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Dielectric properties of $BaTiO_3$–$NaNbO_3$ composites

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Abstract

The barium titanate ($BaTiO_3$) is a ferroelectric material with a perovskite structure. $BaTiO_3$ was largely studied because of its electric properties: ferroelectricity, positive temperature coefficient and piezoelectricity. Generally, $BaTiO_3$ is doped with small amounts of impurities to modify its properties and to widen the number of potential applications. Ceramic samples with composition $(1-x)\ BaTiO_3 + xNaNbO_3$ (where $x = 0$–10 mol%) were prepared by calcinations from appropriate mixture of $BaCO_3$, TiO_2, Na_2CO_3 and Nb_2O_5. The calcined powder was sintered at temperature range 1400–1500 °C. Dielectric measurements and electron microscopy analysis were made for samples characterisations. The addition of $NaNbO_3$ to $BaTiO_3$ causes a considerable change in the microstructure of the sample, i.e. grain growth inhibition and increase in both density and dielectric constant. It was found that Nb substitutes Ti in the $BaTiO_3$ lattice while Na segregates in grain boundaries or into a shell structure. This kind of additive makes the dielectric constant flat in a wide temperature range. A good stability with frequency and a maximum dielectric strength of 65 kV/cm was also achieved.

Keywords: $BaTiO_3$ and titanates; Dielectric properties; Grain boundaries; Niobates; Sintering

1. Introduction

It is well known that impurities or additives incorporation in $BaTiO_3$ (BT) even in quite small proportions may change the dielectric properties appreciably. Sodium niobate $NaNbO_3$ (SN), which melts at 1450 °C, has been added to $BaTiO_3$[1,2] in order to make a composite with very high dielectric constant and dielectric strength. Such a goal may be achieved only if $NaNbO_3$, which is antiferroelectric, melts and coats the grains of $BaTiO_3$. Although a cubic solid solution region exists between BT and SN up to 1350 °C in the composition range 1–10 mol% SN,[1] it is thought that in this composition range a temperature equal or greater than 1450 °C would be sufficient for the formation of an adequate amount of liquid SN to coat the BT grains.[2] Furthermore, it is not clear whether a SN liquid phase at BT grain boundaries can remain after sintering at temperatures ranged between 1400 and 1500 °C, since either niobium segregation near the grain boundaries[3] or its incorporation into the grains has been reported;[4] while no definite conclusions have been drawn regarding the additive segregation phenomena in $BaTiO_3$. Moreover, the effect of higher SN additions on dielectric properties is not well investigated. In this paper, micro-analyses, using the constituents distribution in grain and grain boundaries as well as dielectric properties of the composites are reported.

2. Experimental procedure

Barium titanate was prepared from reagent grade chemical $BaCO_3$ and rutile TiO_2. Sodium niobate was prepared from reagent grade chemical Nb_2O_5 and Na_2CO_3. Mixtures of SN and BT powders were made by varying SN between 1 and 10 mol%. The powders were wet milled in C_2H_5OH medium. The samples in the form of discs were sintered at 1400–1500 °C temperature range for different holding times (30–120 min). Temperature characteristics of the dielectric behaviour were measured in the temperature range 20–300 °C, using an RLC meter, at 1 kHz after the sintered pellets were screen printed with silver electrodes on both surfaces. Moreover, the frequency characteristics are

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also measured between 20 Hz and 1 MHz. The dielectric strength was measured under silicon oil with a 10 kV high voltage generator. A point-to-point nano-analysis has been done using Scanning Transmission Electron Microscope (STEM) with Energy Dispersive X-ray Spectroscopy (EDX) facility.

3. Results and discussions

SEM microstructure of pure BT and BT + 5 mol% SN samples sintered at 1500 °C for 2 h are shown in Fig. 1. This figure shows clearly that SN addition considerably reduces the grain size. Grain growth is believed to be closely related to donor incorporation accompanied by the release of oxygen[5] while grain growth is inhibited as the donor content increases or when the donor segregation occurs. Fig. 2 illustrates STEM/EDX point-to-point analyses across grains for different samples. These results suggest that Nb^{5+} incorporates in the grain core and substitutes Ti^{4+} in association with an appropriate charge compensation mechanism as usually reported,[6,7] while Na^{+} segregates at grain boundaries, particularly at lower sintering temperature (Fig. 2c) and time (Fig. 2a). This is as would be expected, since both ionic radius (0.97 Å) and electro-negativity of Na^{+} cation are very different from those of Ba^{2+} (1.34 Å) and Ti^{4+} (0.68 Å). The Nb^{5+} is not homogeneously distributed inside the grain. Nevertheless, at higher sintering temperature and time, Na^{+} may substitute for Ba^{2+} and become no longer segregated as it can be seen from Fig. 2b. A homogeneous

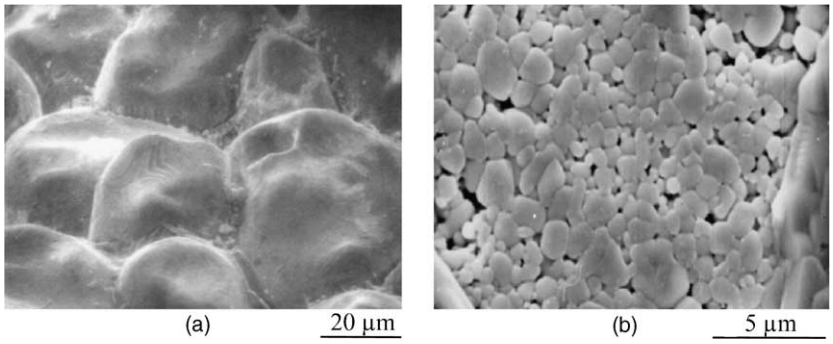

Fig. 1. SEM micrographs of $BaTiO_3$ ceramics sintered at 1500 °C for 120 min: (a) pure BT, (b) with 5 mol% SN.

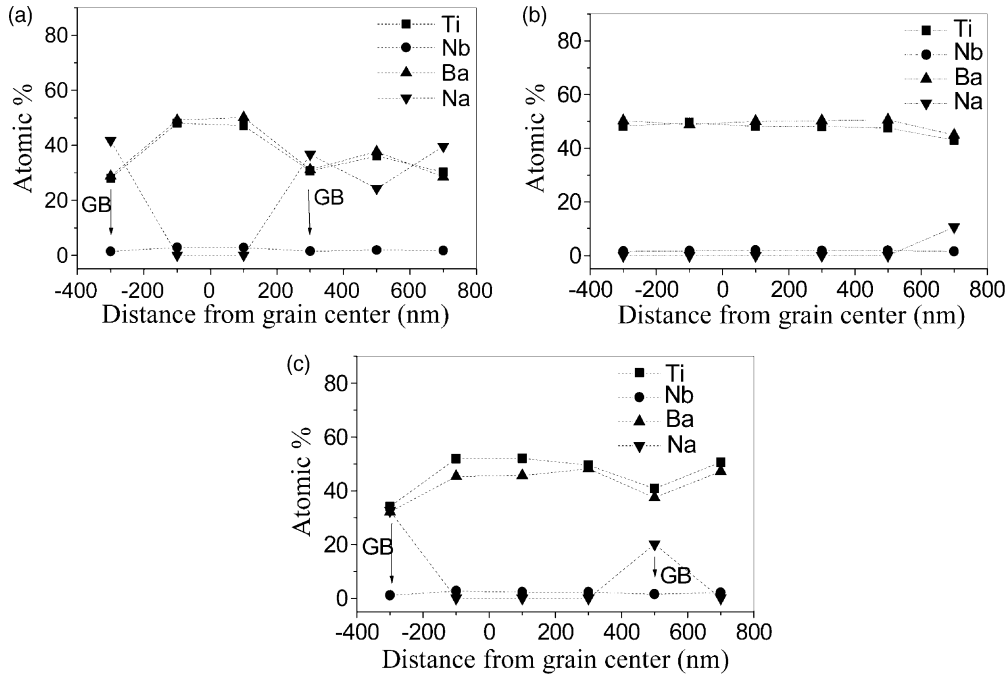

Fig. 2. EDX composition profiles across grain and grain boundaries in 3 mol% NaNbO3 doped $BaTiO_3$ samples (a) sintered at 1500 °C for 30 min, (b) sintered at 1500 °C for 120 min and (c) sintered at 1400 °C for 120 min.

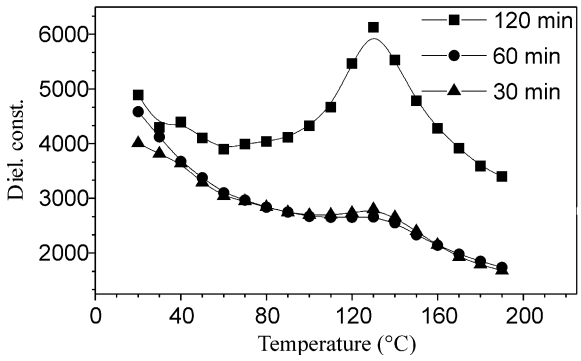

Fig. 3. Temperature dependence of dielectric constant (1 kHz) of $BaTiO_3$ doped with 3 mol% $NaNbO_3$ and sintered at 1500 °C for different times.

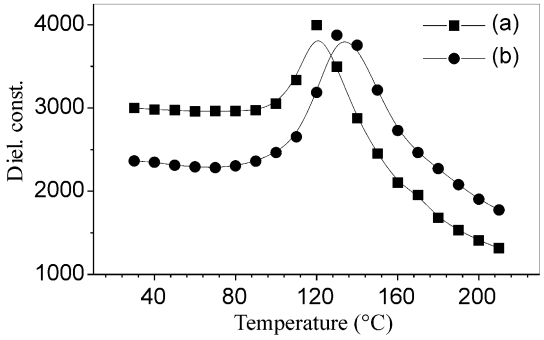

Fig. 4. Temperature dependence of dielectric constant (1 kHz) of $BaTiO_5$ doped (a) 1 mol% $NaNbO_3$ and sintered at 1500 °C for 2 h, (b) 3 mol% $NaNbO_3$ and sintered at 1400 °C for 2 h.

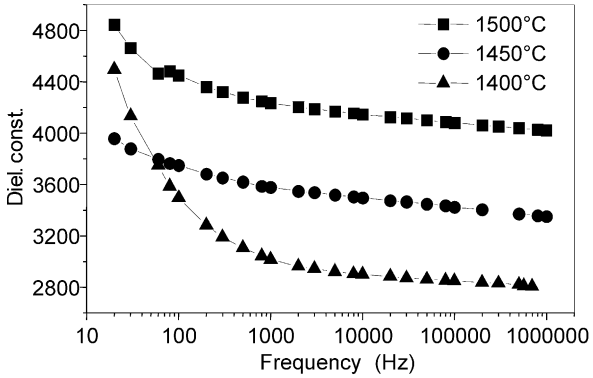

Fig. 5. Frequency dependence of dielectric constant at room temperature of $BaTiO_3$ doped with 5 mol% $NaNbO_3$ and sintered at different temperatures for 2 h.

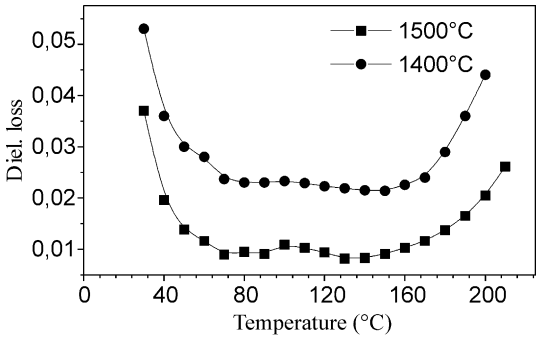

Fig. 6. Temperature dependence of dielectric loss (I kHz) of $BaTiO_3$ doped with 5 mol% $NaNbO_3$ and sintered at different temperatures for 2 h.

distribution of the additions can be obtained with increasing either the sintering temperature or the holding time (Fig. 2b). The relative dielectric constants corresponding to the samples containing 3 mol% SN sintered at 1500 °C for different holding times are shown in Fig. 3. When the sintering time increases, from 30 min to 2 h, the permittivity increases slightly at room temperature, but it increases considerably around the Curie temperature where the peak becomes more pronounced. The diffuse peak at the Curie temperature is reflecting the non-homogeneous composition, which is readily revealed by the results of EDS analysis (see Fig. 2a) which are related to the same samples. At 1400 °C, only 3 mol% SN addition flattens the ε–T curve from room temperature up to 100 °C when the sintering time is 2 h. A flattened ε–T curve in the same temperature range can also be obtained with 1 mol% SN addition but at the expense of higher sintering temperature (1500 °C/2 h). In this case, the dielectric constant is more significant (Fig. 4). The temperature–stable dielectric response of BT dielectric is based on the formation of a core–shell microstructure[6,8] in which individual grains contain a ferroelectric core surrounded by a paraelectric shell. Depending on the sintering conditions, the BT grains may exhibit a concentration gradient of additives from the edge of the grain to the core (Fig. 2a and c).

Furthermore, even when the sintering temperature is raised up to 1500 °C, the highest value of the dielectric strength, which was obtained, is only about 65 kV for samples containing 5 mol% SN.[9] This is similar to the value obtained by Sarkar and Sharma.[2] However, the relative dielectric constant obtained in this work is about 3 times greater than that measured by Sarkar and Sharma[2] These authors suggest that SN is likely to go into solid solution with BT. As a result, the amount of SN left to melt and coat the barium titanate grains is insufficient and leads to a low value for the dielectric strength. This suggestion is confirmed here by STEM/EDX analysis, which clearly shows that SN goes effectively into solid solution, particularly at higher sintering temperature and time.

The frequency dependence of the dielectric constant for the sample with 5 mol% SN and for different sintering temperatures is shown in Fig. 5. It can be seen that the dispersion with frequency decreases as the sintering temperature increases. At 1500 °C, the dielectric constant remains higher than 4000 up to 1 MHz.

This result also indicates a homogeneous doping distribution at higher sintering temperature. Moreover, the loss factor also decreases when the sintering temperature is increased (Fig. 6).

4. Conclusion

STEM/EDX analysis has shown that at relatively lower sintering temperature and time Na segregates at BT grain boundaries and Nb substitutes heterogeneously into Ti sites, being higher in the grain center. At higher sintering temperature or longer holding time, both Na and Nb homogeneously distribute in the grains and grain boundaries without forming any appreciable amount of the liquid phase suited for raising the dielectric strength.

Acknowledgements

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References

1. Newnham, R. E., Skinner, D. P. and Cross, L. E., *Mater. Res. Bull.*, 1978, **13**, 525 (cited by Ref. 2).
2. Sarkar, S. K. and Sharma, M. L., Dielectric strength and dielectric constant of $BaTiO_3$–$NaNbO_3$ composites at room temperature. *J. Mater. Sci. Lett.*, 1989, **8**, 1365–1367.
3. Jida, S., Suemasu, T. and Miki, T., Effect of microwave heating on $BaTiO_3$–Nb ceramics with positive temperature coefficient of resistivity. *J. Appl. Phys.*, 1999, **86**, 2089–2094.
4. Bo, K. P., Jong, H. L., Doh, Y. K. and Nong, M. H., Positive temperature coefficient of resistance effect in heavily niobium-doped barium titanate by growth of the double-twinned seeds. *J. Am. Ceram. Soc.*, 2001, **84**(11), 2707–2709.
5. Drofenik, M., Oxygen partial pressure and grain growth in donor-doped $BaTiO_3$. *J. Am. Ceram. Soc.*, 1987, **70**(5), 311–314.
6. Mccoy, M. A., Lee, W. E., Grimes, R. W. and Keyse, R., Analysis of planar defects in Nb_2O_5- and Bi_2O_3 $BaTiO_3$ ceramics. *J. Mater. Sci.*, 1998, **33**, 5759–5771.
7. Jonker, G. H. and Havinga, E. E., The influence of foreign ions on the crystal lattice of barium titanate. *Mater. Res. Bull.*, 1982, **17**, 345–350.
8. Yoon, S. H. and Kim, H., Experimental evidence for space charge segregation in Nb-doped $BaTiO_3$. *J. Mater. Res.*, 2001, **16**, 1479–1486.
9. Benhamla, N., Achour, S., Harabi, A., Benlahrache, M. T. and Sahli, S., $NaNbO_3$ doped $BaTiO_3$ based dielectric for capacitors application. In: *Proceeding of the Electroceramics IV*, Vol. 1, R. Waser et al. Ed., 1994, pp. 101–104.