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Fabrication and characterization of high permittivity ceramics in the $Ba(Ti_{1-x-y}Sn_xZr_y)O_3$ system

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Ceramics of solid solution compositions in the system $BaTi_{1-x-y}Sn_xZr_yO_3$ have been fabricated using conventional mixed oxide processing routes. Samples with $y = 0$ or 0.01 exhibited maximum relative permittivities, ε_r^{max} of ~ 65 000 and ~ 62 000 respectively. The Curie peaks became broader and ε_r^{max} decreased with increasing zirconium substitutions. The Curie temperature decreased linearly from 35 °C for $y = 0$ to − 40 °C for $y = 0.11$: for the latter, ε_r^{max} was equal to ~ 20 000. The results are interpreted on the basis of microstructural features and on the degree of compositional inhomogeneity in the system.

1. Introduction

It has been known for many years that the electrical properties of $BaTiO_3$ can be modified by a wide range of lattice substitutions. We have been involved in a research programme in which the effects of tin and zirconium substitutions for titanium have been under investigation. Zirconium substitution has been widely studied in the past (see for example, [1–3]), although there are fewer reports regarding the effects of tin [3–5]. In many ways the substitution of tin or zirconium for titanium produces similar results: both lower the cubic to tetragonal transition temperature [6] and raise the temperature of the tetragonal to orthorhombic and orthorhombic to tetrahedral transitions [6]. For certain levels of substituents, the phase transitions, and the corresponding peak maxima in relative permittivity–temperature plots, merge to give a single Curie peak. For the $Ba(Ti_{1-y}Zr_y)O_3$ system this maximum permittivity peak occurs for a composition $y \sim 0.1$ [1]. The diffuse nature of the resulting transition is consistent with the existence of polarized micro-regions for which there is a range of different Curie temperatures. These micro-regions are assumed to be due to local variations in chemical composition [7, 8].

Grain size also contributes to the peak shape and to the maximum value of relative permittivity, ε_r. This is largely a consequence of the influence of grain size on ferroelectric domain formation and domain wall mobility. The domains form on cooling from the cubic paraelectric to the tetragonal ferroelectric state to compensate for the internal stresses accompanying the phase transition. As grain size decreases, for example below ~ 1 μm in $BaTiO_3$, domain formation becomes notably restricted [9, 10] and thus internal stress increases and grain mobility is suppressed. The Curie peak thus becomes broader and lower as grain size decreases.

The present project was motivated by a desire to obtain high permittivities and diffuse Curie peaks in non-lead-containing ceramics. We have selected the $BaTiO_3$–$BaSnO_3$–$BaZrO_3$ system for consideration. In the present paper we report surprisingly high peak permittivity values and examine how a variation in the ratio of the quadrivalent ions affects Curie temperature and peak shape.

2. Experimental procedure

Ceramics of composition $Ba(Ti_{1-x-y}Sn_xZr_y)O_3$ with $x = 0.13$ and $y = 0$, 0.01, 0.06 or 0.11, were fabricated by conventional ball-milling, pressing and sintering techniques.

Powders were prepared by solid state reaction of $BaCO_3$ (purity > 99.9%), TiO_2 (purity > 99.9%), ZrO_2 (Tosoh) and SnO_2 (Aldrich). The physical properties of the powders of the two major components are reported elsewhere [11]. After ball milling in isopropanol with zirconia grinding media for 20 h, the suspensions were dried under a heat lamp and then broken up by passing through a 0.1 mm mesh size nylon sieve. The powders were calcined for 2 h at either 1100, 1200 or 1300 °C, and then sieved once more.

In order to improve compaction behaviour, 0.6 wt % of a binder mixture consisting of equimolar proportions of polyethylene glycol and polyvinyl alcohol was blended with the calcined powders. Powders were compacted at 100 MPa in a 1.25 cm diameter steel die and were fired in a muffle furnace at various temperatures for 4 h ranging from 1350–1500 °C.

Phase analysis of calcined powders and sintered pellets was routinely performed using a Philips 1700 diffractometer (CuK_α radiation; scan speed = 0.3° 2θ min^{-1}).

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The density of sintered pellets was determined using the Archimedes principle. For the $y = 0$ and $y = 0.01$ compositions the lattice parameters were calculated from the (4 0 0) and (0 0 4) d-spacings.

Microstructural features were examined using a Camscan scanning electron microscope (SEM). Surface microstructures were similar to those of polished sections and so for convenience the former were examined routinely.

Specimens were prepared for dielectric property measurements by first polishing pellet faces to a 1 μm finish; gold electrodes were then sputtered on to the cleaned pellet faces. A coating of air-drying silver paint was applied to the gold electrodes in order to improve their mechanical integrity. Relative permittivities were measured as a function of temperature over the range − 60–100 °C, using a Hewlett Packard HP4194 impedance analyser. Data are presented for a frequency of 1 kHz; temperature was controlled using a Delta sample chamber.

3. Results and discussion

Preliminary studies in the $Ba(Ti_{1-x}Sn_x)O_3$ system with $0 < x < 0.15$ showed that very high permittivities occurred for the composition $x \approx 0.13$. This was therefore used as the base composition to examine the effect of partial substitution of zirconium for titanium.

It was found that predominantly single-phase perovskite-type powders were obtained by calcining the ball-milled $Ba(Ti_{0.86}Sn_{0.13}Zr_{0.01})O_3$ powders at ≥ 1200 °C for 2 h, Fig. 1. The 1100 °C powder exhibited peaks due to a $BaSnO_3$ intermediate phase. A faint extra peak at $2\theta \sim 28.3°$ in all samples may indicate residual ZrO_2 or be due to some intermediate phase (e.g. $Ba_4Ti_{13}O_{30}$ [12]). However, there were insufficient data to identify unambiguously the origin of this X-ray diffraction (XRD) peak. The powder calcined at 1200 °C showed a greater degree of broadening of XRD peaks than the 1300 °C calcined powders. From these results, 1300 °C was selected as the calcination temperature for all subsequent experiments.

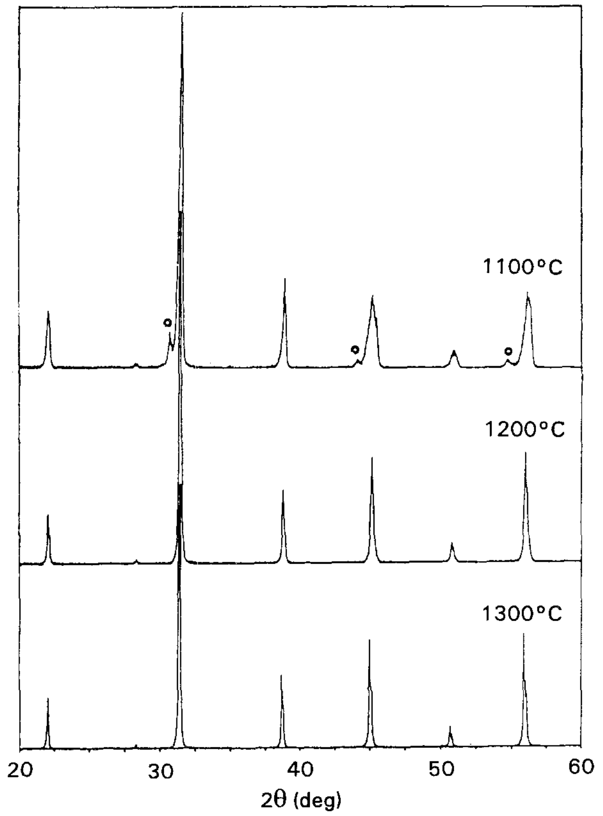

Figure 1 X-ray diffraction patterns of $Ba(Ti_{0.87}Sn_{0.13}Zr_{0.01})O_3$ powders calcined for 2 h at different temperatures. (○) = $BaSnO_3$.

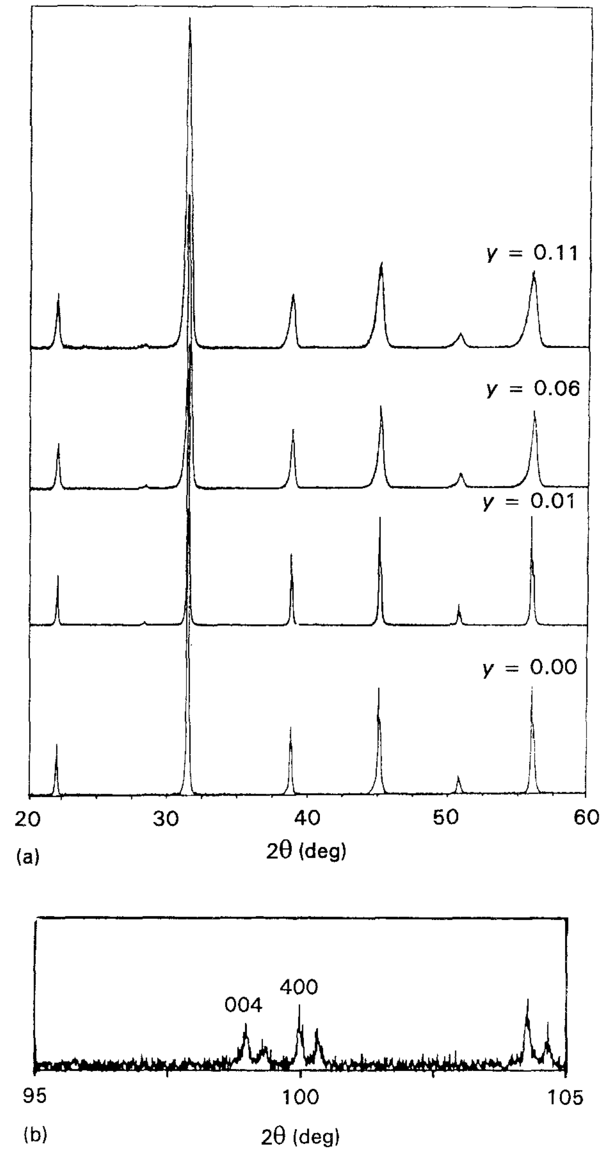

Figure 2 (a) X-ray diffraction patterns of $Ba(Ti_{0.87-y}Sn_{0.13}Zr_y)O_3$ powders calcined at 1300 °C for 2 h. (b) High-angle X-ray diffraction pattern showing tetragonal splitting for $y = 0$.

The XRD patterns of $Ba(Ti_{0.87-y}Sn_{0.13}Zr_y)O_3$ powders at different y compositions calcined at 1300 °C for 2 h are shown in Fig. 2a. The XRD line broadenings for $y = 0.01$ and especially $y = 0.06$ and 0.11, probably indicate that a series of different solid solution phase compositions were present, i.e. the samples were chemically inhomogeneous. Subsequent high-angle XRD data indicated a splitting of what would have been the cubic 4 0 0 peak, Fig. 2b. The patterns shown in Figs 1 and 2a are thus pseudocubic and assuming a tetragonal unit cell, the c/a ratio of the $y = 0$ and 0.01 were calculated from high-angle data to be 1.007 and 1.008, respectively. The XRD peak

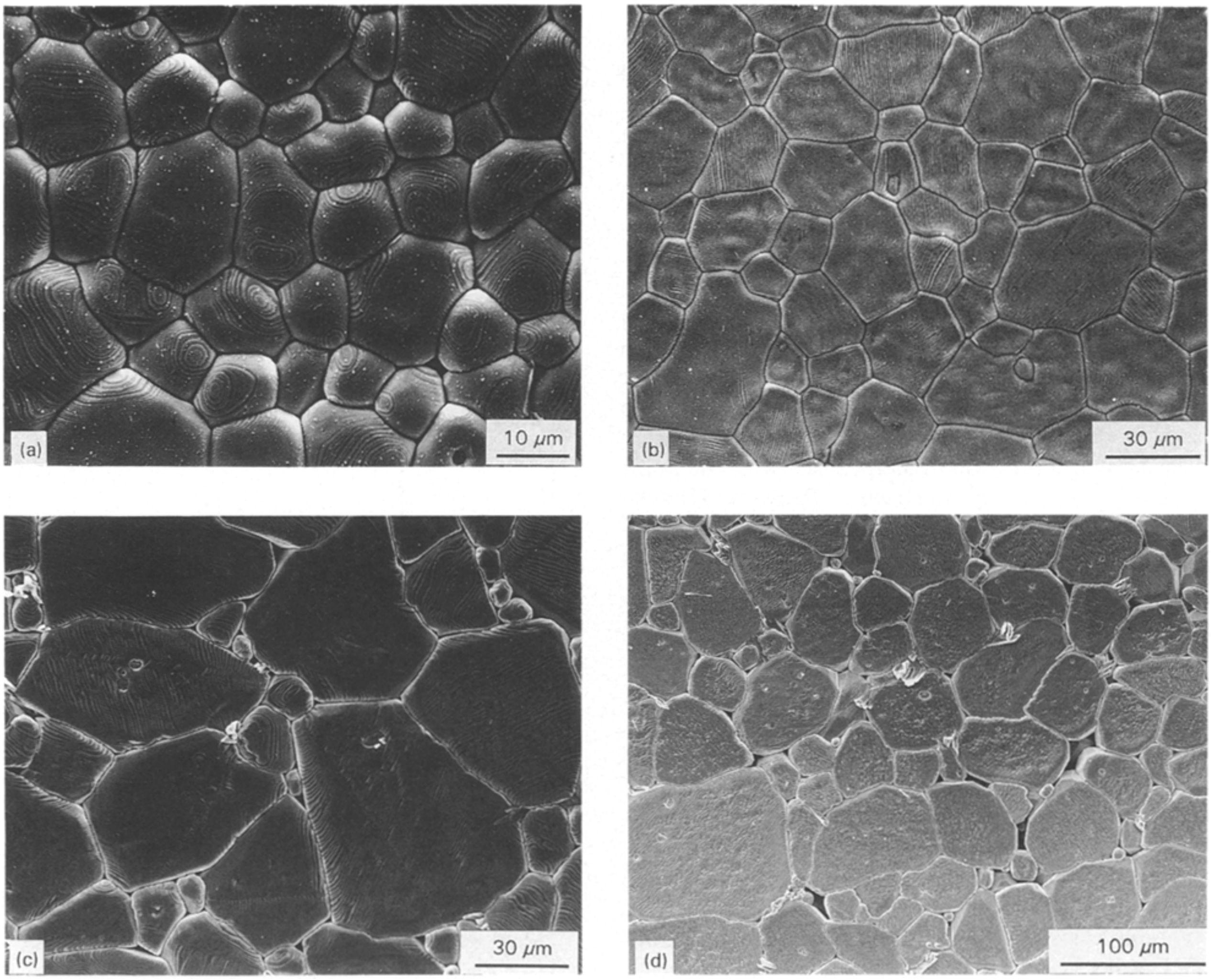

Figure 3 Scanning electron micrographs of "as-sintered" surfaces for $Bn(Ti_{0.87-y}Sn_{0.13}Zr_y)O_3$ ceramics fired at 1400 °C for 4 h: (a) $y = 0$; (b) $y = 0.01$; (c) $y = 0.06$; (d) $y = 0.11$.

broadening in higher y compositions made it difficult to determine their crystal system; however, the Curie temperatures of the $y = 0.06$ and 0.11 compositions (see later) imply that the $y = 0.06$ and 0.11 samples are cubic (paraelectric) at room temperature.

Sintering experiments using various firing temperatures and times indicated that maximum pellet densities were achieved by firing the powder compacts at 1400 °C for 4 h. For the $y = 0$ and $y = 0.01$ compositions, sintered densities were 5.94 and 6.00 g cm^{-3}, corresponding to ~96% and 97% theoretical density. These density values are based on calculated unit cell lattice parameters of $a = 0.4016$ nm and $c = 0.4044$ nm for $y = 0$, producing a theoretical density of 6.17 g cm^{-3}; for $y = 0.01$, $a = 0.4020$ nm and $c = 0.4050$ nm corresponding to a theoretical density of 6.16 g cm^{-3}. For the higher $y = 0.06$ and 0.11 compositions, the measured densities were 6.15 and 6.29 g cm^{-3}. It was not possible to calculate a value of theoretical density from XRD data for these compositions due to the degree of line broadening present. Examination of sintered microstructures suggested that the microstructures of the two highest y compositions were, in fact, less dense than the $y = 0$ and 0.01 samples, Fig. 3.

Grain size increased with increasing zirconium substitution, taking on values of ≤ 15 μm for $y = 0$,

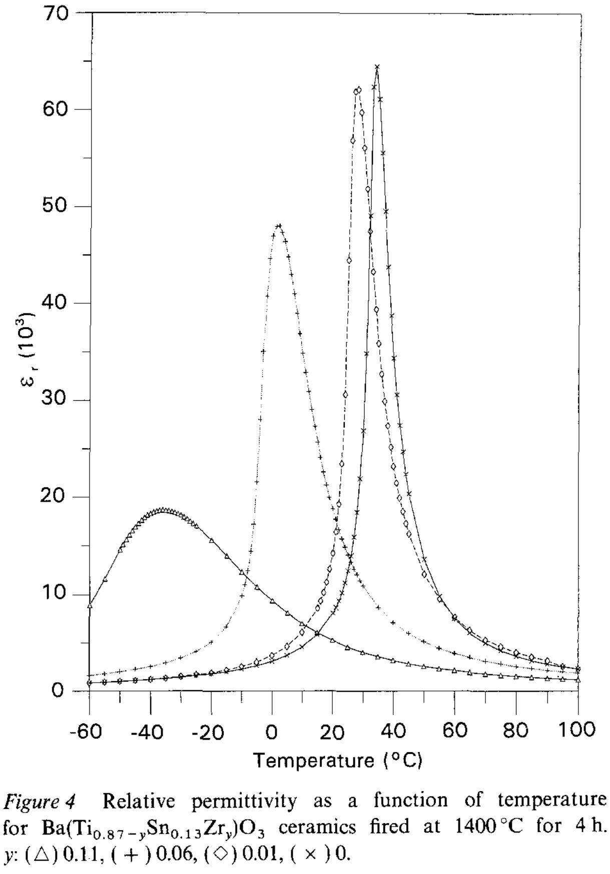

Figure 4 Relative permittivity as a function of temperature for $Ba(Ti_{0.87-y}Sn_{0.13}Zr_y)O_3$ ceramics fired at 1400 °C for 4 h. y: (△) 0.11, (+) 0.06, (◇) 0.01, (×) 0.

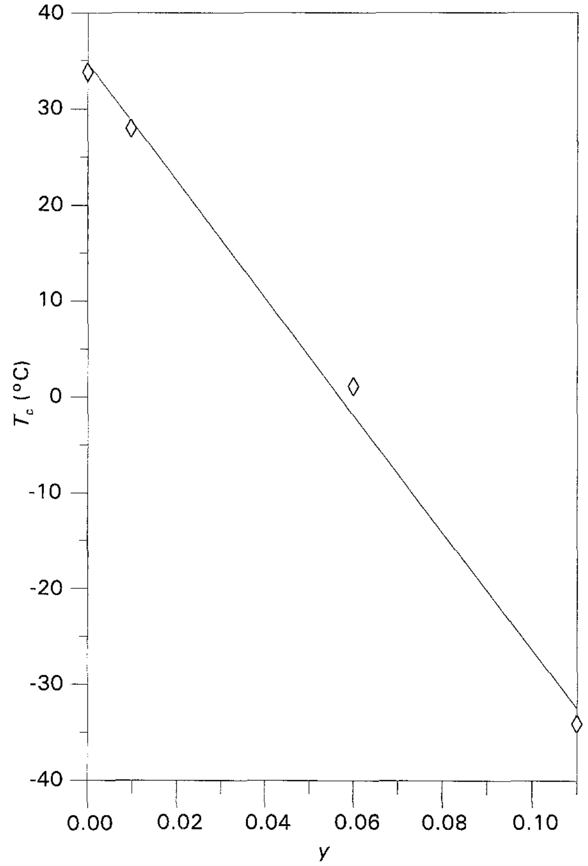

Figure 5 Curie temperatures plotted as a function of composition for $Ba(Ti_{0.87-y}Sn_{0.13}Zr_y)O_3$ ceramics fired at 1400 °C for 4 h.

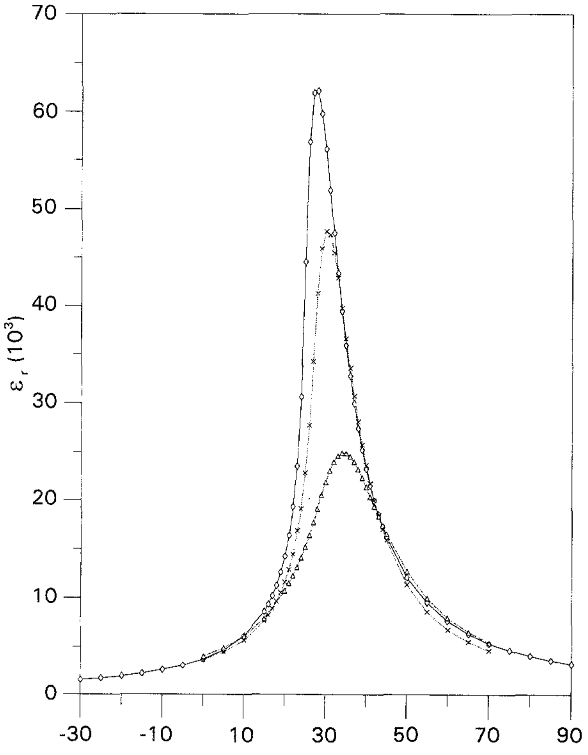

Figure 6 The temperature dependences of relative permittivity for $Ba(Ti_{0.86}Sn_{0.13}Zr_{0.01})O_3$ ceramics prepared from starting powders calcined at different temperatures and fired at 1400 °C for 4 h. (◇) 1300 °C, (×) 1200 °C, (△) 1100 °C.

≤ 50 μm for $y = 0.01$, ≤ 70 μm for $y = 0.06$ and ≤ 100 μm for $y = 0.11$ samples. There was some evidence that grains became more rounded in shape for the highest zirconium composition, Fig. 3d, which may imply some liquid formation during sintering.

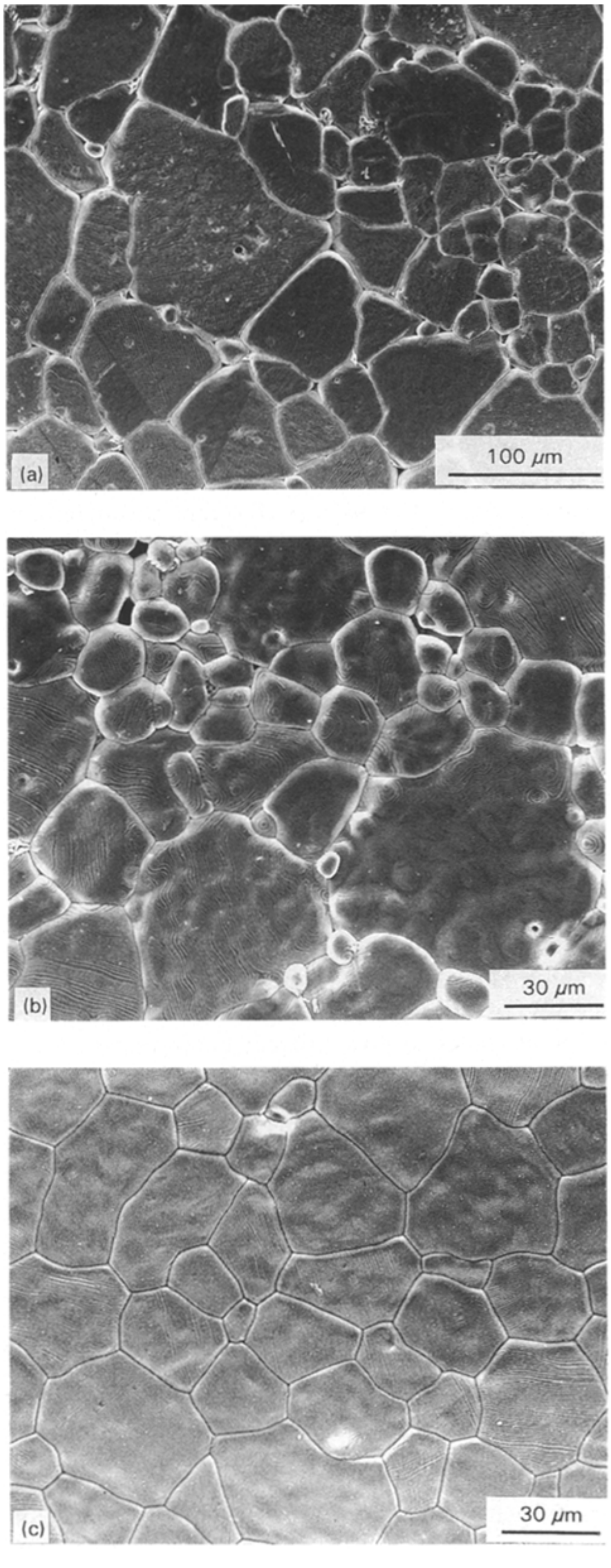

Figure 7 Scanning electron micrographs of "as-sintered" surfaces for $Ba(Ti_{0.86}Sn_{0.13}Zr_{0.01})O_3$ ceramics fabricated from powders calcined at different temperatures: (a) 1100 °C; (b) 1200 °C; (c) 1300 °C for 2 h. All pellets were fired at 1400 °C for 4 h.

Permittivity data for powders calcined at 1300 °C with different y values are presented in Fig. 4. The $y = 0$ composition, $Ba(Ti_{0.87}Sn_{0.13})O_3$ gave rise to the highest and narrowest Curie peak, with a maximum ε_r value of 65 000 and a Curie temperature, T_c, of 35 °C. The peak for the $y = 0.01$ sample was slightly broader with a maximum ε_r of 62000 at ~ 28 °C. Further zirconium substitution decreased T_c and continued to broaden and lower the permittivity peaks, Fig. 4. For $y = 0.11$, ε_r max was ~ 20000 at ~ − 35 °C and the half-peak width extended over a range of ~ 60 °C.

The decrease in T_c with changing zirconium composition was linear, as shown in Fig. 5 with a slope of − 6 K per 0.01 increase in y. This is intermediate, as might be expected, between the − 5 K slope found for $Ba(Ti,Zr)O_3$ and the − 8 K slope found for $Ba(Ti,Sn)O_3$ [6].

The effect of the calcination temperature of the starting powders on the form of the Curie peak was examined for the $y = 0.01$ composition, i.e. $Ba(Ti_{0.86}Sn_{0.13}Zr_{0.01})O_3$. With increasing calcination temperature, the Curie peak of ceramics sintered for 4 h at 1400 °C grew sharper and the peak maximum increased in value and moved to lower temperature, Fig. 6. Interestingly, all three powder calcination temperatures yielded pellets of similar density: 6.0 ± 0.02 g cm^{-3}; grain size decreased from ≤ 100 μm for the 1100 °C sample, to ≤ 50 μm for the sample prepared from powder calcined at 1300 °C, Fig. 7. Thus the results of these calcination experiments imply chemical homogeneity effects have a dominant influence on the permittivity response of $Ba(Ti_{1-z-y}Sn_xZr_y)O_3$ ceramics. It is, however, surprising that structures formed at the calcination temperatures seem to be retained after sintering. These results of chemical homogeneity effects on Curie points and peak shapes are consistent with Neirman's results [13], in which starting powders prepared by different routes to give different homogeneities were used.

The permittivity results are consistent with qualitative information on chemical homogeneity deduced from X-ray diffraction data. The relatively large average particle sizes of the starting powders (> 1 μm) and large grain sizes of the sintered ceramics exclude particle-size XRD broadening effects. It is thus reasonable to conclude that with increasing zirconium substitution, solid solutions are non-uniform in their spatial chemical composition on a scale that leads to severe XRD peak broadening. There is insufficient evidence from this work to establish the extent to which chemical inhomogeneity may be due to gross spatial irregularities or to variations within individual grains such as which might arise from slow diffusion of zirconium.

The diffuse permittivity peaks of the $y = 0.06$ and 0.11 samples may thus reasonably be explained by the overlap of individual Curie peaks that arise from regions of varying chemical compositions.

The observed correlation between chemical inhomogeneity and permittivity peak broadening effects seems a logical result because the formation of ferroelectric domains requires cooperative dipole alignment, a process that is likely to be impeded by any discontinuities in the crystal lattice.

Grain size may also contribute to the high permittivities in this system. Even in the $y = 0$ sample, grain size was relatively large at ~ 15 μm and thus domain formation and domain mobility are unlikely to be constrained by grain size or grain-boundary effects.

4. Conclusions

Very high maximum relative permittivities, ε_r^{max}, of ~ 65000 and ~ 62000 were obtained for $Ba(Ti_{0.87}Sn_{0.13})O_3$ and $Ba(Ti_{0.86}Sn_{0.13}Zr_{0.01})O_3$ ceramics fabricated by a conventional mixed oxide route. An increase in zirconium concentration decreased the Curie temperature and broadened the permittivity peaks. Variations in ε_r^{max} and peak shape were attributed to chemical homogeneity effects.

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References

1. D. HENNINGS, A. SCHNELL and G. SIMON, *J. Am. Ceram. Soc.* **65** (1982) 539.
2. K. TOYODA, F. TAKANA, T. KATA and Y. SAKABE, *Ferroelectrics* **93** (1989) 335.
3. J. N. LIN and T. B. WU, *J. Appl. Phys.* **68** (1990) 985.
4. G. A. SMOLENSKY, *J. Phys. Soc. Jpn* **S28** (1970) 26.
5. K. TOYODA, T. KATO and Y. SAKABE, *Ferrolectrics* **108** (1990) 227.
6. B. JAFFE, W. COOK and H. JAFFE, "Piezoelectric ceramics" (Academic Press, London, 1971).
7. B. N. ROLOV, *Sov. Phys. Solid State* **6** (1965) 1676.
8. N. SETTER and L. E. CROSS, *J. Appl. Phys.* **51** (1980) 4356.
9. W. R. BUESSEM, L. E. CROSS and A. K. GOSWAM, *J. Am. Ceram. Soc.* **49** (1966) 33.
10. G. ARLT, D. HENNINGS and G. de WITH, *ibid.* **67** (1984) 311.
11. N. J. ALI and S. J. MILNE, to be published.
12. H. M. O'BRYAN Jr and J. THOMOSSON Jr, *J. Am. Ceram. Soc.* **57** (1974) 522.
13. S. M. NEIRMAN, *J. Mater. Sci.* **23** (1988) 3973.

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