Ceramics International 24 (1998) 341–346
© 1998 Elsevier Science Limited and Techna S.r.l.
Printed in Great Britain. All rights reserved
0272-8842/98 $19.00 + .00

PII: S0272-8842(97)00020-5

The Influence of CuO–BaO Mixture Addition on the Grain Growth and Dielectric Characteristics of $BaTiO_3$ Ceramics

Cheng-Fu Yang

Department of Electronic Engineering, Chinese Air Force Academy, PO Box 90277-4, Kangshan, Kaohsiung 82012, Taiwan

(Received 20 November 1996; accepted 16 January 1997)

Abstract: Densification, grain growth, and dielectric characteristics of $BaTiO_3$ during liquid-phase sintering of $BaTiO_3$ ceramics was investigated for CuO–BaO (molar ratio, CuO/BaO = 1, 2, and 2.5) mixture addition. Sintering in air for 1 to 16 h at 950 to 1250°C was studied. The grain growth for CuO–BaO mixtures fluxed $BaTiO_3$ was analysed from the kinetic growth equation: $G^n = kot^* \exp(-Q/RT)$. The average grain growth exponents are about 5.3, 5, and 4.3 and grain growth activation energy are 290 ± 60, 314 ± 40, and 348 ± 19 kJ mol^{-1} for $BaTiO_3$ fluxed with CuO/BaO = 1, 2, and 2.5, respectively. For the same sintering condition, as the CuO/BaO ratio increases, the maximum dielectric constant (revealed at Tc) increases, the tetragonal–cubic phase transition (Tc) is shifted to lower temperature, and the orthorhomic–tetragonal phase transition is moved to higher temperature.

1 INTRODUCTION

$BaTiO_3$ is well known for its high dielectric constant. Many efforts have studied the effects of several different oxide additions, though not low melting point oxides, on the densification of $BaTiO_3$ ceramics by the shrinkage of compacts during the initial stages of sintering. Many oxides had been used to promote sintering, including Bi_2O_3, LiF, B_2O_3, and SiO_2.[1-4] Hennings used mixtures of CuO with TiO_2 as sintering aids and found that they led to a lower firing temperature.[5] The binary phase relations of CuO–BaO were uncomplicated as reported in the Eu–Ba–Cu–O system. Roth *et al.*[6] revealed a tentative diagram for the CuO–BaO system involving two binary compounds $BaCuO_2$ and Ba_2CuO_3, the latter apparently being unstable above 800°C.[7] $BaCuO_2$, originally synthesized by Arjomand and Machin,[8] melts incongruently around 1000°C in air. In addition, there is an eutectic between $BaCuO_2$ and CuO at around 900°C, because of the low melting point of the binary CuO–BaO system (or CuO–$BaCuO_2$), so this study concerns the mixtures of CuO–BaO as a new potential candidate for lowering the firing temperature of $BaTiO_3$ ceramics.

In the past, Yang *et al.*[9] were the first researchers to study the effects of CuO/BaO mixtures addition to $BaTiO_3$ for sintering modification. It is confirmed that the addition of CuO/BaO mixtures promote the densification and grain growth of $BaTiO_3$. An addition of 1wt% CuO–BaO mixture to $BaTiO_3$ significantly reduced the sintering rate of $BaTiO_3$ at temperature between 1000°C and 1200°C. However, there is still not any report about the relation between the ratio of CuO–BaO additive and the grain growth. In this paper, the effects of CuO–BaO mixtures (molar ratio, CuO/BaO = 1, 2, and 2.5) on grain growth were studied and discussed exhaustively, to resolve these issues to further understand the role of CuO–BaO mixture addition on the grain growth of $BaTiO_3$ in that system. In this research, a study of the grain growth of $BaTiO_3$ ceramics with systematic CuO–

BaO mixture addition has been undertaken. It is also attempted to determine the influences of different CuO/BaO ratios on the densification and the dielectric characteristics of fired $BaTiO_3$ specimens.

2 EXPERIMENTAL PROCEDURE

Raw materials of $BaCO_3$ and TiO_2 were weighted first in accordance with the composition $BaTiO_3 + 0.5$ mol% TiO_2. The mixture of powders was ball-milled with distilled water, dried and ground to -325 BBS (British standard sieve) mesh. In the past, adding flux former to lower the sintering temperature may result in a significant decrease in the dielectric constant. This may be caused by the formation of low dielectric constant compounds by the reaction between the ceramics and low-melting oxides.[10] To prevent that, high calcining temperature must be used to form ABO_3 ($BaTiO_3$) phase completely.[11] Therefore, the ground powder was calcined in air at 1150°C for 2 h. The calined material was again ground to −325 BBS mesh. X-ray diffraction pattern (XRD) analysis was carried out on the calcined $BaTiO_3$ powder. In the calcined powder only the tetragonal $BaTiO_3$ phase was observed in XRD pattern. Mixtures of 1 wt% CuO–BaO with different CuO/BaO ratios were prepared. CuO–BaO mixtures were added to calcined $BaTiO_3$ powder by wetting mixing. The products were prepared by adding distilled water as a binder and pressing into disk specimens, 10 mm in diameter by 1.5 mm thick. The pellets were sintered at temperature varying 950 to 1250°C in air for 1, 2, 4, 8, and 16 h. The density of fired ceramics were calculated as indices for densification by using Archimedes method. Before the measurement of dielectric characteristics, the microstructural observations of the surfaces of sintered samples were directly observed from the SEM (scanning electronic micrograph). The grain sizes were directly measured from photomicrographs of the SEM pictures. The average grain size G was obtained as[12]

$$G = 1.56L \tag{1}$$

where L is the average grain boundary intercept length of four random lines across the micrograph. After being surface-polished and printed with Ag–Pd paste, the measurements of dielectric characteristics were made and their temperature dependences were determined at 1 kHz using an impendence analyser (HP4192a) in a temperature-humidity-programmable testing chamber.

3 RESULTS AND DISCUSSION

Relative densities of the pellets as a function of CuO/BaO ratio and the firing temperature and with a sintering time of 2 h are presented in Fig. 1. The unadulterated calcined powder-based samples started to densify at about 1150°C and densification was complete at about 1350°C (not shown in Fig. 1), and the density of sintered ceramics possessed about 94% the theoretical density of $BaTiO_3$. The densification curves for $BaTiO_3$ with CuO–BaO mixtures addition were shifted about 200°C lower than that for pure $BaTiO_3$. The compact containing 1 wt% CuO–BaO mixture started to densify at about 1050°C, and the densification behaviour of the compacts reached a saturation value at around 1150°C. The temperature for initial densification to occur was lowered and a higher densification could be observed as the CuO–BaO ratio and the amount of CuO–BaO mixture addition increased. This reveals that at a larger CuO/BaO ratio the temperature for forming CuO–BaO (or CuO–BaCuO) eutectic will be shifted to lower temperature. The densification process was essentially completed at about 1150°C. Sintering at 1150°C, a density of higher than 95% theoretical density of $BaTiO_3$ ($6.03\,g\,cm^{-3}$) was consistently obtained. It is confirmed that the addition of the binary CuO–BaO system can effectively lower the sintering temperature needed for densification of $BaTiO_3$ ceramics.

The sintering surfaces of $BaTiO_3$ specimens that contained 1 wt% of different CuO–BaO mixtures and fired for 1 h at the different temperatures are illustrated in Fig. 2. Effects of CuO–BaO ratio and firing temperature are evident. Several authors had reported that there existed an enhanced propensity

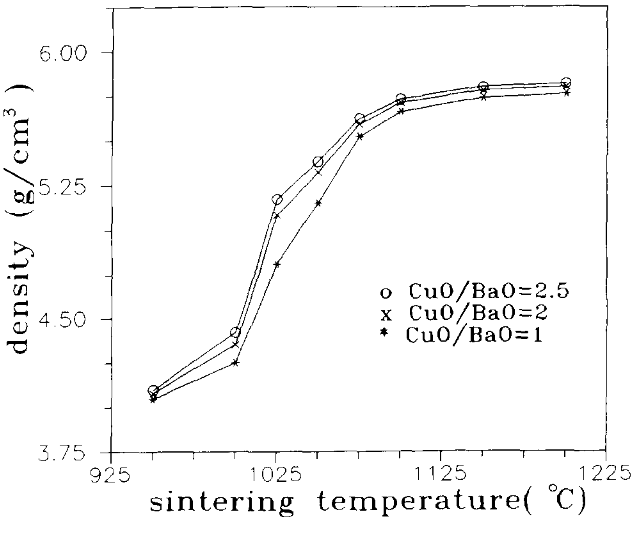

Fig. 1. Density of fired samples as a function of sintering temperature and CuO/BaO ratio.

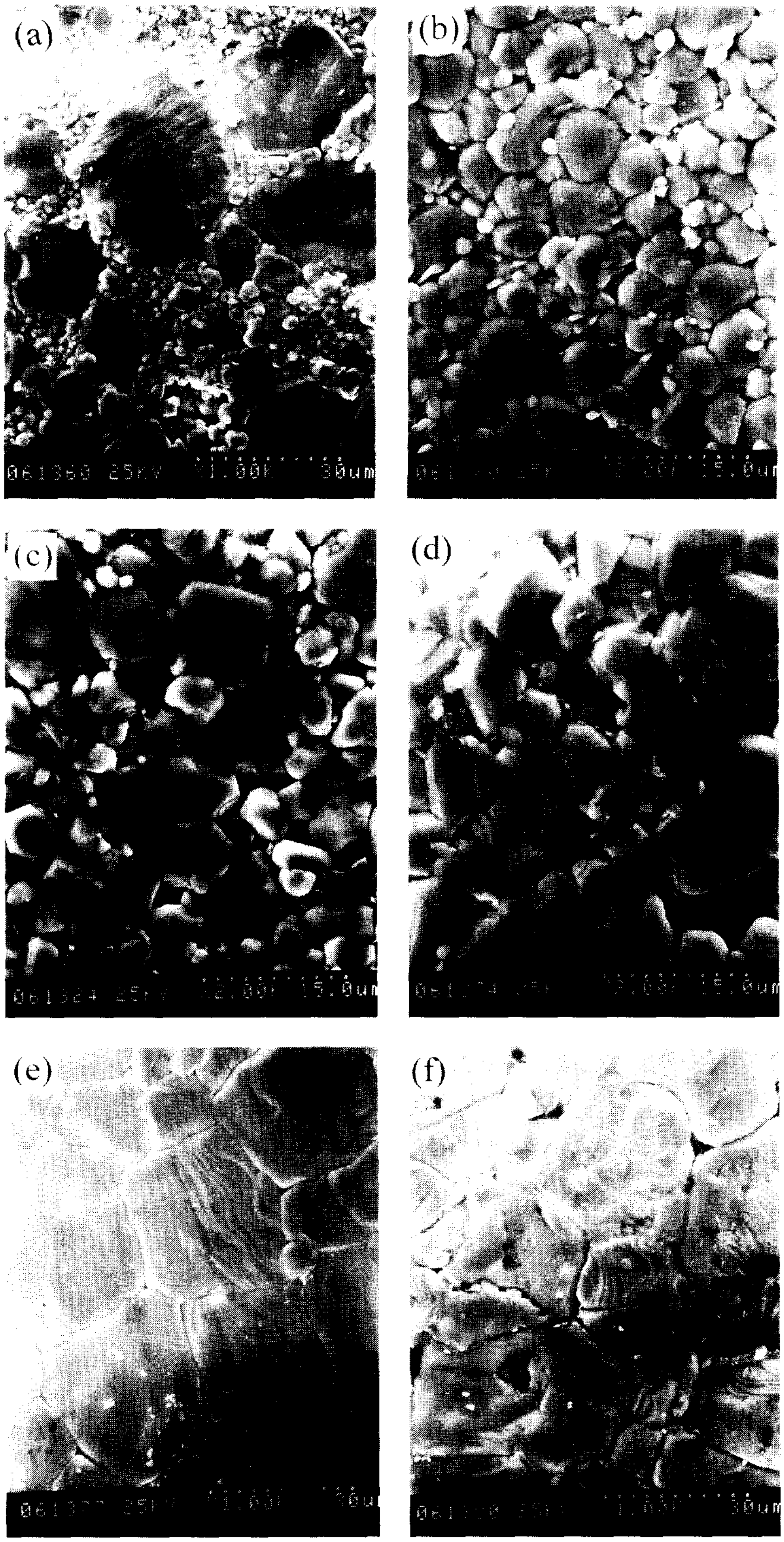

Fig. 2. The sintered micrographs of BaTiO$_3$ ceramics as a function of CuO/BaO ratio and sintering temperature: (a) CuO/BaO = 2, 1100°C; (b) CuO/BaO = 1, 1150°C; (c) CuO/BaO = 2, 1150°C; (d) CuO/BaO = 1, 1200°C; (e) CuO/BaO = 2, 1200°C; (f) CuO/BaO = 2.5, 1200°C.

for discontinuous grain growth (or called abnormal grain) in liquid-phase-sintered systems.[13,14] For BaTiO$_3$ samples fluxed with CuO–BaO mixtures, as the sintering temperature was lower than 1100°C, a bimodal non-uniform distribution of grain size which exhibited exaggerated discontinuous grain in a fine-grained matrix was also observed as shown in Fig. 2(a). As the sintering temperature was high than 1150°C, as Fig. 2(b) and (c) shows, the micrographs revealed homogeneous grain growth for grain size. As the sintering temperature was increased, the sintered surfaces revealed a larger grain size, as Fig. 2(d)–(f) shows. Figure 2(b)–(f) also shows that grain size of sintered surface also increases with the CuO/BaO ratio.

The kinetic of grain growth give the mean grain size vs time as follows:[16]

$$G^n = tK_o\exp(-Q/RT) \qquad (2)$$

where G is the mean grain size, n is the grain growth kinetic exponent, t is time, K_o is the frequency factor, Q is the activation energy, R is the gas constant, and T is the absolute temperature. Equation (2) can be described in the logarium form:

$$n(\log G) = \log[K_o \exp(-Q/RT)] + \log t \qquad (3)$$

The isothermal grain growth results for CuO–BaO-added $BaTiO_3$ from 1150°C through 1250°C are calculated and plotted in the form of a log(R) vs*log*(t) relation and the results are illustrated in Fig. 3. As Fig. 3 show, the average grain growth increased with the CuO/BaO ratio. The average grain size also increased with increasing sintering temperature as well as longer sintering time, as expected from eqn (3). These results can be explained by the following statement. The classic solution for the grain size vs time under diffusion controlled growth at infinite solid dilution is given as:[16]

$$G^n = G_o^n + (4Kt)/9 \qquad (4)$$

where G_o is the initial mean grain size, K is a kinetic constant, and t is time. The mean grain size G increases with increasing tme. On the other hand, K is given as follows:

$$K = 2(DC\Omega\gamma/kT) \qquad (5)$$

where D is the diffusivity of the solid through the liquid, C is the concentration of the solid in the liquid, Ω is the atomic volume of the solid, γ is the solid–liquid surface energy, K is Boltzmann's constant, and T is the absolute temperature. Because both diffusity and concentration of the solid in the liquid have an exponential temperature dependence, the kinetic constant K is very sensitive to temperature. Hence, the mean grain size G also increases with increasing temperature.

The grain growth kinetic exponent n can be determined from the inverse of the slope of the log(G)–log(t) relation. The grain growth exponents obtained by the regression analyses of Fig. 3 are summarized in Table 1. As Table 1 shows, the average grain growth exponent, n-value, decreased with the increase sintering temperature and the CuO/BaO ratio. For example, we could estimate the n value of $BaTiO_3$ added with CuO/BaO = 1 from linear portions of grain growth plots, they appeared to be about 6.4, 5.1, and 4.3 for 1150, 1200, and 1250°C, respectively. The average grain growth exponents were 5.3, 5, and 4.3 for $BaTiO_3$ with the CuO/BaO = 1, 2, and 2.5 added.

The activation energies for $BaTiO_3$ grain growth could be determined from the slopes of the Arrhenius plots of log(G^n/t) vs 1/T, which followed from

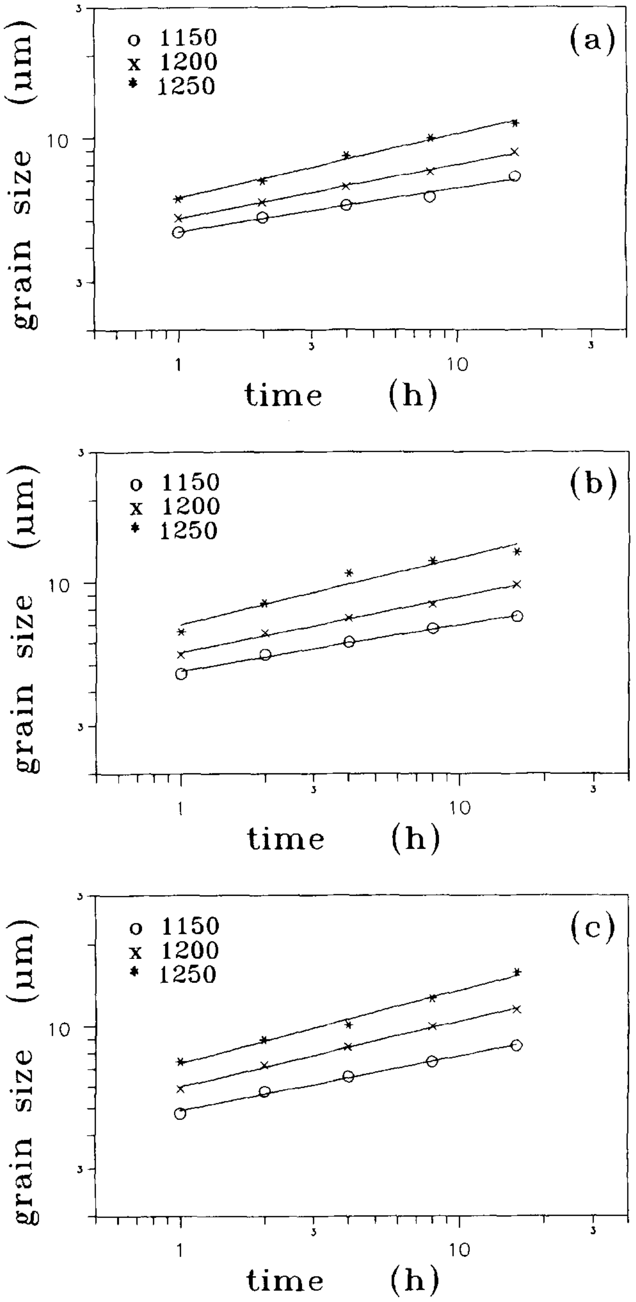

Fig. 3. Log (grain size) vs log (time) plots for $BaTiO_3$ ceramics with different CuO–BaO mixtures added: (a) CuO/BaO = 1; (b) CuO/BaO = 2; (c) CuO/BaO = 2.5.

Table 1. Summary of $BaTiO_3$–1 wt% CuO–BaO grain-growth parameter

Added CuO–BaO	Sintering temperature (°C)	Grain-growth exponent	Average grain-growth exponent	Activation energy (kJ mol^{-1})
	1150	6.4		
CuO/BaO=1	1200	5.1	5.3	290±60
	1250	4.3		
	1150	5.9		
CuO/BaO=2	1200	4.9	5.0	314±40
	1250	4.1		
	1150	4.9		
CuO/BaO=2.5	1200	4.2	4.3	348±19
	1250	3.7		

eqn (2) and used the average exponents (5.3, 5, and 4.3 were used for CuO/BaO = 1, 2, 2.5, respectively). These plots are shown in Fig. 4 for the four types of CuO–BaO mixtures addition. These exhibited a linear relationship between the log(G^n/t) and 1/T from 1150 to 1250°C. The activation energies obtained from the regression analyses of the slopes of these lines are also summarized inTable I. The activation energies were 290 ± 60, 314 ± 40, and 348 ± 19 kJ mol^{-1} for CuO/BaO = 1, 2, and 2.5. The value was increased with the increase of CuO/BaO ratio. It is apparent that the slopes of the Arrhenius plots are not identical in this study. However, it implies that the activation energies derived from the slopes of the Arrhenius plots are not the same and supports the idea that the mechanism of grain growth is not identical for all compositions.

Figure 5 shows the maximum dielectric constant (i.e. tested at Curie temperature) and the loss tangent (tested at Curie temperature) as a function of sintering temperature and different ratios of CuO–BaO mixtures addition. As the sintering temperature was increased, the dielectric constant increased significantly and the loss tangent also decreased significantly. Higher sintering temperature resulting in more densification may dominate these results. The loss tangent decreased with the sintering temperature and decraesed slightly with the increasing in CuO/BaO ratio. It may be caused by the fact that as the CuO/BaO ratio increases, the more liquid-phase flux is formed for full densification by the grain growth.

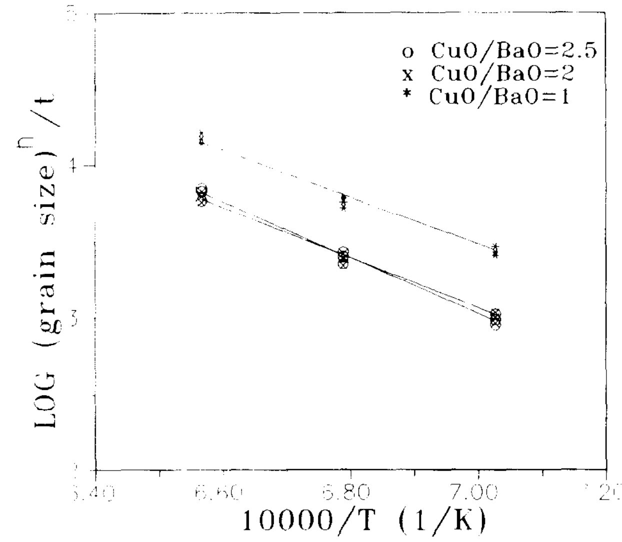

Fig. 4. Log (G^n/t) vs 1/T Arrhenius plots for the $BaTiO_3$ ceramics with different CuO–BaO mixtures added.

For a sintering temperature of 1100°C the evolution of dielectric characteristics vs temperature is closely related to different ratios of CuO–BaO mixtures, and the results are shown in Fig. 6. The dielectric constant was increased when the CuO–BaO mixture with higher ratio was used. The tetragonal–cubic phase transition (or the Curie temperature) accompanying the maximum dielectric constant was shifted to lower temperature, the orthorhombic–tetragonal phase transition was

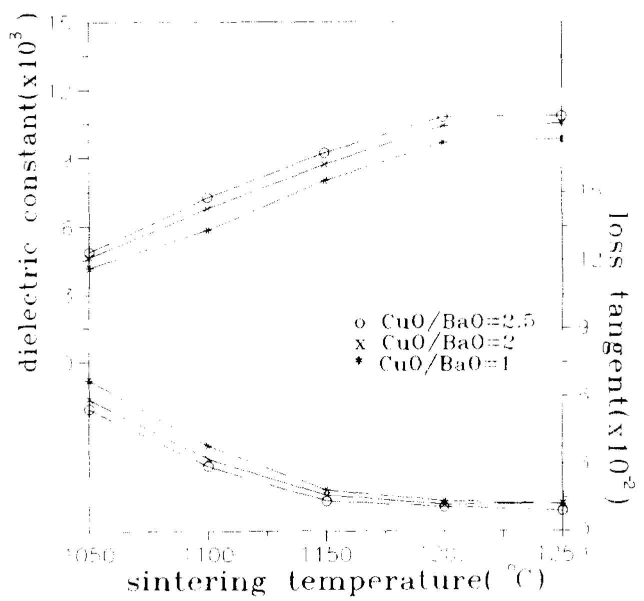

Fig. 5. The maximum dielectric constants and loss tangents of $BaTiO_3$ ceramics as a function of sintering temperature and CuO/BaO ratio.

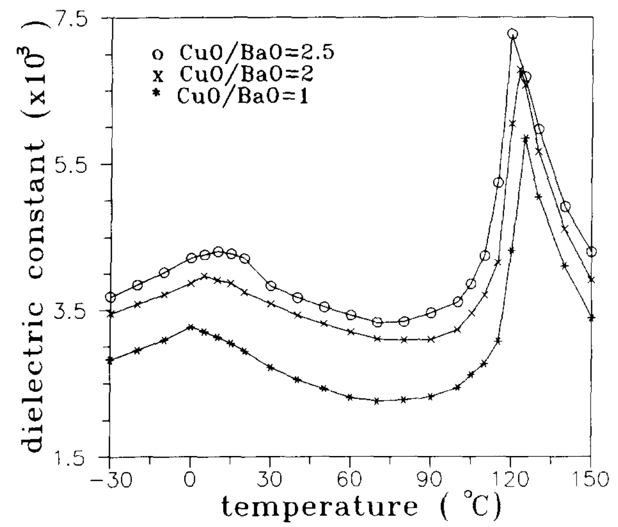

Fig. 6. The dielectric constant for $BaTiO_3$ ceramics as a function of CuO/BaO ratio.

moved towards higher temperature. The permittivity peak at both phase transitions is broadened and broader and fainter dielectric curves can be observed. However, in this study, the εr-T (dielectric constant vs temperature) curves of the sintered CuO–BaO/$BaTiO_3$ ceramics showed broad curves, especially when the temperatures are lower than 110°C.

4 CONCLUSION

The binary system CuO–BaO mixture can be used as the liquid-phase flux former for lowering the sintering temperature of $BaTiO_3$. The grain growth exponent decreases with the increases of sintering temperature and the CuO/BaO ratio, but the average grain size increases with the increase of sinetring temperature and CuO/BaO ratio. The activation energy also increases with the increase of CuO/BaO ratio. As the CuO/BaO ratio increases, the greater densification, larger dielectric constant, lower loss tangent, and fainter dielectric curve for $BaTiO_3$ ceramics can be achieved.

REFERENCES

1. BURN, I., *J. Mater. Sci.*, **17** (1982) 1398.
2. HAUSSONNE, J. M., DESGARDIN, G., BAJOLET, P. H. & RAEAU, B., *J. Am. Ceram. Soc.*, **66** (1983) 801.
3. TOLINO, D. A. & BLUM, J. B., *J. Am. Ceram. Soc.*, **68** (1985) c-292.
4. BURN, I., US Patent 4283753, 1981.
5. HENNINGS, D., *Ber. Dt. Keram. Ges.*, **55** (1978) 359.
6. ROTH, R. S., DAVIS, K. L. & DENNIS, J. R., *Adv. Caram. Mater.*, **2**(3B) (1987) 295.
7. PIECZULEWSKI, C. N., McADAMS, J. E. & MASON, T. O., *J. Am. Ceram. Soc.*, **73** (1990) 3088.
8. ARJOMAND, M. & MACHIN, D. J., *J. Chem. Soc., Dalton Trans.*, (1975) 1061.
9. YANG, C. F., WU, L. & WU, T. S., *J. Mater. Sci. Lett.*, **11** (1992) 1246.
10. BURN, I., *Bull. Am. Ceram. Soc.*, **50** (1971) 501.
11. YANG, C. H., WU, L. & WU, T. S., *Jpn J. Appl. Phys.*, **31** (1992) 2170.
12. SENDA, T. & SRADT, R. C., *J. Am. Ceram. Soc.*, **73** (1990) 106.
13. WONG, J., *J. Appl. Phys.*, **51** (1980) 4453.
14. OLSSON, E., FALK, L. K. L., DUNLOP, G. L. & OSTERLUND, R., *J. Mater. Sci.*, **20** (1985) 4091.
15. NUNES, S. I. & BRADT, R. C., *J. Am. Ceram. Soc.*, **78** (1995), 2469.
16. GERMAN, R. M. (ed.), *Liquid Phase Sintering*. Plenum Press, New York, 1985, p. 134.