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Dielectric properties and microstructural behaviour of B-site calcium-doped barium titanate ceramics

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Dielectric properties and microstructural behaviour of $Ba_{1-x}Sr_xTi_{1-y}Ca_yO_{3-y}$ ceramics, where strontium and calcium were doped on the barium and titanium sites, respectively, within the range $0 \leqslant x \leqslant 0.24$ and $0 \leqslant y \leqslant 0.05$, were investigated. Calcium addition decreased the tetragonality, *c/a*, increased the unit cell volume, and lowered the Curie temperature, which were all attributed to the occupancy of Ca^{2+} ions on titanium sites. When sintered at a low oxygen partial pressure of 10^{-9} MPa, a resistivity higher than 10^{11} Ω cm was maintained for the formulations containing B-site calcium substitution more than 0.5 mol %. With increasing the amount of calcium addition, the Curie peak was depressed and completely broadened for the compositions with calcium addition more than 3 mol %, where the average grain size was smaller than 1 μm. Co-firing with nickel electrodes in a reducing atmosphere also depressed the Curie peak and inhibited the grain growth due to the diffusion of nickel into the dielectrics.

1. Introduction

Dielectric formulations and process technologies for multilayer ceramic capacitors have been extensively investigated in the electronics industry, because multilayer ceramic capacitors have large capacitance per unit volume and can be soldered directly on the printed circuit boards by surface mounting technology [1–6]. Recently, multilayer capacitors with base-metal internal electrodes, such as nickel and ion, have been developed to reduce the process cost [3–5]. In this case, dielectrics should be co-fired in a reducing atmosphere to prevent the oxidation of the internal electrodes. However, $BaTiO_3$ ceramics become semiconducting and lose their high insulation resistance due to the unlocalized electrons produced by the formation of oxygen vacancies during sintering in a reducing atmosphere [3–5, 7]. For the fabrication of multilayer capacitors with base metal electrodes, the most important factor is, therefore, the dielectric formulations where high insulation resistance can be maintained even after sintering in a reducing atmosphere.

Calcium-doped $BaTiO_3$ ceramics, where the A-site to B-site ion ratio is larger than 1, have been developed for this purpose [5, 7, 8]. The following mechanism of reduction inhibition for these dielectric formulations has been proposed: Ca_{Ti}'' ions are formed by substitution of Ca^{2+} ions on titanium sites and act as acceptors to trap the unlocalized electrons [5, 7]. However, it was also suggested that the substitution of smaller Ca^{2+} ions on barium sites suppressed the formation of oxygen vancancies by increasing the binding energy of oxygen, resulting in maintenance of the high insulation resistance after sintering at low oxygen partial pressure [8, 9]. Previous investigations have been based on the A-site excess formulations of $(Ba_{1-x}Ca_x)_mTiO_{2+m}$, $m > 1$ [5, 7, 8]. Thus calcium was substituted simultaneously on the A- and B-sites of $BaTiO_3$, and it was difficult to characterize the effects of calcium substitution at the titanium site on the electrical properties of $BaTiO_3$ ceramics systematically.

In our study, the dielectric properties and microstructural behaviour of $BaTiO_3$ ceramics by B-site calcium substitution were investigated using dielectric formulations of $Ba_{1-x}Sr_xTi_{1-y}Ca_yO_{3-y}$, where strontium and calcium were doped on barium and titanium sites, respectively, within the range $0 \leqslant x \leqslant 0.24$ and $0 \leqslant y \leqslant 0.05$. Strontium is well known as a useful shifter for the Curie temperature and cannot be substituted on the titanium site due to the large difference in ionic radii [10]. Reduction inhibition of $BaTiO_3$ by B-site calcium substitution, after sintering in a reducing atmosphere, was confirmed and the effects of co-firing with a nickel electrode on the dielectric properties were also studied.

2. Experimental procedure

The starting powders used in this study were 99.8% $BaCO_3$, $SrCO_3$ and TiO_2 and 98% $CaCO_3$. Formulations of $Ba_{1-x}Sr_xTi_{1-y}Ca_yO_{3-y}$ were weighed and wet mixed for 12 h in a polyethylene jar using zirconia balls. After drying, the mixed powder was calcined at 1100 °C for 2 h and ball-milled for 24 h and dried. The powder was then mixed with a small amount of PVA binder and pressed at 1200 kg cm^{-2} to form disc-type samples 1 cm diameter and 1 mm thick. After complete burn-out of the binder at 500 °C in air, sintering was conducted at 1400 °C for 2 h in air or a reducing atmosphere. The oxygen partial pressure in a reducing atmosphere, which was produced by a CO/CO_2 gas mixture, was measured using a zirconia sensor. After sintering, termination electrodes were formed by sputtering gold on both sides of the disc-type samples.

Dielectric properties and insulation resistance were measured using an LCR meter (HP 4262A, Hewlett Packard) at 1 kHz and high-resistance meter (HP 4329A, Hewlett Pakcard) at 100 V d.c., respectively. Lattice parameters were characterized by X-ray diffraction (XRD) on the ground powder of sintered samples and microstructure was observed using scanning electron microscopy (SEM).

3. Results and discussion

3.1. Effect of B-site calcium substitution on the dielectric properties

Fig. 1 shows that lattice parameters of the *c*-axis were linearly decreased and those of the *a*-axis were increased for both $x = 0$ and $x = 0.08$ formulations sintered in air when the amount of calcium substitution, *y*, in $Ba_{1-x}Sr_x\ Ti_{1-y}Ca_yO_{3-y}$ formulations was varied from 0 to 0.02. As indicated by the variation in lattice parameters, the tetragonality, c/a, was decreased with increasing calcium addition. Here, the rate of lattice-parameter change for $x = 0$ compositions is higher than that for $x = 0.08$ formulations.

As shown in Fig. 2, the unit cell volume was increased linearly up to 2 mol % calcium substitution. When Ca^{2+} was substituted on the barium site, which is larger than the Ca^{2+} ion, the unit cell volume was reported to be reduced with decreasing lattice parameters of *c*- and *a*-axis [10–13]. With linear increase of unit cell volume and the variation of lattice parameters, it can thus be concluded that up to 2 mol % Ca, doped on the B-site of $BaTiO_3$, was completely substituted on the titanium sites without depending on the presence of Sr^{2+} ions at the barium sites. The rate of unit-cell volume change with B-site calcium substitution is also affected by the substitution of strontium on the barium site. The radius of the Sr^{2+} ion is smaller than that of the Ba^{2+} ion, and the unit-cell volume was linearly decreased by increasing the amount of strontium addition to the barium sites, up to 0.24 mol % (Fig. 3). Thus the difference in the rate of the unit-cell volume change between $x = 0$ and $x = 0.08$ compositions, shown in Fig. 2, may be due to the fact that the expansion of the unit cell by calcium substitution at the titanium site, which is smaller than the Ca^{2+} ion, could be partly compensated by the shrinkage of the unit cell with A-site strontium substitution in $x = 0.08$ compositions.

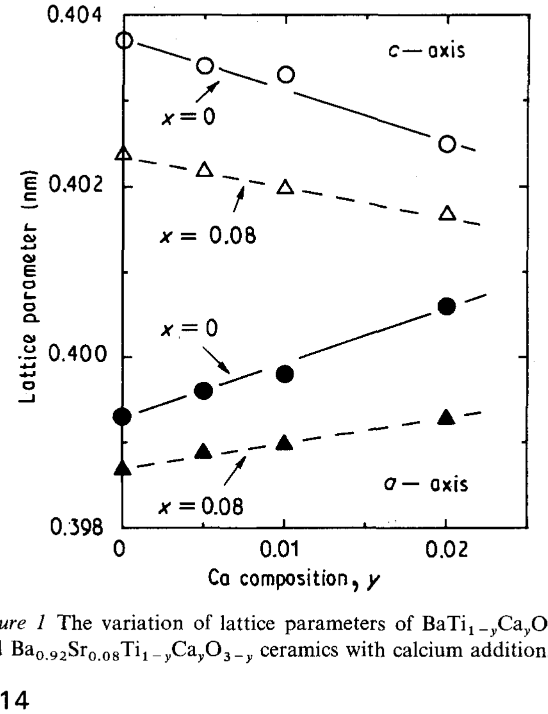

Figure 1 The variation of lattice parameters of $BaTi_{1-y}Ca_yO_{3-y}$ and $Ba_{0.92}Sr_{0.08}Ti_{1-y}Ca_yO_{3-y}$ ceramics with calcium addition.

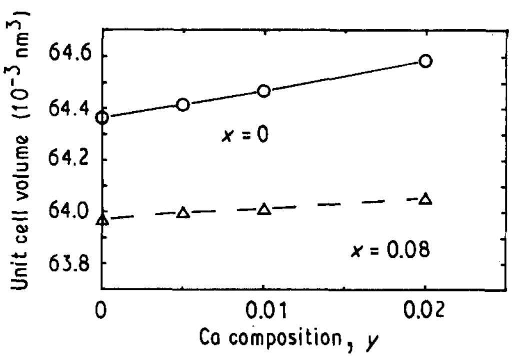

Figure 2 The variation of unit cell volume of $BaTi_{1-y}Ca_yO_{3-y}$ and $Ba_{0.92}Sr_{0.08}Ti_{1-y}Ca_yO_{3-y}$ ceramics with calcium addition.

When calcium was doped to more than 3 mol %, second-phase particles, containing more calcium compared to the matrix, were observed without depending on A-site strontium substitution and characterized as orthotitanate using XRD and EDS. The enhanced intensities of the second phase in the XRD patterns with increasing calcium substitution have indicated that the solubility limit of calcium on the titanium site of $BaTiO_3$ ceramics is about 2 mol %.

The lowering of the Curie temperature with B-site calcium substitution for $x = 0$ and $x = 0.08$ dielectric compositions, sintered in air, is illustrated in Fig. 4. When the barium sites of $BaTiO_3$ were not substituted with Sr^{2+} ions ($x = 0$), the Curie temperature decreased linearly at a rate of − 20 °C/mol % Ca substitution, up to $y = 0.03$. With A-site strontium substitution, however, the rate of Curie-temperature lowering was changed to − 16 °C/mol % Ca substitution. When calcium was substituted at the barium site, the Curie temperature was reported to be little changed [11–13]. Thus the rapid lowering of the Curie temperature in Fig. 4 was caused by calcium substitution at the titanium site. As proposed by Zhuang *et al.* [14], lattice distortion by B-site calcium substitution built up compressive stresses on the unit cells adjacent to B-site calcium-substituted unit cells, which lowered the Curie temperature as did hydrostatic pressure on $BaTiO_3$ [15].

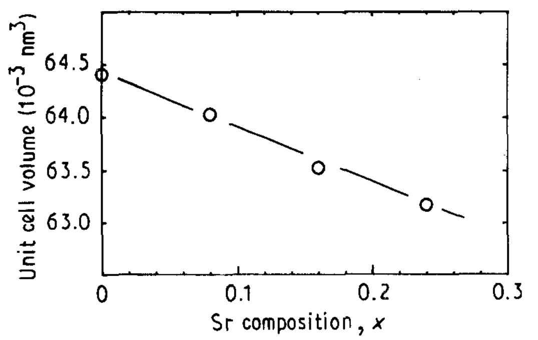

Figure 3 The variation of unit cell volume of $Ba_{1-x}Sr_xTi_{0.995}Ca_{0.005}O_{2.995}$ as a function of strontium addition.

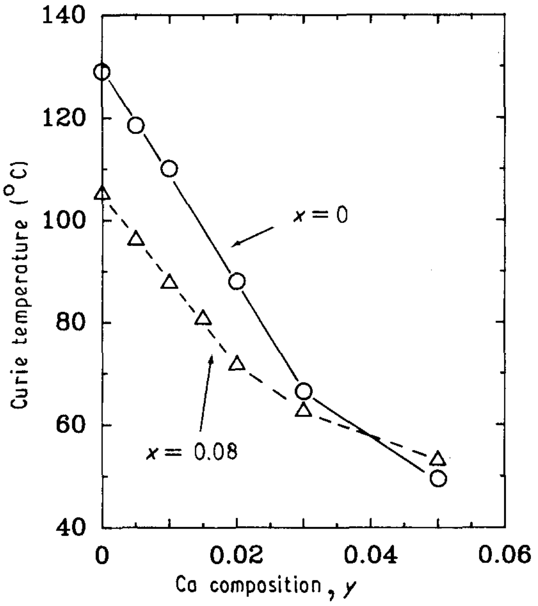

Figure 4 The lowering of the Curie temperature of $BaTi_{1-y}Ca_yO_{3-y}$ and $Ba_{0.92}Sr_{0.08}Ti_{1-y}Ca_yO_{3-y}$ ceramics as a function of calcium addition.

For $Ba_{1-x}Ti_{1-y}Ca_{x+y}O_{3-y}$ formulations where calcium was substituted on A- and B-sites of $BaTiO_3$, rapid lowering of the Curie temperature has been reported for A-site calcium-doped compositions compared to $x = 0$ formulations [14]. When A-sites of $BaTiO_3$ were substituted by smaller Ca^{2+} ions, it was found that more Ca^{2+} ions could be substituted at the titanium sites for the same amount of B-site calcium addition, resulting in the faster Curie temperature shift [14]. With a linear decrease of Curie temperature and an increase in unit-cell volume with calcium addition up to 2 mol % in our study, however, up to 2 mol % Ca^{2+} ions could be thought to be completely substituted at titanium sites without depending on the A-site strontium substitution. Because the rate of unit-cell volume change with B-site calcium substitution was affected by A-site strontium substitution (Fig. 2), the lattice distortion by B-site calcium substitution could be partly absorbed by the shrinkage of the unit cell with A-site strontium substitution and this, in turn, reduced the compressive stresses on the adjacent unit cells and the rate of Curie temperature change for $x = 0.08$ compositions compared to that of $x = 0$ compositions.

3.2. Effects of grain size on dielectric properties

Figs 5 and 6 show the temperature dependence of dielectric constant for $x = 0$ and $x = 0.08$ formulations sintered in air, respectively. The maximum Curie peak was reduced with increasing the amount of calcium dopant and complete broadening of the Curie peak was obtained with $y = 0.03$ and 0.05 for $x = 0$ compositions and only with $y = 0.05$ for $x = 0.08$ formulations. Scanning electron micrographs, illustrated in Fig. 7 for $x = 0$ and in Fig. 8 for $x = 0.08$ formulations, indicate that such complete broadening of the Curie peak was mainly due to the grain-size effect. With increasing the amount of B-site calcium dopant in the dielectric formulations, grain growth

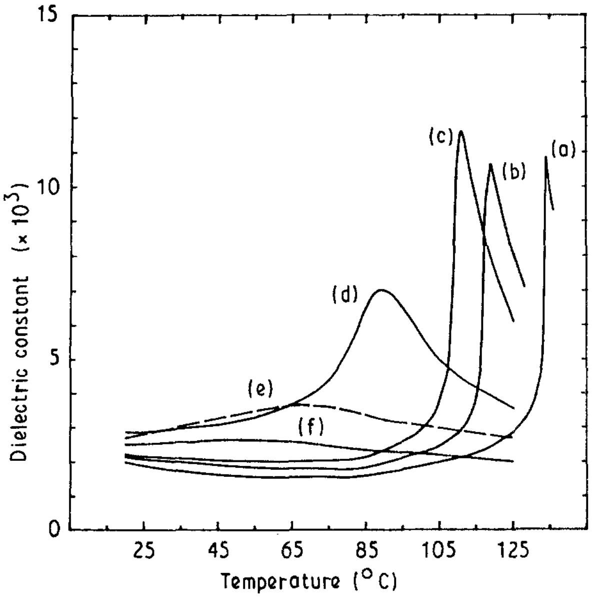

Figure 5 The temperature dependence of the dielectric constant of $BaTi_{1-y}Ca_yO_{3-y}$ ceramics, sintered in air, at 1 kHz. $y =$ (a) 0, (b) 0.005, (c) 0.01, (d) 0.02, (e) 0.03, (f) 0.05.

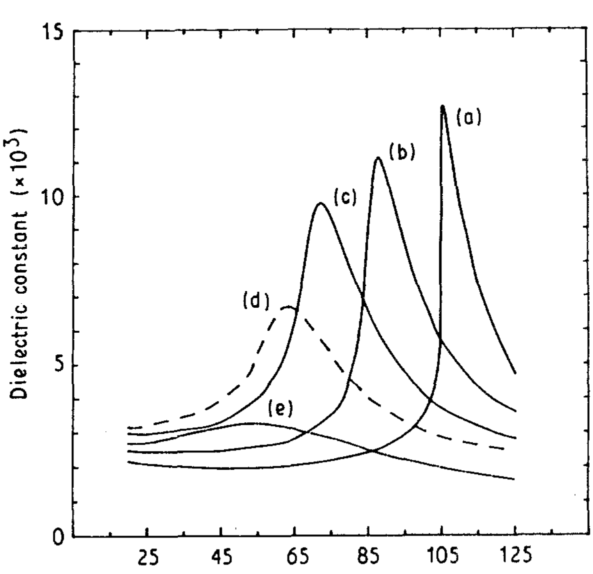

Figure 6 The temperature dependence of the dielectric constant of $Ba_{0.92}Sr_{0.08}Ti_{1-y}Ca_yO_{3-y}$ ceramics, sintered in air, at 1 kHz. $y =$ (a) 0, (b) 0.01, (c) 0.02, (d) 0.03, (e) 0.05.

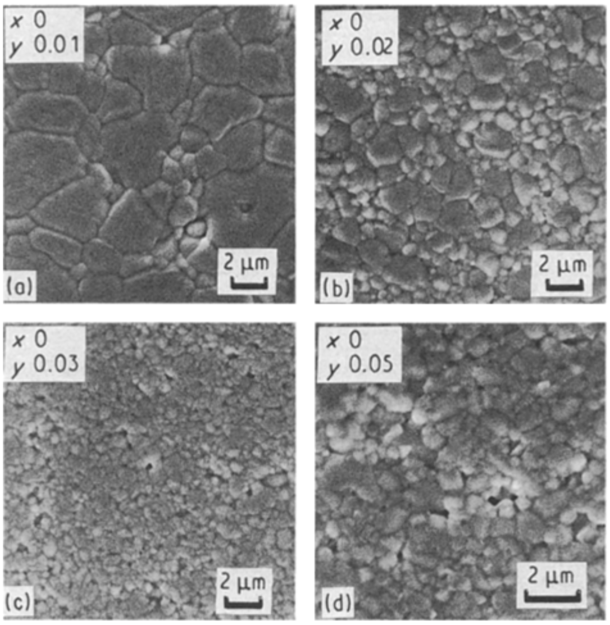

Figure 7 Scanning electron micrographs of polished and thermally etched surfaces of $BaTi_{1-y}Ca_yO_{3-y}$ ceramics, sintered in air, for (a) $y = 0.01$, (b) $y = 0.02$, (c) $y = 0.03$, and (d) $y = 0.05$.

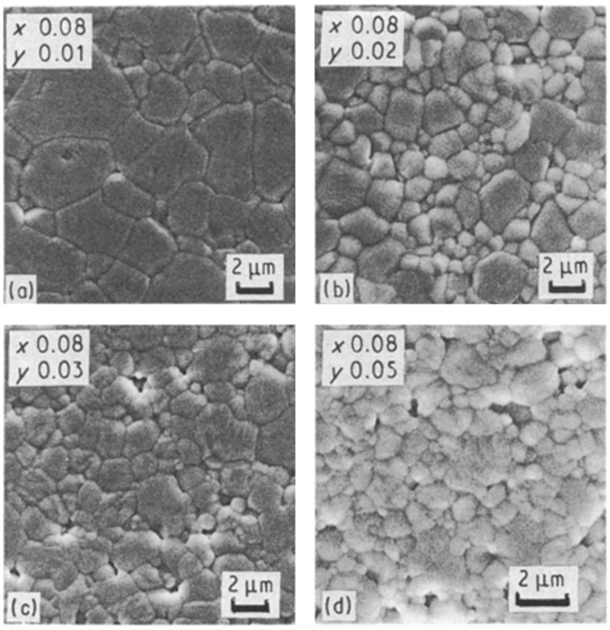

Figure 8 Scanning electron micrographs of polished and thermally etched surfaces of $Ba_{0.92}Sr_{0.08}Ti_{1-y}Ca_yO_{3-y}$ ceramics, sintered in air, for (a) $y = 0.01$, (b) $y = 0.02$, (c) $y = 0.03$, and (d) $y = 0.05$.

was inhibited and the grain size became smaller than 1 µm for $y = 0.03$ and 0.05 with $x = 0$ and for $y = 0.05$ with $x = 0.08$. With a grain size smaller than 1 µm in $BaTiO_3$, the internal stress during ferroelectric phase transition was not relaxed, because the formation of ferroelectric 90° domains was difficult, resulting in a change of lattice from tetragonal to pseudo-cubic phase and a broadening of the Curie peak [16, 17].

To confirm that the Curie peak was completely depressed by the grain-size effect, dielectric formulations with $x = 0$ were sintered in a reducing atmosphere of 10^{-9} MPa oxygen partial pressure. Contrary to the results obtained by sintering in air (Fig. 5), complete broadening of the Curie peak could be observed only for the $y = 0.05$ composition (Fig. 9). As shown in the micrographs of each composition sintered at low oxygen partial pressure of 10^{-9} MPa (Fig. 10), the grains generally became larger than those of air-fired samples in Fig. 7. Although the grains for $y = 0.05$, where complete broadening of the Curie peak was observed, were still smaller than 1 µm, the average grain size for $y = 0.03$ became larger than 1 µm. Non-uniform stress distribution on adjacent unit cells by calcium substitution at the titanium site might cause the Curie peak broadening [14]. However, complete broadening of the Curie peak, observed with calcium additions of more than the solubility limit of $y = 0.02$, could not be explained by the stress-distribution effect.

The dissipation factor, tan δ, was below 1% for most formulations in the temperature range 20–125 °C.

3.3. Effects of co-firing with nickel electrodes

Fig. 11 shows the temperature dependence of disc-type samples with $x = 0$ and $y = 0.02$ composition sintered in a reducing atmosphere of 10^{-9} MPa oxygen partial pressure with and without nickel electrodes. For samples co-fired with nickel electrodes, nickel paste was screen-printed on both sides of disc-type samples before sintering. The Curie peak was more depressed by diffusion of nickel into the dielectrics during co-firing with the nickel electrode, which was confirmed by EDS analysis on the cross-sectioned samples. As shown in Fig. 12, where microstructures of the polished and thermally etched cross-section are illustrated, the grain size became smaller in the area closer to the nickel electrodes. This indicates that nickel diffusion inhibited the grain growth of the dielectrics, resulting in a depressed Curie peak. Such effects of nickel diffusion to the dielectrics on the microstructure and dielectric properties will be exaggerated in

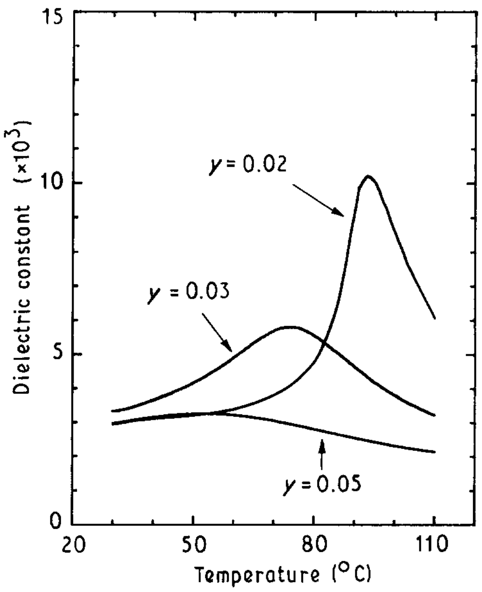

Figure 9 The temperature dependence of dielectric constant of $BaTi_{1-y}Ca_yO_{3-y}$ ceramics, sintered at a low oxygen partial pressure of 10^{-9} MPa, at 1 kHz.

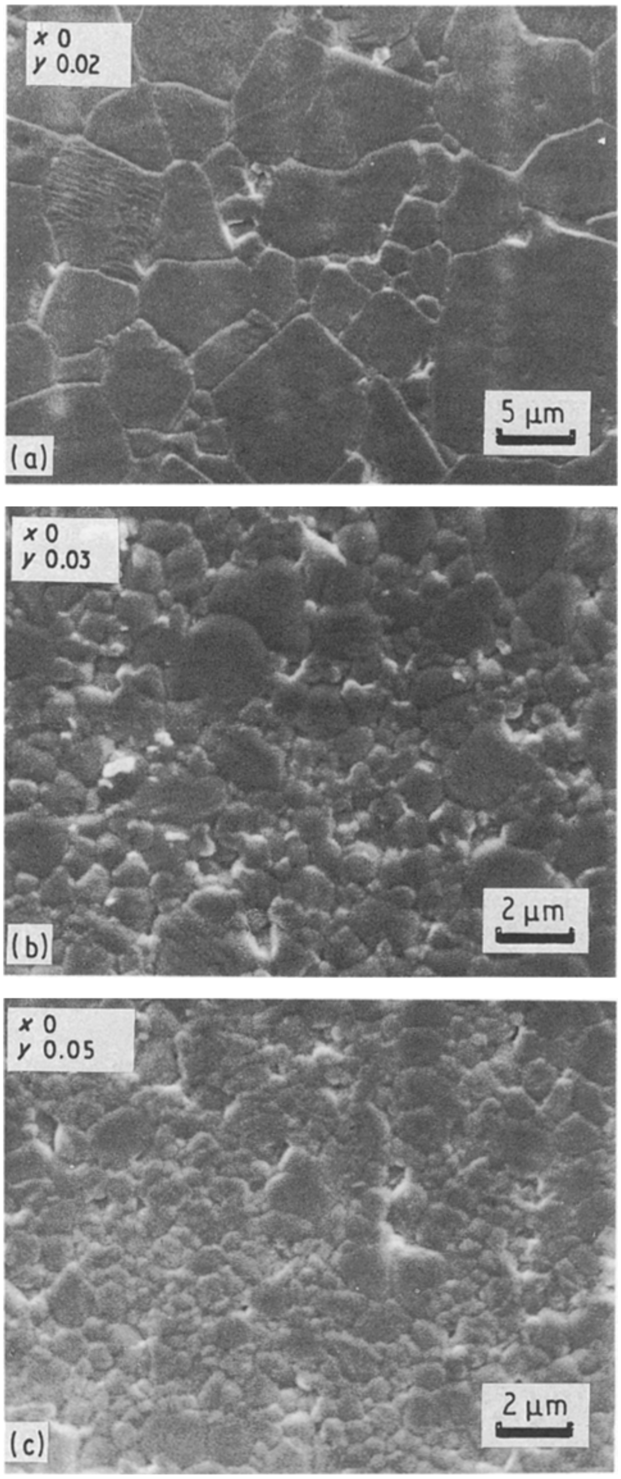

Figure 10 Scanning electron micrographs of polished and thermally etched surfaces of $BaTi_{1-y}Ca_yO_{3-y}$ ceramics, sintered at a low oxygen partial pressure of 10^{-9} MPa, for (a) $y = 0.02$, (b) $y = 0.03$, and (c) $y = 0.05$.

the fabrication of multilayer capacitors where thin dielectric layers should be used to obtain a large capacitance per unit volume.

3.4. Variation of resistivity with B-site calcium substitution

As shown in Fig. 13 where the resistivity of $x = 0.08$ compositions is illustrated as a function of the calcium addition, a resistivity higher than 10^{11} Ω cm could be maintained with a B-site calcium substitution, y, of more than 0.005, even when sintered in a reducing atmosphere of 10^{-9} MPa oxygen partial pressure. Such a high resistivity was also obtained for dielectric formulations without A-site strontium substitution. For dielectric compositions where calcium was not doped ($y = 0$), the resistivity dropped to about 10^7 Ω cm when sintered in a reducing atmosphere. From the XRD results and dielectric behaviour of $Ba_{1-x}Sr_xTi_{1-y}Ca_yO_{3-y}$ ceramics in our study, it was confirmed that up to 0.02 mol % calcium doped on the B-site was completely substituted at the titanium site without the formation of any second phase. Thus the high resistivity after sintering in a reducing atmosphere was maintained by the acceptor-like behaviour of Ca''_{Ti}, which trapped the unlocalized electrons produced by the formation of oxygen vacancies during sintering in a reducing atmosphere [5, 7].

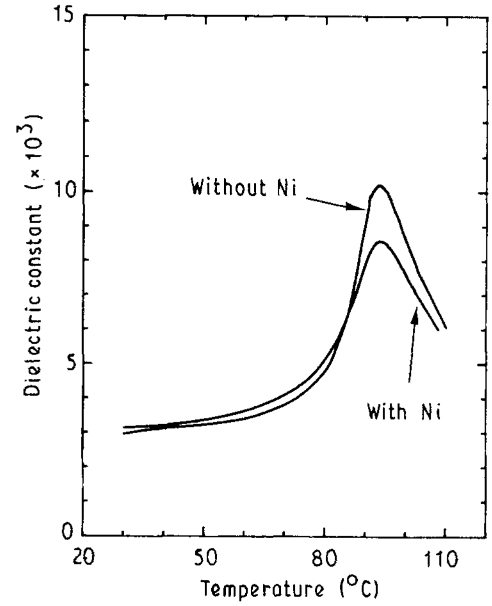

Figure 11 The temperature dependence of the dielectric constant of $BaTi_{0.98}Ca_{0.02}O_{2.98}$ ceramics, sintered at a low oxygen partial pressure of 10^{-9} MPa with and without a nickel electrode, at 1 kHz.

4. Conclusions

Based on an experimental study of the dielectric and microstructural behaviour of $BaTiO_3$ ceramics by B-site calcium substitution, the following conclusions can be drawn.

1. With increasing amount of calcium addition to $Ba_{1-x}Sr_xTi_{1-y}Ca_yO_{3-y}$ formulations, the unit-cell volume was increased with a linear decrease of the c-axis and an increase of the a-axis, which could be attributed to the calcium substitution at the titanium site. The solubility limit of calcium at the B-site of $BaTiO_3$ was found to be about 2 mol %.

2. The rate of Curie temperature change with B-site calcium substitution was affected by strontium substitution at the barium site; within 2 mol % Ca addition, the Curie temperature was lowered at a rate of − 20 and − 16 °C/mol % Ca at $x = 0$ and $x = 0.08$ formulations. Such a difference in the rate of Curie temperature shift may be due to the fact that the lattice

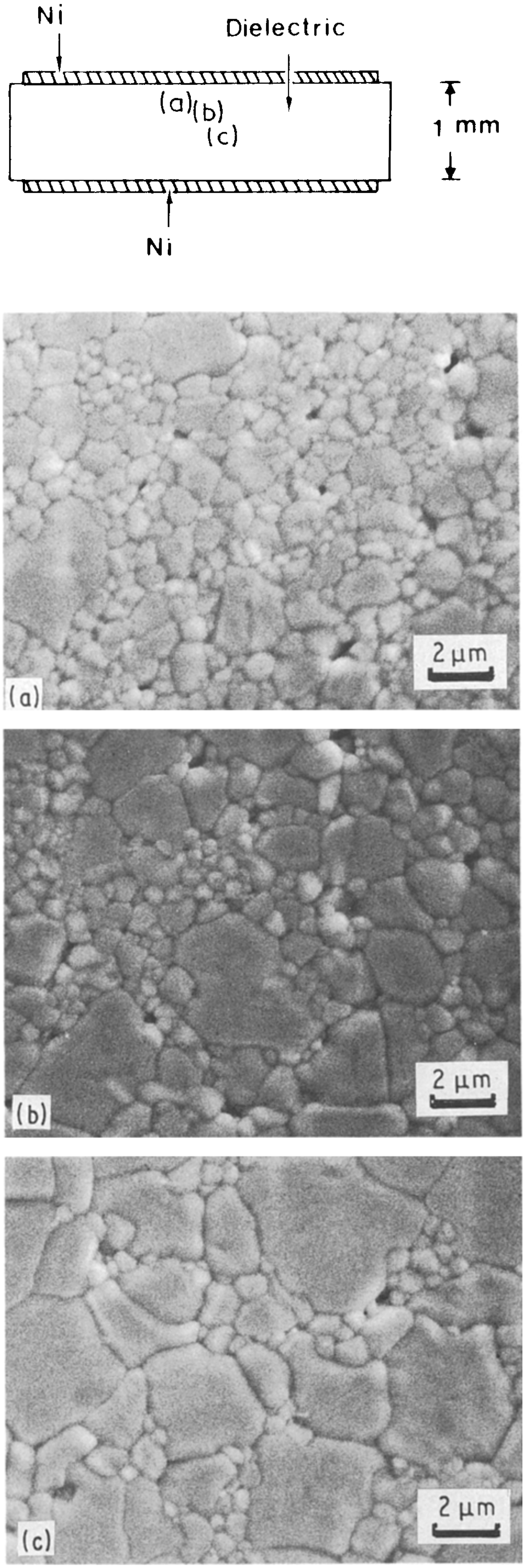

Figure 12 Scanning electron micrographs of a polished and thermally etched cross-section of a $BaTiCa_{0.02}O_{2.98}$ disc-type sample, co-fired at a low oxygen partial pressure of 10^{-9} MPa with nickel electrodes.

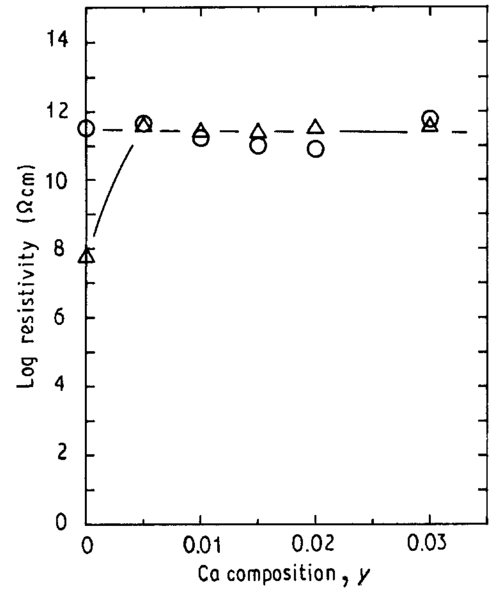

Figure 13 The resistivity of $Ba_{0.92}Sr_{0.08}Ti_{1-y}Ca_yO_{3-y}$ ceramics sintered in (○) air and (△) a reducing atmosphere of 10^{-9} MPa oxygen partial pressure.

distortion by calcium substitution at the titanium site was partly relaxed by the shrinkage of the unit cell on the compositions of $x = 0.08$ where smaller Sr^{2+} ions were substituted at the barium sites.

3. With increasing amount of B-site calcium substitution, the grain growth was inhibited and the Curie peak was depressed. Complete broadening of the Curie peak was obtained with calcium additions of more than the solubility limit of 2 mol %, where the average grain size was smaller than 1 µm. When co-fired with nickel electrodes in a reducing atmosphere, the Curie peak was depressed and grain growth was inhibited by diffusion of nickel into the dielectrics.

4. After sintering in a reducing atmosphere, a resistivity higher than 10^{11} Ωcm, which was obtained by sintering in air, was maintained by B-site calcium substitution to more than 0.5 mol %, due to the acceptor-like behaviour of Ca''_{Ti} ions.

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