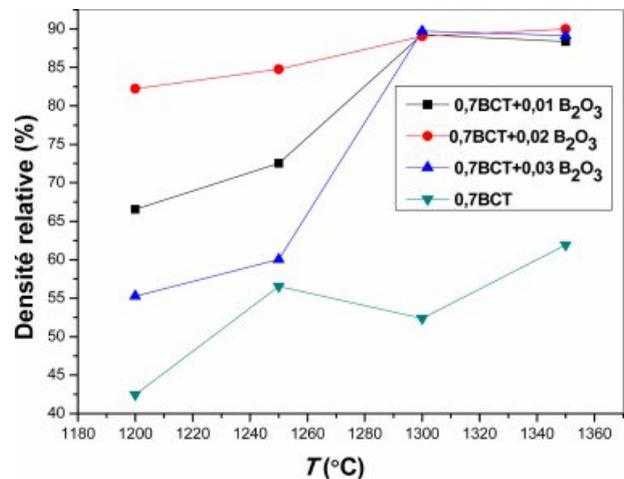


Fig. 5. Relative density of different  $((1 - y)(0.3 BaTiO_3 + 0.7 CaTiO_3) + yB_2O_3)$  pellets as function of sintering temperature.

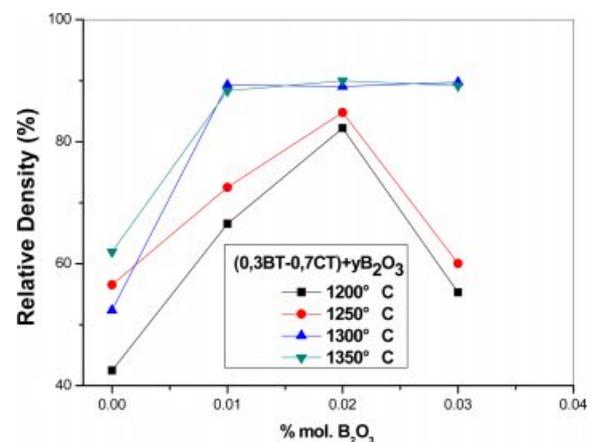
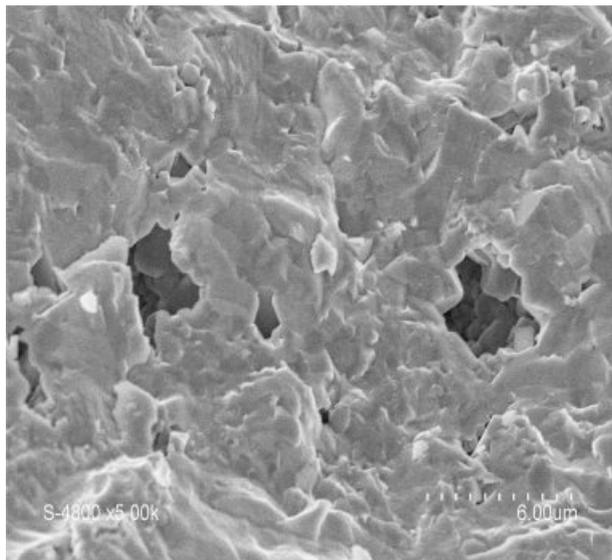
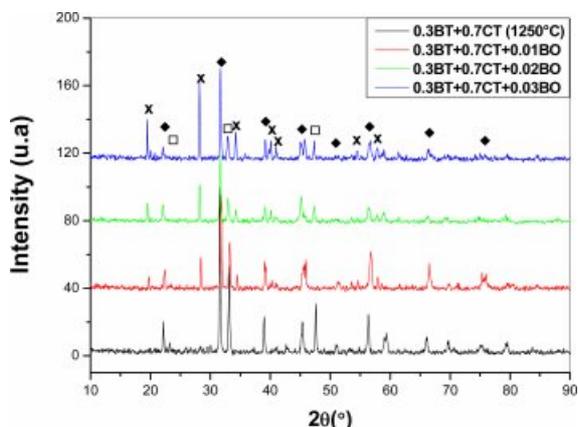


Fig. 6. Relative density of different  $((1 - y)(0.3 BaTiO_3 + 0.7 CaTiO_3) + yB_2O_3)$  pellets as function of proportion of added  $B_2O_3$ .



**Fig. 7.** MEB micrograph of BT-0.7 CT + 3% B<sub>2</sub>O<sub>3</sub> pellet sintered at 1,200 °C for 3 h.



**Fig. 8.** X-Ray diffraction spectra recorded from different  $((1 - y) (0.3 \text{ BaTiO}_3 + 0.7 \text{ CaTiO}_3) + y\text{B}_2\text{O}_3)$  pellets sintered at 1,250 °C for 3 h; BT, ?CT, X unidentified phase.

increases with added percentage of B<sub>2</sub>O<sub>3</sub>.

Nonetheless, it is important to remark that the proportion of BT solid solution seems not be affected by B<sub>2</sub>O<sub>3</sub> addition, while, CT proportion manifestly diminishes as mol.% of B<sub>2</sub>O<sub>3</sub> is increased. Therefore, we can say that the unidentified phase principally forms by reaction between CT and B<sub>2</sub>O<sub>3</sub>.

In the case of pellets sintered at 1,300 or 1,350 °C, the corresponding curves reveal, at the beginning, an increase in the relative density with added B<sub>2</sub>O<sub>3</sub> then the relative density achieves a maximum of about 90% as B<sub>2</sub>O<sub>3</sub> addition exceeds 1% mol.

## Conclusion

The relative density of  $(1-x) \text{ BaTiO}_3 - x \text{ CaTiO}_3 - y \text{ B}_2\text{O}_3$

(where  $x$  is 3 or 7% mol. respectively and  $0 \leq y \leq 3$  mol.%) composite materials depends on both chemical composition of the initial mixtures and sintering conditions.

The reaction between BT, CT and BO powder conduces to the formation of liquid phase which enhances the densification of pellets, since its proportion is moderate. Inversely, the liquid phase inhibits the densification when its proportion became so important.

In the case of pellets containing 30% of CT, the obtained results reveal an increase in the relative density of about 20% corresponding to an increase of 150 °C in the sintering temperature. A maximum of densification (~95%) is obtained in pellet containing 1% mol. of B<sub>2</sub>O<sub>3</sub> and sintered at 1,300 °C.

The addition of 1% mol. of B<sub>2</sub>O<sub>3</sub> provokes an increase of about 20% in the relative density for all considered sintering temperature. At the opposite, the relative density decreases for higher percentage of B<sub>2</sub>O<sub>3</sub> addition.

In the case of pellets containing 70% of CT, the obtained results also reveal an increase in the relative density with sintering temperature of about 20% corresponding to an increase of 150 °C.

Like in the case of pellets containing 30% CT, the addition of B<sub>2</sub>O<sub>3</sub>, up to 2% mol, enhance the densification, but the relative density decreases over this percentage in the case of pellets sintered at 1,200 or 1,250 °C. For higher sintering temperature, the relative density reaches a maximum of about 90% as B<sub>2</sub>O<sub>3</sub> addition exceeds 1% mol.

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