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# Effect of CuO on the sintering and dielectric characteristics of $(Ba_{1-x}Sr_x)$ $(Ti_{0.9}Zr_{0.1})O_3$ ceramics

CHENG-FU YANG, LONG WU, TIEN-SHOU WU
*Department of Electrical Engineering, National Cheng Kung University, Tainan, Taiwan*

In order to lower the temperature required to densify $(Ba_{1-x}Sr_x)$ $(Ti_{0.9}Zr_{0.1})O_3$ (BSTZ-series) and to avoid the formation of a low dielectric constant phase, copper oxide is added as liquid-phase promotor after BSTZ-series are calcined. The *a*-axis lattice constant at room temperature elongates with both increasing amount of CuO added and higher sintering temperature, while the *c*-axis lattice constant elongates only slightly under the same condition. The dielectric constant increases with sintering temperature. However, for different amounts of CuO added, the dielectric constant increases with increasing amount of CuO at lower sintering temperatures (below ~ 1100 °C). When a higher sintering temperature is used (above ~ 1200 °C), the dielectric constant reaches a maximum at ~ 1 wt% CuO added, and decreases slightly on further addition of CuO.

## 1. Introduction

Barium titanate ceramics have exceedingly high dielectric constants with low dissipation factors, so they may be used as the basic ingredient for many ceramics capacitor dielectrics. Barium titanate has a high Curie point temperature of 130 °C, and for this reason has little practical use, unless a Curie point shifter is provided. This is commonly done by substitution of the isovalent cation $Ti^{4+}$ by $Zr^{4+}$, $Sn^{4+}$ and/or $Ba^{2+}$ by $Mg^{2+}$, $Sr^{2+}$ to form such materials as $BaZrO_3$, $SrZrO_3$, $MgTiO_3$, $SrTiO_3$ or $BaSnO_3$ [1, 2]. These form a solid solution with $BaTiO_3$ and alter the lattice constant. The phase change from tetragonal to cubic, accompanying the maximum permittivity, would occur near room temperature.

The initial purpose of this study was to try to form a $(Ba_{1-x}Sr_x)(Ti_{0.9}Zr_{0.1})O_3$ composition for $x = 0$, 0.1, 0.2 and 0.3 (BSTZ-series) which had maximum permittivity at 25 °C. Unfortunately, incorporation of zirconium and strontium into barium titanate raises the firing temperature required for full densification of the sintered samples [2]. However, if a liquid-phase formation occurs in the sintering process, the ceramics can be sintered at lower temperature. In the past, oxides were added as flux in order to lower the sintering temperature, e.g. $B_2O_3$, $Bi_2O_3$, LiF, $SiO_2$, etc. [3–6]. Copper oxides have been used previously as flux formers [7].

Unfortunately, a lower sintering temperature may be accompanied by a significant decrease in dielectric constant caused mainly by two reasons: (1) the dilution of high dielectric constant ceramics with low dielectric constant flux or glass, which virtually cannot be avoided as flux is added; and/or (2) the formation of low dielectric constant compounds by the reaction of the ceramics with low-melting oxide. The low dielectric compound can be prevented by the formation of $ABO_3$ phase completely. The purpose of this study was to sinter BSTZ-series with added CuO without causing suppression of the dielectric constant.

## 2. Experimental procedures

$BaCO_3$, $SrCO_3$, $TiO_2$ and $ZrO_2$ (> 99.8% purity) were used as raw materials, and weighed first in accordance with the composition $(Ba_{1-x}Sr_x)$ $(Ti_{0.9}Z_{0.1})O_3$, for $x = 0$, 0.1, 0.2 and 0.3, respectively. To prevent the formation of low dielectric compound between BSTZ-series and CuO, a high calcining temperature was used to form $ABO_3$ phase completely. The calcination temperatures of $(Ba_{1-x}Sr_x)$ $(Ti_{0.9}Zr_{0.1})O_3$ were selected as 1150, 1160, 1170 and 1180 °C for BSTZ-series ceramics $x = 0$, 0.1, 0.2 and 0.3, respectively. From the X-ray diffraction patterns, only (Ba, Sr)$TiO_3$ and $BaZrO_3$ were revealed.

After calcination, followed by crushing, grinding and sieving with 325 mesh screen, BSTZ-series powder was obtained. Different amounts of copper oxide (CuO) were then added to the BSTZ powder by wet-mixing. After drying and grinding, the powder was pressed into disc-shaped samples using distilled water as binder. Sintering was conducted at 1050–1200 °C in air for 4 h. Surface observation and elemental analysis were carried out using the SEM. After surface polishing, the crystalline structure of the sintered specimens was again examined by X-ray diffraction analysis. Then the sintered samples were printed with Ag–Pd paste, fired at 700 °C for 15 min, and then placed in the temperature–humidity programmable testing chamber, the capacitance (dielectric constant)

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and loss tangent (tan δ), together with their temperature dependence, were measured using an impedance analyser (HP4192a).

## 3. Results and discussion

### 3.1 Microstructure and electron probe microanalysis (EMPA)

The first evidence of liquid-phase effect can be judged by grain growth. For BSTZ-series without added CuO, even with a sintering temperature of 1250 °C, densification was not complete; only a uniform fine-grained microstructure with grain size smaller than 1 μm could be seen. However, for CuO-modified BSTZ-series, while sintering proceeded at 1100 °C with the addition of 1 wt % CuO, a non-homogeneous grain size distribution, which exhibited exaggerated discontinuous grains in a fine-grained matrix, was observed, as shown in Fig. 1a.

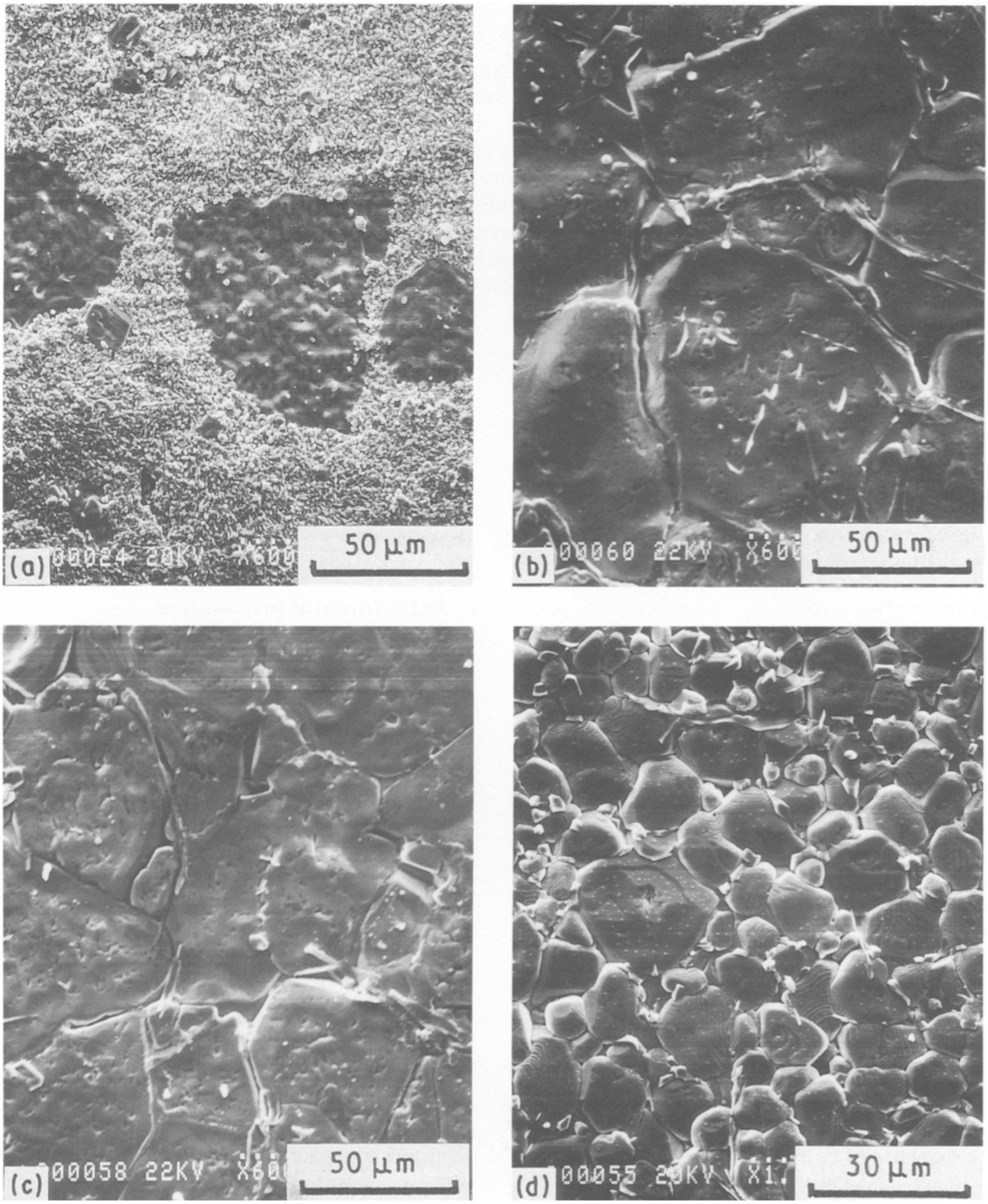

*Figure 1* Scanning electron micrographs of "as-fired" surfaces of CuO-modified $(Ba_{1-x}Sr_x)(Ti_{0.9}Zr_{0.1})O_3$: (a) $x = 0$, 1 wt % CuO added, sintered at 1050 °C; (b–d) 1 wt % CuO added, sintered at 1200 °C for $x = 0$, 0.1 and 0.2, respectively; (e, f) for $x = 0.1$, sintered at 1200 °C, 0.5 and 2 wt % CuO added, respectively.

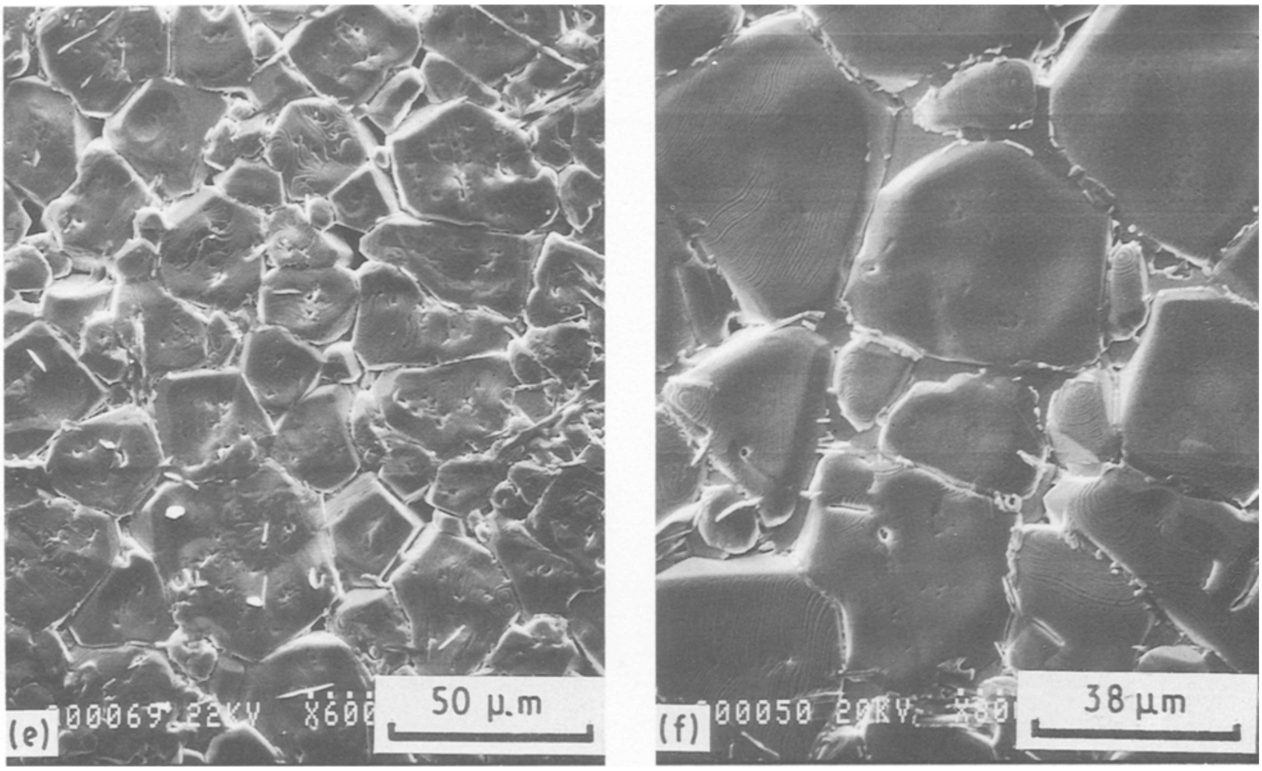

*Figure 1* Continued

The abnormal grain growth (also called secondary recrystallization) is characterized by the rapid growth of only a small number of grains. This may have resulted from the presence of a small amount of liquid eutectic formed by the additive or certain impurities. For the composition of BSTZ-series with added CuO, there are two conditions under which this kind of bimodal microstructure may form. The first condition causing liquid-phase formation is that a small excess of $TiO_2$ reacts with $BaTiO_3$ to form the other phases, and they then form a eutectic with $BaTiO_3$. For example, $Ba_6Ti_{17}O_{40}$ would form a eutectic with $BaTiO_3$ and melt at 1312 °C [8]. The second condition is the liquid-phase effect of CuO. The first condition is impossible because the sintering temperatures used here are lower than 1250 °C. Therefore, the abnormal grain growth caused by the liquid-phase effect of CuO is proved.

Fig. 1b–d show the grain growth of sintered samples with 1 wt % CuO added and sintered at 1200 °C. The grain size decreases significantly with increasing Sr/Ba ratios. It reveals that for more barium substitution by strontium, a higher sintering temperature is required. Fig. 1e and f show the microstructure of $(Ba_{0.9}Sr_{0.1})(Ti_{0.9}Zr_{0.1})O_3$ with 0.5 and 2 wt % CuO added and sintered at 1200 °C. For 0.5 wt % CuO added, small-sized grains can be observed (cf. Fig. 1e and c), for less liquid phase engaged in the grain growth. Thus, the liquid-phase effect of CuO on BSTZ-series would be clearly known. For 2 wt % CuO added, a smaller grain size compared with Fig. 1c, was also seen, and the grain boundaries seem discontinuous for the second phase to segregate. However, it suggests that a large amount of CuO is unnecessary, because the amount of grain-boundary phase will increase, and normal grain growth will be inhibited because, when the inclusions increase, the energy for grain-boundary movement also will be increased, and the grain growth will thus be inhibited.

To determine whether the distribution of Cu(CuO) will segregate as liquid-phase flux at the grain boundary, or melt into the grain, EPMA analysis at the grain-boundary-grained structure was carried out; the results are shown in Fig. 2. EPMA shows an obvious inhomogeneity in the distribution of barium, strontium, titanium, zirconium and copper. For $(Ba_{0.8}Sr_{0.2})(Ti_{0.9}Zr_{0.1})TiO_3$ sintered at 1200 °C and with 2 wt % CuO added, the concentrations of barium, strontium, titanium and zirconium show a homogeneous distribution throughout each grain, and decrease substantially at grain boundaries, as shown in Fig. 2a and b. However, the concentration of copper reveals a directly opposite distribution. As Fig. 2c shows, the concentration of copper increases substantially at grain boundaries, but it is almost undetectable in the grains. This suggests that CuO, as predicted, would not react with BSTZ-series to form other unknown phase.

### 3.2. The variation in lattice constant

Table I shows the variations of lattice constants, *a* and *c*, as a function of the amount of CuO added and sintering temperature. The lattice constant *a* and *c* are calculated from the X-ray diffraction peaks for the BSTZ-series system mainly by examination of the behaviour of the (3 1 0) and (2 1 1) planes. Because the value of sin θ is higher for larger values of θ, the change in the 2θ value can be accurately observed, and it will offer the best basis for reaction studies.

As shown in Table I, the $a$-axis lattice constant is elongated as a higher sintering temperature and greater amounts of CuO are used. The $c$-axis also slightly elongates for both conditions. For $x = 0, 0.1$, the crystal structure of $(Ba_{1-x}Sr_x)(Ti_{0.9}Zr_{0.1})O_3$ displays clearly a tetragonal phase with a $c/a$ ratio larger than 1. But for $x = 0.2$, the phase moves from the tetragonal phase to the cubic (or pseudo-cubic) structure for higher sintering temperatures and greater amounts of CuO added. For $x = 0.3$, the specimens clearly display the cubic phase for with no splitting at $(3\bar{1}0)$ and $(2\,1\,1)$ planes.

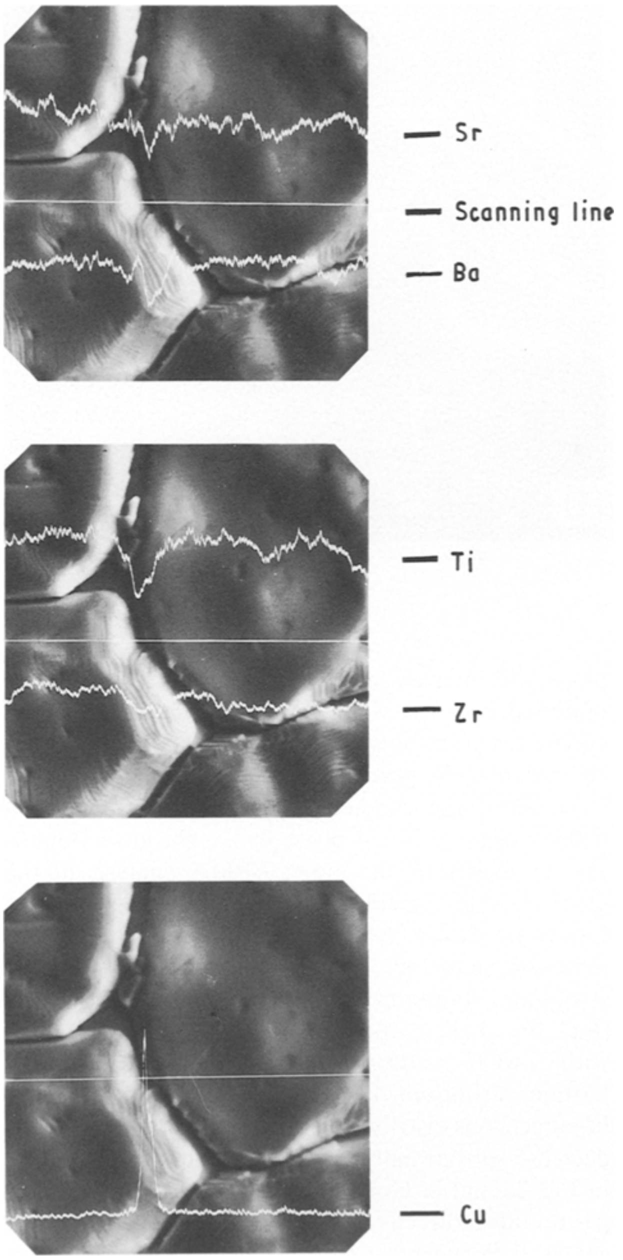

*Figure 2* Line scanning of barium, strontium, titanium, zirconium and copper at the grain-boundary-grained structure for $(Ba_{0.8}Sr_{0.2})$-$(Ti_{0.9}Zr_{0.1})O_3$ with 2 wt % CuO added and sintered at 1200 °C.

The variations in the lattice parameters can be determined from the X-ray patterns of the fired ceramics by observing the intensity of $BaZrO_3$. Jackson and Jonker's studies on $BaZrO_3$ and $SrTiO_3$ prohibit the formation of a complete solid solution with $BaTiO_3$ [9]. However, the $BaZrO_3$ phase is found. Thus the calcining process cannot permit the formation of a solid solution between $(Ba, Sr)TiO_3$ and $BaZrO_3$. When a higher sintering temperature is used and more CuO is added, the intensity of $BaZrO_3$ will be lower: this could explain the variation in lattice constant as a function of sintering temperature and amount of CuO added. Another important result is also revealed; CuO due to its liquid-phase flux effect, may improve the formation of a solid solution of $(Ba, Sr)TiO_3$ (or $BaTiO_3$) with $BaZrO_3$.

### 3.3. The dielectric characteristics

Fig. 3 shows the temperature-dependent dielectric characteristics of BSTZ-series ceramics with 1 and 2 wt % CuO added and sintered at 1150 °C. Many factors will affect the dielectric characteristics, including the microstructure, the doping effect of the impurities, the porosity and the second phase. As the Sr/Ba ratio is changed, a morphotrophic phase boundary (MPB) exists where optimum electrical properties can be generated [10]. As shown in Fig. 2, although the grain size for $Ba(Ti_{0.9}Zr_{0.1})O_3$ is larger than the other BSTZ-series with identical sintering temperature and amount of added CuO, the maximum dielectric constant will be found at $(Ba_{0.9}Sr_{0.1})(Ti_{0.9}Zr_{0.1})O_3$ rather than at $Ba(Ti_{0.9}Zr_{0.1})O_3$.

Table II shows the maximum dielectric constant of BSTZ-series with different amounts of added CuO, fired at different temperatures. As Table II shows, at lower sintering temperatures, for example 1100 °C, the dielectric constant will increase with increasing CuO content. It may be caused by the lower sintering temperature, as more liquid-phase flux is needed for full densification by the normal and/or abnormal grain growth. For higher sintering temperatures, for example if 1200 °C is used as the firing temperature,

TABLE I The lattice constants of sintered $(Ba_{1-x}Sr_x)(Ti_{0.9}Zr_{0.1})O_3$

| Sintering temperature (°C) | CuO content (wt %) | $x = 0$ |  | $x = 0.1$ |  | $x = 0.2$ |  | $x = 0.3$ |
|---|---|---|---|---|---|---|---|---|
|  |  | $a$ (Å) | $c$ (Å) | $a$ (Å) | $c$ (Å) | $a$ (Å) | $c$ (Å) | $a$ (Å) |
| 1100 | 1 | 4.005 | 4.032 | 3.994 | 4.009 | 3.982 | 3.992 | 3.974 |
|  | 2 | 4.007 | 4.032 | 3.996 | 4.009 | 3.984 | 3.992 | 3.976 |
| 1150 | 1 | 4.010 | 4.032 | 3.999 | 4.009 | 3.987 | 3.994 | 3.979 |
|  | 2 | 4.014 | 4.032 | 4.002 | 4.009 | 3.994 |  | 3.981 |
| 1200 | 1 | 4.019 | 4.036 | 4.004 | 4.012 | 3.996 |  | 3.981 |
|  | 2 | 4.021 | 4.036 | 4.006 | 4.012 | 3.996 |  | 3.983 |

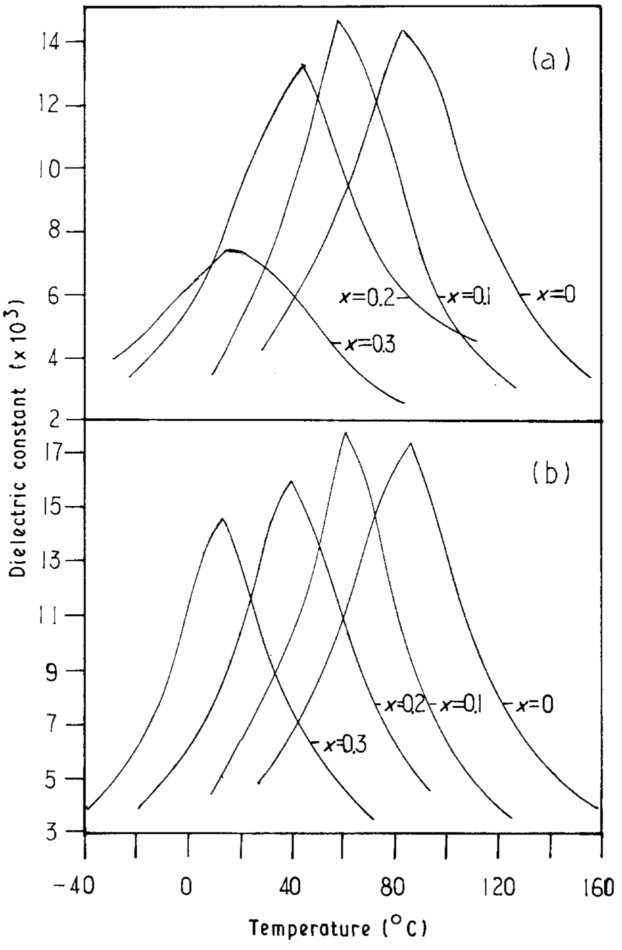

*Figure 3* Dielectric constant for BSTZ-series sintered at 1150 °C as a function of CuO added: (a) 1 wt % CuO, (b) 2 wt % CuO.

TABLE II The maximum dielectric constants of $(Ba_{1-x}Sr_x)(Ti_{0.9}Zr_{0.1})O_3$ as a function of sintering temperature and amount of CuO added

| Composition | CuO content (wt %) | Maximum dielectric constant | | |
|---|---|---|---|---|
| | | 1100 °C | 1150 °C | 1200 °C |
| 0 | 0.5 | 4820 | 10300 | 13120 |
| | 1 | 7070 | 14600 | 21040 |
| | 1.5 | 9920 | 18970 | 20320 |
| | 2 | 12120 | 17500 | 18820 |
| 0.1 | 0.5 | 4460 | 10110 | 14720 |
| | 1 | 7530 | 14980 | 22370 |
| | 1.5 | 11230 | 19370 | 21510 |
| | 2 | 12910 | 17980 | 18820 |
| 0.2 | 0.5 | 4060 | 6890 | 10150 |
| | 1 | 5450 | 12090 | 19570 |
| | 1.5 | 8920 | 13940 | 19020 |
| | 2 | 11240 | 15390 | 18400 |
| 0.3 | 0.5 | 2870 | 4520 | 7940 |
| | 1 | 3640 | 7440 | 13340 |
| | 1.5 | 5450 | 11890 | 15320 |
| | 2 | 6890 | 14530 | 17090 |

the maximum dielectric constant in the BSTZ-series for $x = 0$, 0.1 and 0.2, will be reached at 1 wt % CuO added, and will decrease when more CuO is added.

Because almost no reaction would occur between BSTZ-series and CuO, the variation of dielectric constant can be explained by the microstructure of the polycrystalline ceramics in Fig. 1f, as illustrated in Fig. 4a. The microstructure may be approximated by

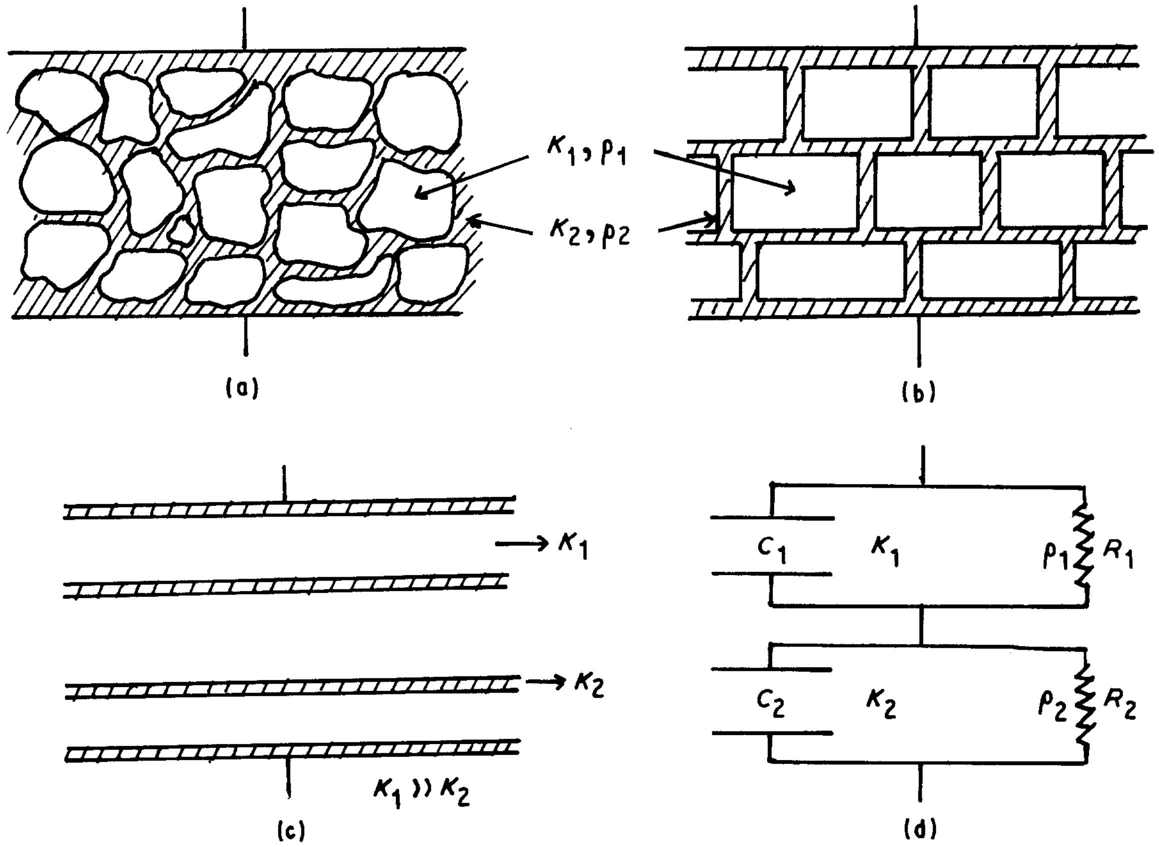

*Figure 4* The model of equivalent circuits for diphase ceramics: (a) microstructure, (b) brick-wall model, (c) parallel mixing rule, (d) ideal two-layer model.

a brick-wall model, as shown in Fig. 4b if the boundary phase is continuously connected. In this model, cubes of the major phase (BSTZ-series) are separated by an intergranular boundary phase. When $\chi_1 \gg \chi_2$, the lines of flux prefer the major phase ($\chi_1$ and $\chi_2$ are the dielectric susceptibility of BSTZ-series and CuO, respectively), and only the susceptibility boundaries ($\chi_2$) normal to the flux path are important. So series mixing rules ([11] p. 947), as shown in Fig. 4c, would be applied for the dielectric constant.

By collecting like impedences together, Maxwell simplified the diphasic stratified dielectric, shown in Fig. 4c, to a two layered model ([11], p. 956). The equivalent circuit for such a model is shown in Fig. 4d, where each layer has a capacitance parallelled by resistance. For perfectly insulating phases ($\rho_1 = \rho_2 = \infty$) the a.c. capacitance, $\bar{C}$, of series-connected layers is reciprocally given by

$$\frac{1}{\bar{\bar{C}}} = \frac{1}{C_1} + \frac{1}{C_2} \tag{1}$$

In terms of dielectric constants

$$\frac{d}{\varepsilon_0 \bar{\bar{K}} A} = \frac{d_1}{\varepsilon_0 K_1 A} + \frac{d_2}{\varepsilon_0 K_2 A} \tag{2}$$

or

$$\bar{K} = \frac{d K_1 K_2}{K_1 d_2 + K_2 d_1} \tag{3}$$

where $d_1$ and $d_2$ are the total thickness of BSTZ-series and CuO, $\bar{K}$, $K_1$ and $K_2$ are the dielectric constants of the composite, BSTZ-series and CuO, respectively. The value of the composite dielectric constant, $\bar{K}$, depends upon the ideal displacement of constituent dielectric layers, which depends especially on the low dielectric constant grain-boundary layer.

When the amount of CuO added is less than 1 wt %, the grain size will be the dominant factor for controlling the dielectric constant: the larger the grain size (compare Fig. 1c, e and Table II) the higher will be the dielectric constant. If the amount of CuO added is more than 1 wt %, the segregation of CuO at the grain boundaries will be apparent and can no longer be ignored when higher sintering temperatures are used. Thus the equivalent circuit of the dielectric in Equation 3 will be considered. When a greater amount of CuO is added, the thickness of the constituent boundaries (the thickness of $d_2$) is increased, and the composite dielectric constant, $K$, will be lowered for $K_2$ and $K_1$. This also suggests that a large amount of CuO is unnecessary for depression on the dielectric constant.

## 4. Conclusion

The liquid-phase effect of CuO on BSTZ-series ceramics was studied. Because the BSTZ-series is calcined, the reaction between CuO and BSTZ-series is prevented and CuO is only segregated at the grain boundary. The maximum dielectric constant is obtained at $(Ba_{0.9}Sr_{0.1})(Ti_{0.9}Zr_{0.1})O_3$, rather than $Ba(Ti_{0.9}Zr_{0.1})O_3$. A large amount of CuO is unnecessary for depression of the dielectric constant and inhibition of grain growth. The optimum amount of CuO added is about 1 wt % in this research. On sintering at 1150 °C with 1 wt % CuO, the peak dielectric constants obtained were 14 600, 15 000, 12 100 and 7400 for $x = 0$, 0.1, 0.2 and 0.3, respectively.

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