Dielectric properties of liquid phase sintered $0.98BaTiO_3$-$0.02Ba(Mg_{1/3}Nb_{2/3})O_3$ ceramic

A. MUNPAKDEE, J. TONTRAKOON*, K. SIRIWITAYAKORN, T. TUNKASIRI
Department of Physics, Faculty of Science, Chiang Mai University, Chiang Mai, 50200, Thailand
E-mail: anochamun@yahoo.com

In earlier work [1], the 2 mol% $Ba(Mg_{1/3}Nb_{2/3})O_3$ doped $BaTiO_3$ specimens sintered at 1300 °C exhibited the highest dielectric constant, ε_r, value of about 43000. The obtained results are in good agreement with those of Weill *et al.* [2, 3] who employed the chemical method. The present work thus aims at lowering the sintering temperature of $0.98BaTiO_3$-$0.02Ba(Mg_{1/3}Nb_{2/3})O_3$ (abbreviated as (BT)(BMN)) ceramic in order to reduce the fabrication cost particularly in the manufacture of MLC capacitors.

The liquid phase sintering technique had been used by many researchers [4–8] to decrease the sintering temperature down to about 1000 °C. Additives of relatively low melting temperatures such as Bi_2O_3, PbO and Li_2CO_3 were used to promote the densification. Unfortunately, a lower sintering temperature is often accompanied by a significant decrease in ε_r of the ceramics. It is expected, however, that the reactions between the base compounds and appropriate flux contents will possibly yield high ε_r ceramics.

Consequently, effects of various flux contents on the microstructural and dielectric properties of (BT)(BMN) ceramic were investigated. The chosen fluxing agents were Bi_2O_3, Li_2CO_3 and PbO whose melting temperatures are 825, 618 and 880 °C, respectively.

The raw materials used were 99% pured and the calcined powder (BT)(BMN) was obtained by a conventional oxide-mixing process, the details of which had already been described in [1]. Mixtures of powder Bi_2O_3/Li_2CO_3 and PbO were then blended with the calcined powder (BT)(BMN) according to the sample compositions shown in Table I.

The powder samples were ball milled once more in ethyl alcohol for 24 h, dried and pressed to form disc-type pellets under 60 MPa pressure. The obtained green compact samples were then sintered at various temperatures for 2 h in air. They were heated by controlling the furnace temperature at the rate of 5°C/min. The linear shrinkage and densities, determined by the Archimedes method, of the sintered samples were recorded and their microstructures were investigated via X-ray diffractometry (XRD) and scanning electron microscopy (SEM). Silver paste was applied on both polished faces of the disc samples for electrical measurements. Evolution of the dielectric constant against temperature was measured at various ambient temperatures ranging from room temperature to around 200 °C, using an LCZ meter (Hewlett Packard 4276A) operated at 1 kHz.

TABLE 1 Sample compositions in wt%

	Sample composition		
Code	(BT)(BMN)	Bi_2O_3/Li_2CO_3	PbO
(BT)(BMN)	100	–	–
A	98.25	1.32	0.43
B	96.50	2.63	0.87
C	92.99	5.26	1.75

n.b.: Sample compositions are of the form $(100\text{-}x\text{-}y)0.98BaTiO_3$-$0.02Ba(Mg_{1/3}Nb_{2/3})O_3$-$xBi_2O_3/Li_2CO_3$-$yPbO$.

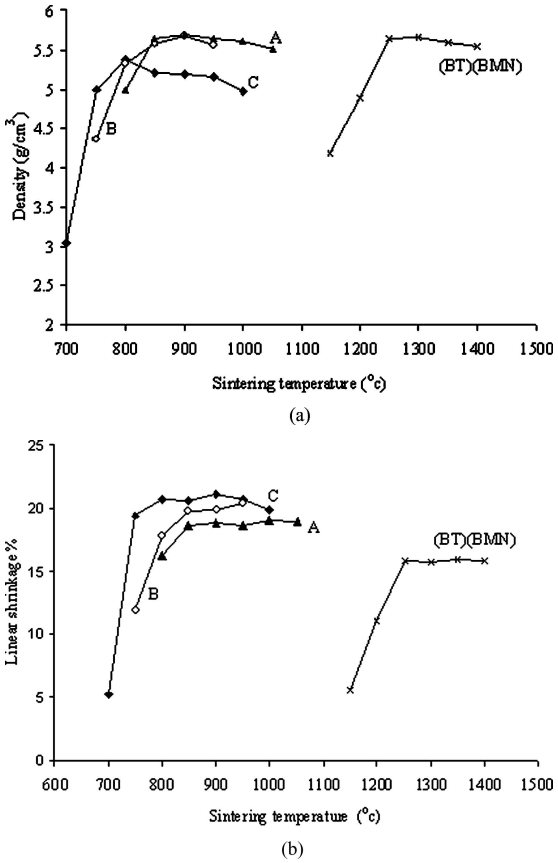

Figure 1 Density (a) and linear shrinkage (b) of fired samples containing different amounts of fluxing agents against sintering temperature.

Fig. 1 shows the effect of the sintering temperature on the densities and linear shrinkages of the samples

* Author to whom all correspondence should be addressed.

0022-2461

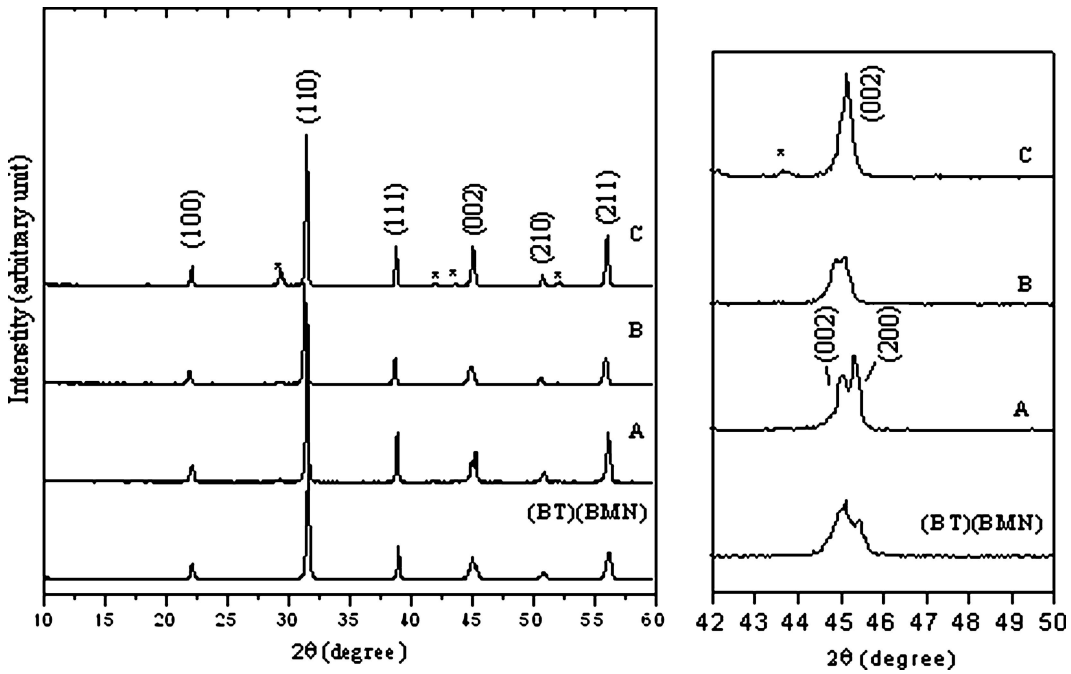

Figure 2 XRD patterns of specimens sintered at 950 °C. (* identified as $Bi_4 Ti_3 O_{12}$).

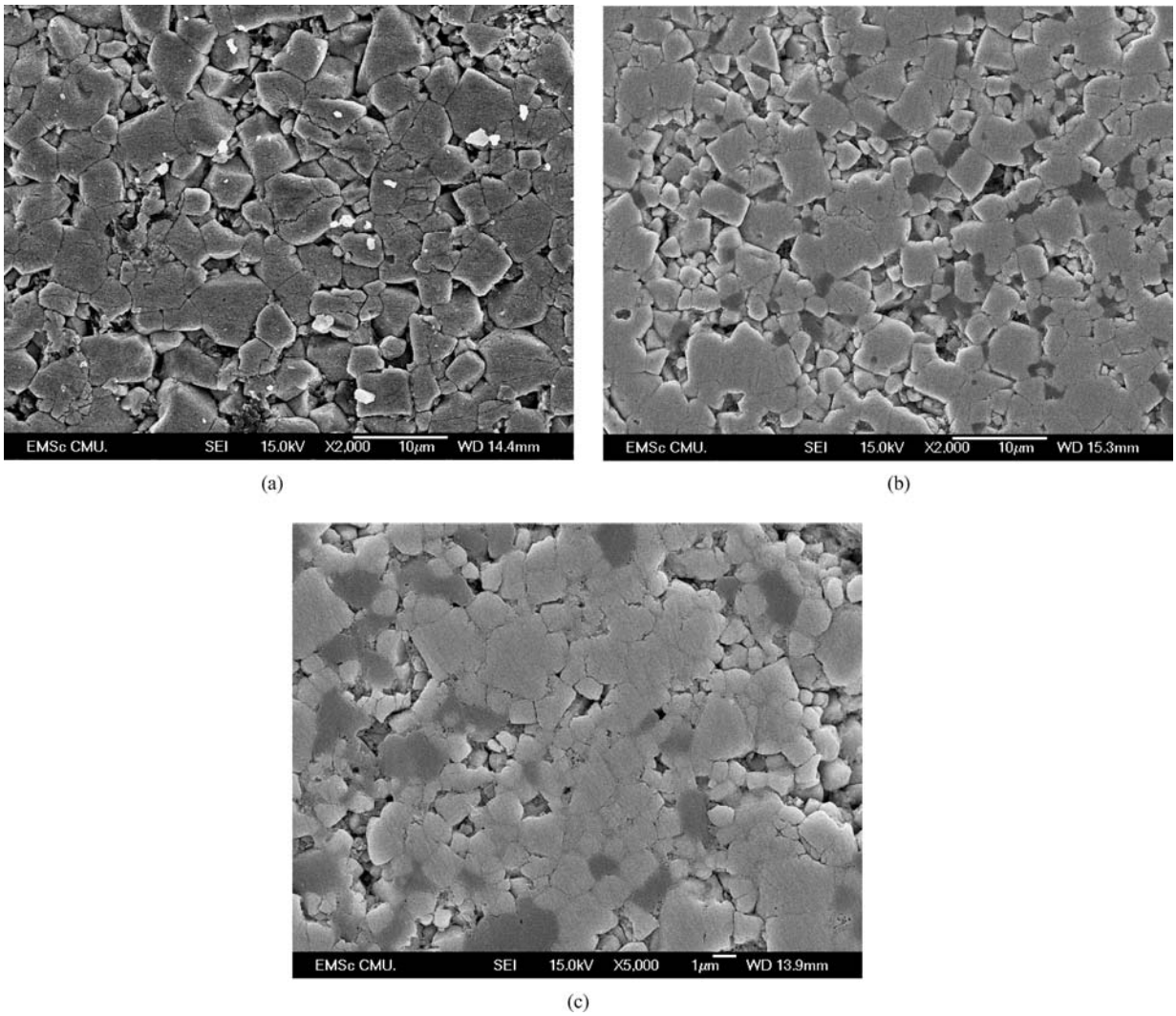

Figure 3 Microstructures of Bi_2O_3/Li_2CO_3 and PbO added (BT)(BMN) ceramics sintered at 950 °C for 2 h.

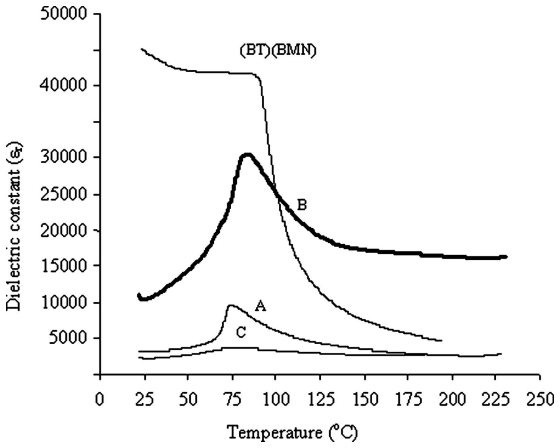

Figure 4 Dielectric constant at 1 kHz as a function of temperature for Bi_2O_3/Li_2CO_3 and PbO - added (BT)(BMN) and pure (BT)(BMN).

containing various flux concentrations. It can be seen that the density and shrinkage reach saturation at the temperature as low as 850 °C, i.e., the additives used can significantly reduce the sintering temperature of the ceramic down to around 900 °C. The XRD patterns of specimens containing various flux concentrations are shown in Fig. 2. These patterns reveal that the sample containing small amounts of fluxes (Sample A) has the tetragonal perovskite structure. This can be attributed to the diffusion of some amounts of fluxes into the (BT)(BMN) lattices and as a result the ceramic can not retain the coexistence of tetragonal and cubic phases at room temperature. It is also evident that the tetragonal-cubic transformation occurred in Sample B at room temperature while Sample C contained multiphases, with the cubic structure as a major phase and $Bi_4Ti_3O_{12}$ as a second phase. This is quite agreeable with Maher [6] who detected the same second phase of bismuth in $BaTiO_3$ system. Fig. 3 reveals the observation of chemically etched, polished ceramic surfaces of Sample A, B and C by scanning electron microscopy. The size distribution in each sample is reasonably homogeneous and the average grain sizes of Sample A, B and C are 5.64, 2.85 and 0.92 μm, respectively. The inhibition of grain growth caused by the added fluxes was also observed in all samples. This same result was realised by Li and Cheng [7, 9]. Comparison of the temperature dependent dielectric characteristics of the ceramic samples with various flux concentrations and pure (BT)(BMN) is depicted in Fig. 4. The dielectric temperature peak of Sample B is seen much higher than that of Sample A due to the smaller average grain size of Sample B, according to Moulson [10], and the coexistence of tetragonal and cubic phases in this sample. It should also be noted that this Sample B possesses a relatively high (exceeding 16500) and invaried ε_r over the temperature range of 100 to 225 °C. This is suitable for MLC capacitors whose applications are in high temperature environment. For samples with large amounts of fluxes (demonstrated by Sample C), the dielectric temperature peak is suppressed and broadened appreciably due to the presence of the second phase, evidently confirmed by the X-ray diffractogram.

Inconclusion, the sintering temperature of (BT)(BMN) ceramics could be lowered from around 1300 to 900 °C via liquid phase sintering by adding Bi_2O_3/Li_2CO_3 and PbO. The XRD data confirmed the ferroelectric phase of the so prepared ceramics using lower amount of additives (1.32wt%Bi_2O_3/Li_2CO_3-0.43wt%PbO). The transformation from ferroelectric to paraelectric phase occurred when flux concentration was double the amount used to cause the ceramic ferroelectric state. The XRD data confirmed the presence of the second phase, $Bi_4Ti_3O_{12}$, in cases where flux concentrations were too high (Sample C). Apart from acting as the liquid phase formers, the additives apparently had influence on the mirostructure and hence the dielectric constant-temperature characteristic of the ceramic. Inhibition of grain growth was observed and subsequently the average grain sizes of all specimens were not larger than 6 μm but the grain size distribution was quite homogeneous. In general, the dielectric constant of the ceramic was considerably decreased except for Sample B (additives used were 2.63 wt% Bi_2O_3/Li_2CO_3-0.87wt%PbO) whose ε_r was found to be relatively high (>16500) and invaried over the temperature range around 100 to 225°C.

Acknowledgements

The authors wish to express their sincere thanks to the Thailand Research Fund, the Graduate School of Chiang Mai University for the financial support and to the Centre for Microanalysis in the Materials Research Laboratory at the University of Leeds for the use of their facilities

References

1. A. MUNPAKDEE, J. TONTRAGOON, K. SIRIWITAYAKORN and T. TUNKASIRI, *J. Mater. Sci. Lett.* **22** (2003) 1307.
2. F. WEILL, J. L. REHSPRINGER, P. POIX, C. KIPELEN and J. C. BERNIER, *J. Mater. Sci.* **27** (1992) 2316.
3. F. WEILL, J. L. REHSPRINGER, P. POIX and J. C. BERNIER, *ibid.* **27** (1992) 2321.
4. I. BURN, *ibid.* **17** (1982) 1398.
5. E. M. LEVIN and C. L. MCDANIEL, *J. Amer. Ceram. Soc.* **45** (1962) 355.
6. G. H. MAHER, *J. Amer. Ceram. Soc. Bull.* **60** (1981) 401.
7. Q. LI, J. QI, Y. WANG, Z. GUI and L. LI, *J. Eur. Ceram. Soc.* **21** (2001) 2217.
8. G. F. CHEN and S. L. FU, *J. Mater. Sci.* **25** (1990) 424.
9. S. Y. CHENG, S. L FU and C. C. WEI, *Ceram. Int.* **13** (1987) 223.
10. A. J. MOULSON and J. M. HERBERT, "Electroceramics: Materials, Properties and Application," 2nd ed. (Chapman and Hall, London, 2003) p. 82.

Received 27 July 2004
and accepted 3 February 2005