Effects of B_2O_3 addition on the structural and dielectric properties of 0.7BaTiO$_3$ - 0.3 CaTiO$_3$ ceramics

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The effects of B_2O_3 addition on the structural and dielectric properties of (0.7) BaTiO$_3$-0.3CaTiO$_3$ composite materials were investigated. (0.7) BaTiO$_3$-0.3CaTiO$_3$-y B$_2$O$_3$ ($0 \leq y \leq 3$ mol. %) pellets were prepared from BaTiO$_3$ (BT) and CaTiO$_3$ (CT) powders mixture and sintered. The obtained results pointed out three distinct domains in the evolution of the relative density as a function of mol. % B_2O_3. Hence, in pellets containing between 0 and 1 mol. % B_2O_3 an important increase in the relative density is remarked for all sintering temperatures. In the second domain corresponding to pellets containing between 1 and 2 mol. % B_2O_3, the densification rate was clearly less important. In the third domain corresponding to mol. % $B_2O_3 > 2$, a decrease in densification was observed for all considered temperatures. X-rays diffraction (XRD) analysis revealed the presence of BT and CT solid solutions together with an unknown secondary phase. Furthermore, XRD patterns revealed a net decrease in the CT proportion with added of mol. % of B_2O_3, while, the proportion of the unidentified phase increased.

Key words: BT-CT composites, B_2O_3 addition, Relative density, Secondary phase permittivity, Dielectric loss.

Introduction

The nonlinear properties of ferroelectrics materials are subjects of intense research activity both in fundamental and practical domains. These materials are now, currently, used in manufacturing of divers microwave devices, such as varactors, voltage-controlled oscillators (VCO), tunable filters, tunable resonators, phase shifters, lens antennas. [1-3]. In these applications, the first important characteristic of nonlinear dielectric materials is their tunability defined as the mean variation of the relative permittivity as function of bias field. For devices design, the tunability may be as high as possible. At the opposite, the materiel may have a low dielectric loss tan$\ddot{a}$ together with a feeble temperature dependence of the relative permittivity. Up to now, a particular attention was given to (Ba, Sr)TiO$_3$ systems based materials where a high tunability ($> 60\%$ for ceramics and $> 30\%$ for thin films) has been obtained [4]. Nevertheless, these systems suffer of two major inconvenient; a relatively high dielectric loss at microwave frequency and relatively large å$_r$ temperature dependence. CaTiO$_3$ is well established as a typical depressor in BaTiO$_3$ ceramics, which conduces to a significant decrease both in the dielectric loss and in the temperature coefficient of the dielectric constant. Furthermore, CaTiO$_3$ introduces only slight change in Curie point when Ca^{++} substitutes Ba^{++} in A sites [5, 6], but, at the opposite, causes an important shift to lower temperature when Ca^{++} substitutes Ti^{4+} in B sites [7-9].

In this later case, it would be possible to obtain like diffuse phase structure conferring good dielectric and relaxor properties in these materials. Consequently, (Ba, Ca)TiO$_3$ systems are expected as alternative candidates for tunable microwave dielectric materials with low dielectric loss and small temperature dependence [10]. Unfortunately, BCT sintering is usually performed at high temperatures. High densified BCT ceramics have to be sintered over 1300 ºC, consequently refractory metals (as platinum) are the only inner conductors witch can be used in BCT based devices. These materials are expensive, so the cost-effective fabrication of high-quality components is thus higher. For example, in MLCC component, the inner electrodes account for approximately 60% of the total cost [11]. Different, base metal systems such as Ni or Cu [12-14] and Cu [15] have been proposed as a replacement for Ag/Pd systems. Nevertheless, if such base metal systems are used, the devices have to be sintered in a reducing atmosphere and at low temperature to evict electrode oxidation. So, it has become imperative to lower the sintering temperature in device production, in the objective that cheaper electrode materials will be used instead. A decrease in the sintering temperature of ceramic materials is, commonly, achieved via adding some glass or glass-ceramics that soften at rather low temperature. The liquid phase that forms during sintering enhances densification and grain coarsening at lower temperatures, but, generally, degrades electrical properties. Boron oxide has been used by different authors [16, 17] to lower the sintering temperature of BaTiO$_3$ based systems and other dielectric materials. For example, Castellize et al. [16] found that the addition of up to 20 mol % of B_2O_3

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significantly lowered the sintering temperature of BaTiO$_3$, and improved, at the same time, the mechanical properties and insulation resistance. At the opposite, a decrease in the dielectric constant of such materials was observed. B_2O_3 has, also, been used as lowering sintering temperature by Rhim et al. [18] in BST systems. The authors found that 0.5 wt% B_2O_3, allowed to decreases the sintering temperature of BST, prepared by the conventional oxide mixing preparation method, down to 1150 °C. Moreover, the B_2O_3-doped BST samples sintered at 1150 °C had the same dielectric and ferroelectric properties as pure BST sintered at 1350 °C. Nevertheless, the formation of two secondary phases in BST samples over-doped with B_2O_3 (> 1.0 wt. %) degraded the dielectric and ferroelectric properties of the ceramics. Most recently, Qi et al. [19] studied the effect of B_2O_3 vapour on the sintering and the PTCR effect of Y-doped BaTiO$_3$ based ceramics. Semiconductors with 30 W.cm resistivity room temperature have been obtained in ceramics sintered at 1150 °C through doping with 1 mol. % B_2O_3 vapour. In term of their investigation, the authors concluded that B_2O_3 vapour promotes the surface or boundary diffusion as a consequence of the formation of active liquid phases in grain surface or boundary and accelerates the grain growth. At the opposite, when materials were sintered at temperatures higher than 1250 °C, the grain growth was depressed because too much B_2O_3-contained liquid phases are formed which wrap the grains and decrease the driving force of sintering.

The principal objective of the present investigation was to study the effect of B_2O_3 addition on the microstructure evolution and dielectric properties of 0.7BaTiO$_3$-0.3CaTiO$_3$ (BCT) system sintered at different temperatures.

Experimental

BaTiO$_3$ (BT) powder used in this investigation was commercial reagent (Fluka, Japan) while used CaTiO$_3$ (CT) powder was prepared in laboratory following the conventional procedure of milling and calcination. The starting raw materials used to prepare CT powder were high purity commercial anatase TiO$_2$ powder (Fluka, Japan) and local pure CaCO$_3$ powder (extracted out from Khroub locality in Algeria). The starting powders were weighed and mixed in a stochiometric proportion. The mixtures were then ball-milled for 6 hrs using alumina balls in methanol alcohol. The obtained slurry was dried at 70 °C in electrical furnace and calcined in air at 1100 °C for 8 hrs. XRD analysis was carried out on calcined powders to control the formation of CT phase. After that, (0.7) BaTiO$_3$-0.3 CaTiO$_3$-y B$_2O_3$ (where $0 \leq y \leq 3$ mol.%) mixtures were prepared from BaTiO$_3$ (BT), CaTiO$_3$ (CT) and B_2O_3 powders and re-milled by the same route. 1 mm high and 13 mm diameter pellets were fabricated by uniaxially cold

pression under 70 MPa. The pellets were, then, sintered at 1200-1350 °C temperature range in air for 3 hrs. The obtained sintered samples were characterised in terms of apparent density by direct measure of mass and volume. X-rays diffraction analysis (D8 Advanced Bruker-Siemens Diffractometer, with Cu Kα radiation) was carried out on different sintered samples to follow the microstructure evolution.

Results and Discussion

The relative densities of samples sintered for 3 hrs at different temperatures are shown in Fig. 1. The obtained curves reveal quite identical evolution of the pellets relative density as a function of the sintering temperature for different mol. % B_2O_3 used in this investigation. One can remark an increase of about 20% in the relative density of pellets containing 1 and 3 mol. % B_2O_3 respectively when the sintering temperature is increased from 1200 to 1350 °C. In the case of pellets containing 2 mol. % B_2O_3, the increase in the relative density between 1200 and 1200 °C is more moderate (~18%) probably because the pellet density attained at 1200 °C is so important that the densification rate beyond this temperature is less important than in other doped pellets.

Fig. 2 shows the variation of the relative density as a function of mol.% B_2O_3, for different sintering temperatures. At 1200 °C, the maximum of the relative density is obtained in pellets containing 2 mol.% of addition, then the relative density decreases for over-doped samples. In the case of sintering temperatures higher than 1200 °C, the maximum of the densification is obtained in pellets containing 1 mol.% B_2O_3. On the other hand, the curves in Fig. 2 reveal three distinct domains in the evolution of the relative density as a function of mol. % B_2O_3. In the first domain, corresponding to doping with 0-1 mol. % B_2O_3, a manifest increase in the pellets density is remarked for all considered temperature. In fact, a densification rate of about ~22% in the relative density by mol. % of
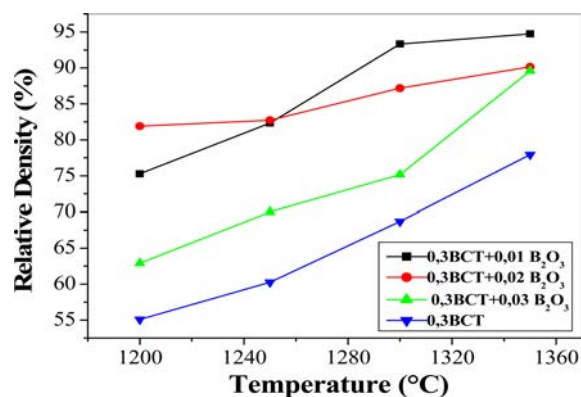

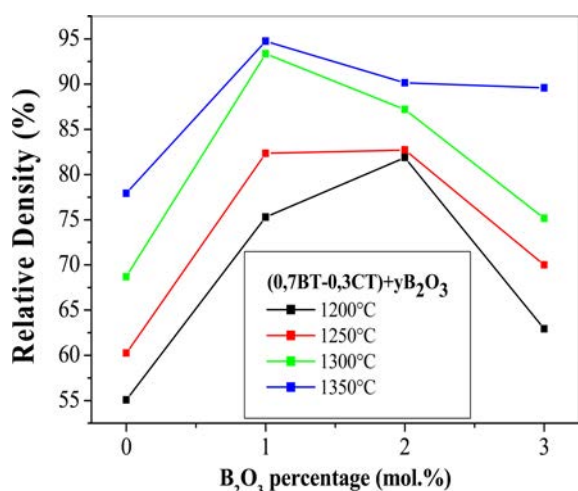**Fig. 1.** Relative density of different (0.7 BaTiO$_3$ + 0.3 CaTiO$_3$) + yB$_2O_3$ pellets as function of sintering temperature.

Fig. 2. Relative density of different (0.7 BaTiO$_3$ + 0.3 CaTiO$_3$) + yB$_2$O$_3$ pellets as function of B$_2$O$_3$ percentage (mol. %).
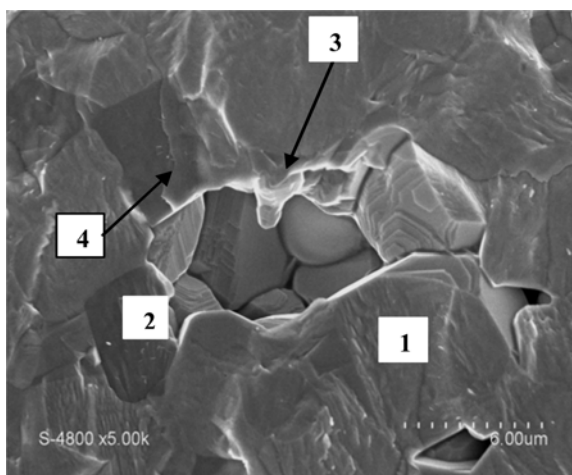
Fig. 3. SEM micrograph of 0.7BT-0.3 CT + 3 mol. % B$_2$O$_3$ pellet sintered at 1250 °C for 3 hrs.

Fig. 4. XRD spectra recorded for different (0.7 BaTiO$_3$ + 0.3 CaTiO$_3$) + yB$_2$O$_3$ pellets sintered at 1200 °C for 3 hrs; ◆ BT, □ CT, X un-identified phase.

Fig. 5. XRD spectra recorded from 0.7 BaTiO$_3$ + 0.3 CaTiO$_3$ + y B$_2$O$_3$ samples sintered at 1350 °C for 3 hrs; ◆ BT, □ CT, X un-identified phase.

B$_2$O$_3$ is obtained in pellets sintered at 1200, 1250 and 1300°C respectively and a densification rate of 17% in those sintered at 1350 °C. In the second domain corresponding to doping with 1-2 mol. % B$_2$O$_3$, the densification rate of pellets is clearly less important. Moreover, a decrease in the densification is observed when pellets are sintered at 1300 and 1350 °C respectively. In the third domain corresponding to mol. % B$_2$O$_3$ > 2%, a depressed densification is observed for all considered sintering temperatures. However, the decrease in density became, in this case, less important that sintering temperature is higher. These results agree with those obtained by other workers on different BT systems [18] who attributed the increase in the density to the development of liquid phase in the case of moderate-doped samples and the decrease in the density for over-doped samples to the apparition of secondary phases. For Qi al. [19] the decrease in the densification (in the case of over-doped pellet) is accompanied by a depress in grain growth and must be linked to the grains
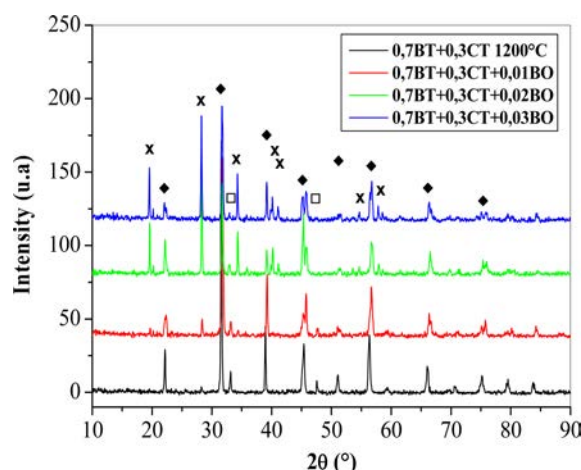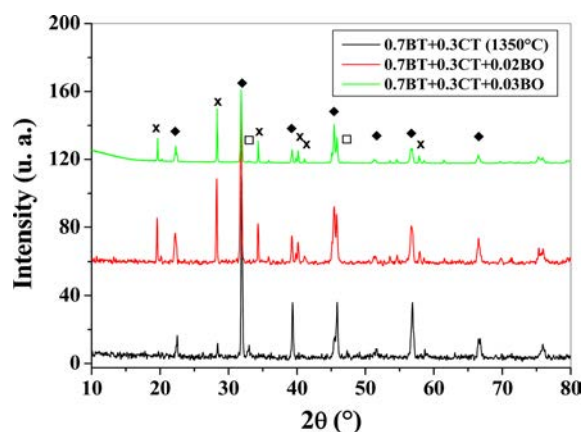
wrapping in consequence of the important liquid phase proportion formed which decreases the driving sintering force. In our case, the formation of secondary glass-ceramic phase which melted during sintering treatment is clearly point out by SEM observation.

In fact, Fig. 3 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 the arrow. Furthermore, it can be seen that the melting phase wraps a great area of a CT grain in zone (4) and is neighboured by secondary porosity which probably appears as a consequences of the shrinkage of the liquid phase during pellet cooling. So, it must be concluded that the formation of secondary liquid phase enhances the sdensification of pellets for moderate proportion of B$_2$O$_3$ by developing liquid sintering process. On the contrary, when liquid phase content augments, the proportion of the secondary porosity, induced by the liquid phase shrinkage, increases too and conduces by this fact to a diminution of pellets density.
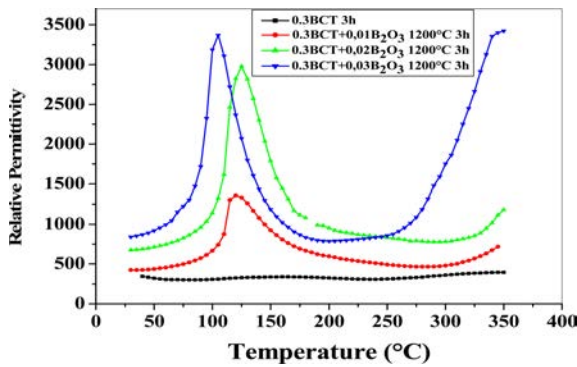
Fig. 6. Relative permittivity of 0.7 BaTiO₃ + 0.3 CaTiO₃ + y B₂O₃ samples sintered at 1200 °C for 3 hrs.

Fig. 7. Dielectric loss in 0.7 BaTiO₃ + 0.3 CaTiO₃ + y B₂O₃ pellets sintered at 1200 °C for 3 hrs.

The development of secondary phase in sintered pellets is confirmed by XRD analysis which reveals the formation of BT and CT solution together with an un-identified secondary phase (Fig. 4). Furthermore, the recorded spectra reveal a net decrease in the intensity of peaks corresponding to CT solutions as function of added B₂O₃, while, peak intensities corresponding to the un-identified phase increases. This result proves that the un-identified phase is formed, principally, as a consequence of reaction between B₂O₃ and CT. X-rays diffraction analysis carried out on pellets sintered for 3 hrs at 1300 °C reveals identical phases as those obtained in pellets sintered at lower temperatures, while spectra recorded from pellets sintered at 1350 °C (Fig. 5), show only diffraction peaks corresponding to BT solutions and the un-identified phase. In this later case, one can remark that the proportion of the unidentified phase increases with B₂O₃ while BT proportion slightly decreases. This means that a certain proportion of BT, probably, incorporates the un-identified phase lattice. In conclusion, we can say that the presence of the un-identified phase controls in great part the density evolution of pellets with added B₂O₃.

Concerning the influence of B₂O₃ on the dielectric properties, Fig. 6 shows the relative permittivity $\varepsilon_r(T)$ for different B₂O₃ doped pellets sintered at 1200 °C for 3 hrs. The reported curves reveal an obvious increase in the room temperature dielectric constant with mol.% B₂O₃. In fact, ε_r varies from ~350 in un-doped pellet to 830 in pellet containing 3 mol.% B₂O₃. This result would not be only related to the increase in density because, and as it has been seen above, the density of 3 mol.% B₂O₃ doped pellet is lower than that corresponding to 2 mol.% B₂O₃ doped pellet. On the other hand, one can remark that the peak of the permittivity (ε_m), also, increases as function of mol.% B₂O₃ and shifts, at the same time towards lower temperature. Hence, e_m changes from 340 in un-doped BT-CT pellet to ~3400 in 3 mol.% B₂O₃ doped pellet, while the corresponding temperature lowers from ~ 140 to 105 °C. The shift of curie peak to lower temperature (in pellets sintered at 1200 °C) can be attributed either to
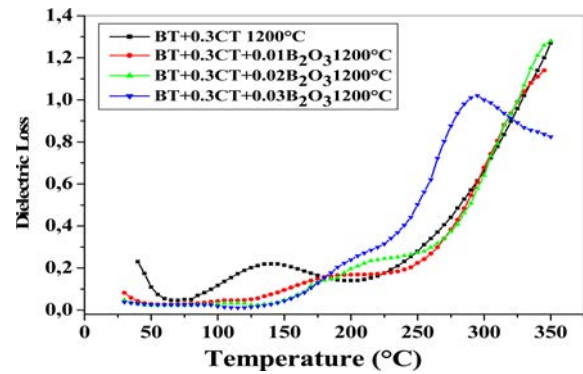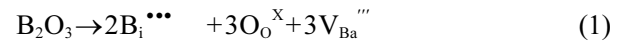
a more important substitution of Ti⁴⁺ by Ca⁺⁺ in B sites in presence of B₂O₃ or to the insertion of B³⁺ in interstitial site as it has been suggested by J. Q. Qi et al. [20]. In this later assumption, the B³⁺ incorporation in BT lattice leads to the formation of barium vacancies as indicated by the following equation (in Kroger-Vink notation):

$$B_2O_3 \rightarrow 2B_i^{\bullet\bullet\bullet} + 3O_O^X + 3V_{Ba}^{'''} \tag{1}$$

Consequently, a relaxation phenomenon linked to the bore interstitial hopping must be behind the increase in the relative permittivity observed from 250 °C and whose corresponding temperature lowers as mol.% B₂O₃ in pellet is increased. Let's remark that such a behavior appeared at lower temperature than that observed in other BT systems and supposed to be related to the hopping of oxygen vacancy charges [21].

The dielectric loss evolution as function of B₂O₃ addition in the precedent pellets is reported in Fig. 7. It can be seen that the room temperature dielectric loss manifestly diminish from tangδ~0.3 in un-doped pellet to tangδ~ 0.04 in doped pellet. While, the loss peak corresponding to ferro-para transformation decreases with mol.% B₂O₃ and his position is moved toward high temperature. So, we can say that ,at the opposite of many investigation carried out on different BT systems [16, 17], mol.% B₂O₃ has, rather, positive effects on the dielectric properties of BT-CT pellets sintered at 1200 °C.

The evolution of dielectrics properties in pellets sintered at 1250 °C is somewhat different (Fig. 8). Here, the room temperature dielectric constant is not affected by 1 mol. % B₂O₃, but fairly diminishes when pellet are more doped. For example, the relative permittivity decreases from ~690 in un-doped pellet to ~550 in 3 mol.% doped pellet. Nevertheless, an important increase in ε_r is observed in all doped pellets near the curie transformation leading to an important temperature coefficient of ε_r in this range of temperature. The maximum of the permittivity is obtained, here, in pellets containing 1 mol. % B₂O₃, while, the curie temperature
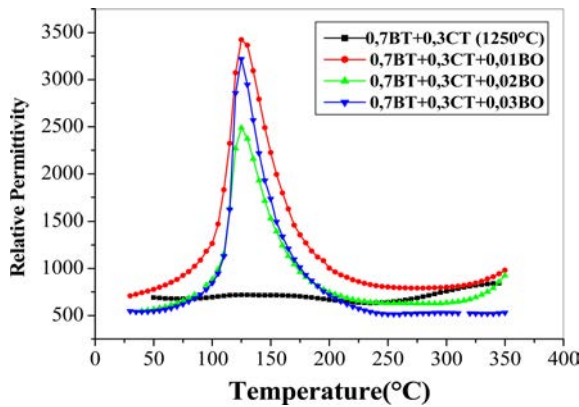
Fig. 8. Relative permittivity of 0.7 $BaTiO_3$+0.3 $CaTiO_3$+y B_2O_3 samples sintered at 1250 ºC for 3 hrs.

Fig. 9. Relative permittivity of 0.7 $BaTiO_3$ + 0.3 $CaTiO_3$ + y B_2O_3 samples sintered at 1350 ºC for 3 hrs.

Fig. 10. Dielectric loss in 0.7 $BaTiO_3$ + 0.3 $CaTiO_3$ + y B2O3 pellets sintered at 1350 ºC for 3 hrs.

appears to be unaffected by added B_2O_3 percentage. On the other hand, $\varepsilon_r(T)$ curves did not reveal any other increase in the dielectric constant (similar to that obtained in pellets sintered at 1200 ºC) up to 350 ºC.

At the opposite of ε_r, the evolution of the dielectric loss in pellets sintered at 1250 ºC as function of mol.% B_2O_3 is similar to that observed in pellets sintered at 1200 ºC, even though, room temperature dielectric loss values are lesser (tangδ~0.09 in un-doped pellet and tangδ ~0.02 in pellet containing 3 mol.% B_2O_3 are obtained). So, one can concludes that mol.% B_2O_3 addition> 1% enhances the loss proprieties of BCT pellets sintered at 1250 ºC, but, at the opposite, degrades the room temperature permittivity and increases at the same time their temperature coefficient.

Finally, measures carried out on pellets sintered at 1300 and 1350 ºC respectively reveal identical evolution of the relative permittivity as a function of both mol.% B_2O_3 and sintering temperature. For example, Fig. 9, corresponding to pellets sintered at 1350 ºC, shows that the room temperature ε_r in 1 mol.% B_2O_3 doped pellet is equal to that of un-doped pellet. At the opposite, a net decrease in the room temperature dielectric constant is observed when the added mol.% B_2O_3 pass from 1 (ε_r~ 970) to 2 mol.%(ε_r~ 550). This decrease in the permittivity could not be attributed to the densification of pellets since 1 mol. % doped pellet is more densified than 2 mol.% B_2O_3 doped pellet but probably to the apparition of the non ferroelectric secondary glass- phase. On the other hand, the important increase in ε_r observed in the precedent pellets near the curie transformation is also observed in these pellets, but, the high of the peak is, in this case, faintly modified by the added mol. % B_2O_3. At the opposite, the position of the peak clearly shifts toward high temperature; from 78 ºC in un-doped sample until 120 ºC in the 3 mol. % B_2O_3 doped sample. Such a behavior can be explained as follow; in un-doped pellet, the Ca^{++} insert B site leading to a lowering in curie temperature as has been proposed by different authors. On the contrary, in doped pellets the added B_2O_3 principally reacts with CT (as it has been
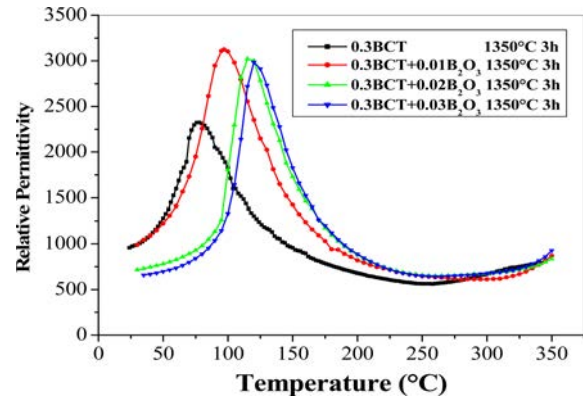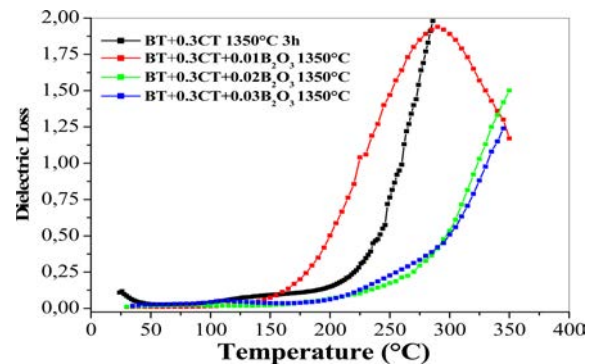
observed by XRD analysis) and conduces to the formation of BT solid solutions the more and the more poor in Ca^{++} cation that mol.% B_2O_3 in pellet is higher. Consequently, the curie transformation moves to the corresponding temperature in pure BT.

Dielectric loss evolves in pellets sintered at 1350 ºC in a distinctly manner (Fig. 10). It can be remarked that tangδ markedly decreases when 1 mol.% B_2O_3 are added but remains sensibly constant in over doped pellets (tangδ~ 0.1 in un-doped pellet and tangδ~ 0.008 in 1 mol.% B_2O_3 doped pellet). On the other hand, loss curves reveal that tangδ slightly changes with temperature up to 160 ºC, after that an important increase in the loss is observed in all considered pellets. Moreover, the temperature corresponding to such a phenomenon somewhat decreases in 1 mol.% B_2O_3 doped pellet but, at the opposite, shifts to higher values in over doped pellets. So, we can conclude that 1 mol.% B_2O_3 promotes both ε_r and tangδ in pellets sintered at 1300 and 1350 ºC respectively, but deteriorates, at the same time, the ε_r temperature dependence.

Conclusions

The main results of the present investigation are

1. B_2O_3 enhances densification of sintered pellet for added mol.%≤ 2% at 1200 ºC. At sintering temperatures higher than 1200 ºC, the maximum of the density is

obtained in pellet containing 1 mol.%. The benefit effect of B_2O_3 on the relative density may be linked to the formation of a glass phase with low melting point. This phase forms as a consequence of a principal reaction between B_2O_3 and CT. At the opposite, when excess B_2O_3 is added, the pellets density decreases probably owing to a secondary porosity induced by liquid phase shrinkage during cooling.

2. In the case of pellet sintered at 1200 °C, The added % mol.B_2O_3 has benefit effect on both room temperature dielectric constant and dielectric loss. At the opposite, B_2O_3 addition favourites the ferroelectric behaviour in these pellets and consequently enhances the temperature dependence of the permittivity. At the same time, the curie peak corresponding to Ferro- Para transformation shifts to lower temperature probably in consequence of B^{3+} incorporation in BT lattice.

3. In pellets sintered at temperature higher than 1200 °C, 1 mol.%.B_2O_3 does not clearly affect the room temperature permittivity but promotes, at the same time, dielectric loss and develops Ferroelectric characteristics of pellets, i.e., increases dielectric constant versus temperature.

4. For over doped pellets sintered at temperature > 1200 °C, added B_2O_3 decreases room temperature permittivity, ameliorates tangδ but increases, at the same time, the temperature dependence of the permittivity.

Acknowledgments

References

1. G.H. Haertling, J. Am. Ceram. Soc. 82 (1999) 797-818.
2. A.K. Tagantsev, V.O. Sherman, K.F. Astafiev, J. Venkatesh and N. Setter, J. Electroceram. 11 (2003) 5-66.
3. F.D. Flaviis, N.G. Alexopoulos and O.M. Stafsudd, IEEE Trans. Micro. Theo. Tech. 45 (1997) 963-969.
4. L.B. Kong, S. Li, T.S. Zhang, J.W. Zhai, F.Y.C. Boey, J. Mad: Prog. Mater. Sci. 55 (2010) 840-893.
5. J.N. Lin, T.B. Wu, J. Appl. Phys. 68 (1990) 985-993.
6. M.S. Yoon, S.C. Ur, Ceram. Int. 34 (2008)1941-1948.
7. S. Yun, X. Wang, Mater. Lett. 60 (2006) 2211-2213.
8. Y. Li, Xi Yao, L. Zhang, Ceram. Int. 30 (2004) 1283-1287.
9. J.S. Park, T.S. Oh and Y.H. Kim, J. Kor. Ceram. Soc.38 (1991) 689-695.
10. X.M. Chen, T. Wang and J. Li, Mater. Sci. Eng. B.113 (2004) 117-120.
11. H. Kanai, O. Furukawa, S. I. Nakamura and Y. Yamashita, J. Mater. Sci. 31 (1996) 1609-1614.
12. I. Burn and G. M. Maher, J. Mater. Sci. 10 (1975) 633-637.
13. H.J. Hagemann and D. Hennings, J. Am. Ceram. Soc. 64 (1981) 590-594.
14. Y. Sakabe, K. Minai and K. Wakino: Jpn. J. AppI. Phys. Suppl. 20 (1981) 147-150.
15. J. Kato, Y. Yokotani H. Kagata and H. Niwa, Jpn. J. Appl. Phys. Suppl. 26 (1987) 90-92.
16. L.M. Castelliz and R. J. Routil, J. Can. Ceram. Soc. 35 (1969) 69-74.
17. I. Burn, J. Mater. Sci. 17 (1982) 1398-1408.
18. S.M. Rhim, S. Hong, H. Bak, O.K. Kim, J. Am. Ceram. Soc. 83 (2000) 1145-1148.
19. J. Qi, W. Chen, H. Wang, Y. Wang, L. Li, H. L.W. Chan, Sensors and Actuators A. 116 (2004) 215-218.
20. J.Q. Qi, W.P. Chen, Y. Wang and H.L.W. Chan, J. Appl. Phys. 96 (2004) 6937-6939.
21. O. Bidault, P. Goux, M. Kchikech, M. Belkaoumi, and M. Maglione, Phys. Rev. B.49 (1994) 7868-873.