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The Curie point temperature of $Ba(Ti_{1-x}Zr_x)O_3$ solid solutions

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The Curie point temperature of solid solutions made by firing mixtures of $BaTiO_3$ and $BaZrO_3$ powders was found to depend markedly on sintering conditions. However, when the ceramic was made from a homogeneous powder, wherein each particle of powder had the same chemical composition, the Curie point temperature was only slightly dependent on the firing schedule. Using chemically homogeneous powders, $Ba(Ti_{1-x}Zr_x)O_3$ with $x = 0.05$, 0.10 and 0.20, the Curie point temperature shift was found to be a non-linear function of x.

1. Introduction

$BaTiO_3$, the basic ingredient for many ceramic capacitor dielectrics, has a Curie point temperature of ~ 125° C. At this temperature the crystal lattice undergoes a tetragonal to cubic phase change, accompanied by a sharp peak in the dielectric constant. Most practical ceramic formulations require a Curie point shifter, a material that forms a solid solution with $BaTiO_3$ and alters the lattice so that the phase change and therefore the permittivity maximum occurs at a more appropriate temperature. This is commonly done by substitution of isovalent cations for Ti^{4+} and/or Ba^{2+}; that is to say, by the addition of such materials as $BaZrO_3$, $SrZrO_3$, $SrTiO_3$ or $CaZrO_3$.

The initial intent of the author was to form a $Ba(Ti_{1-x}Zr_x)O_3$ material with maximum permittivity at ~ 20° C. A literature review disclosed disagreement concerning the magnitude of the effect of Zr^{4+} substitution in $BaTiO_3$ on the Curie point temperature [1–5], so the required composition was uncertain. Because of this, an initial series of Curie point temperature shift experiments was done with powders prepared in-house. The results of this investigation supported the contention that the Curie point temperature of $(1-x)BaTiO_3 + (x)BaZrO_3$ $(0 \leqslant x \leqslant 0.25)$ solid solutions was influenced by sintering conditions. It was not clear, however, whether this variation with firing parameters was due to grain size or the degree of chemical homogeneity of the sintered piece. Indeed, it is difficult to separate the two when starting with a mixture of $BaTiO_3$ and $BaZrO_3$ powders. So a second investigation of the $Ba(Ti_{1-x}Zr_x)O_3$ system was done with a series ($x = 0$, 0.05, 0.10, 0.20) of chemically uniform powders; that is to say, powders with each particle having the same composition. Within solubility limits, the chemical homogeneity of each fired piece would then be assured, and the phenomena of grain growth and chemical homogenization distinguished.

2. Experimental details

$BaTiO_3$ (particle diameter ~ 0.15 μm; Curie point temperature ~ 126° C) and $BaZrO_3$ (diameter ~ 0.1 μm) powders prepared in-house by an emulsion-char method [6] were used for the mixture samples with composition $(1-x)BaTiO_3 + (x)BaZrO_3$ ($x = 0$, 0.05, 0.10, 0.15, 0.20 and 0.25). $Ba(Ti_{1-x}Zr_x)O_3$ powders ($x = 0$, 0.05, 0.10 and 0.20; particle diameter ~ 0.1 μm; Curie point temperature ~ 127° C) prepared by a hydrothermal process [7] and supplied by Sakai Chemical Industry Co., Ltd. were used for the homogeneous composition specimens. X-ray diffraction confirmed that the Sakai powders were single phased, and not mixtures of $BaTiO_3$ and $BaZrO_3$ (Fig. 1). Furthermore, the claimed compositions of these powders were checked by analysis of several diffraction peak positions. (The 321 reflection is shown in Fig. 2.) The calculated lattice constants (in nm) are shown in Table I. As has been observed by others [8], the lattice spacings of hydrothermally prepared powder are too large until they have been heat treated. The as-received powders were all cubic. After being heated to 1100° C for 1 h, the $BaTiO_3$ became tetragonal, and the $Ba(Ti_{0.95}Zr_{0.05})O_3$ slightly so. Assuming

TABLE I Lattice constants and composition of hydrothermally prepared powders, $Ba(Ti_{1-x}Zr_x)O_3$

Composition	As-received (±0.00006)	1100° C, 1 h (±0.00006)	x
$BaTiO_3$	0.40128	$a_0 = 0.39947$	0
		$c_0 = 0.40338$	
$Ba(Ti_{0.95}Zr_{0.05})O_3$	0.40230	0.40178	0.0055
$Ba(Ti_{0.90}Zr_{0.10})O_3$	0.40331	0.40271	0.0105
$Ba(Ti_{0.80}Zr_{0.20})O_3$	0.40563	0.40464	0.021

TABLE II Common impurity content of some powders

Element	Emulsion $BaTiO_3$	Hydrothermal $BaTiO_3$	Hydrothermal $Ba(Ti_{0.90}Zr_{0.10})O_3$	Emulsion $BaZrO_3$
Sr	0.0009	0.0017	0.0030	0.0008
Ca	< 0.0001	< 0.0001	0.0001	0.0004
Si	0.0011	0.0010	0.0008	0.0038
Al	0.0006	0.0005	0.0034	0.026
Fe	0.0004	0.0007	0.0005	0.0002

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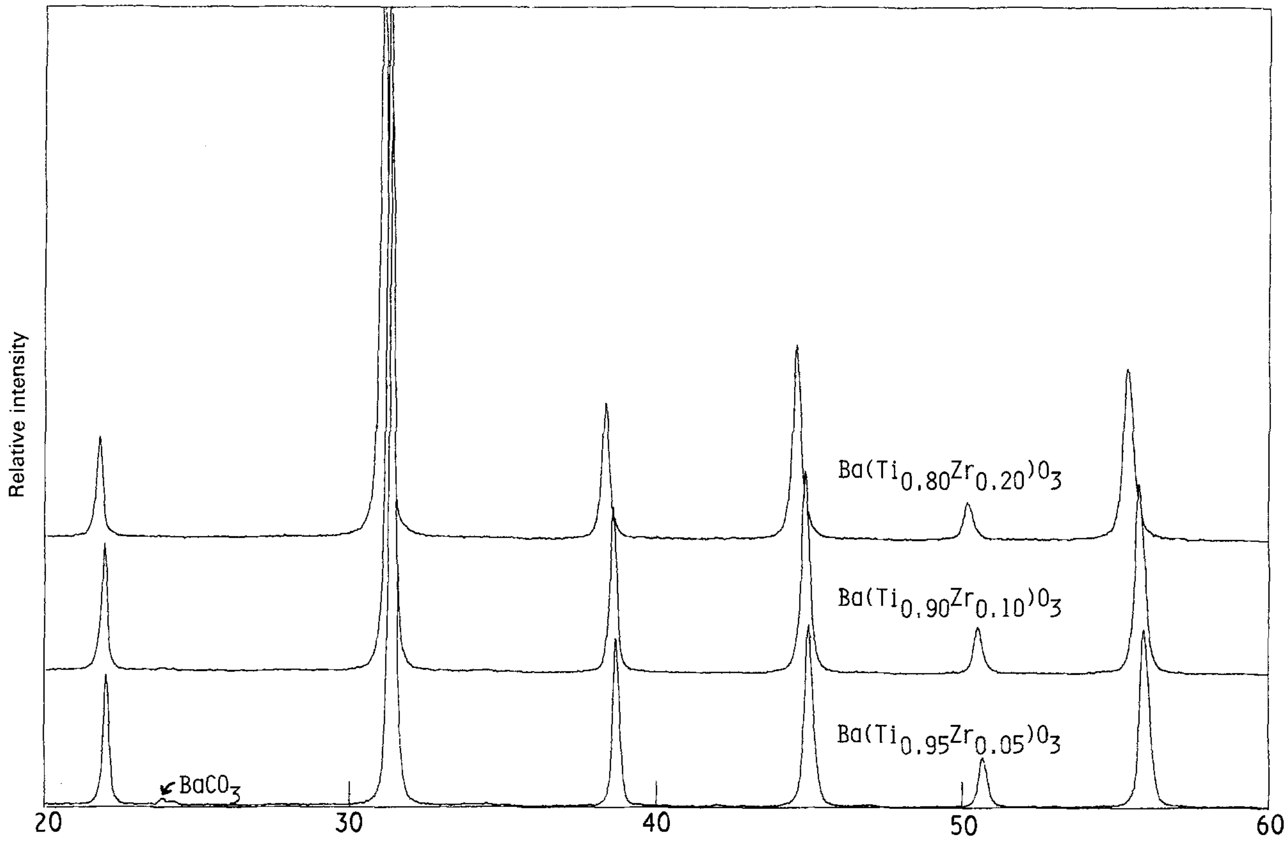

Figure 1 X-ray diffraction patterns for $Ba(Ti_{1-x}Zr_x)O_3$ ($x = 0.05$, 0.10 and 0.20) powders.

a variation in cell dimensions in accord with Vegard's law, and using an equivalent cubic a_0 corresponding to the same unit cell volume as the tetragonal $BaTiO_3$, the x values in the last column were calculated.

Inductively coupled plasma analysis for common impurities was done for some of the powders, and the results are shown in Table II. The entries are in terms of wt.%. The high aluminium content of the emulsion $BaZrO_3$ is unfortunate, although it not believed to have affected the results of this investigation.

Powders were dispersed by wet milling in high density polyethylene jars with ZrO_2 balls. Test squares approximately 0.7 × 0.7 × 0.5 cm were made by the doctor-blade technique. These were slowly heated (~35 h) in air to 700° C to remove organic binders, and then sintered, also in air, at various temperatures (in the range 1250–1400° C) for at least 2 h in platinum-lined alumina boats.

Electrical contact was made to the mixed powder composition ceramics by firing on (at ~800° C) a fritless 70 wt.% Ag–30 wt.% Pd paste applied to the major surfaces. For the homogeneous powder samples, platinum electrodes were applied by RF sputtering.

Capacitance (from which the dielectric constant could be calculated) was measured in the temperature range 130° C to −55° C using an HP-4274A LCR meter controlled by an HP-85 computer. The measurements were made approximately every 15° C while the samples were being cooled, except in the vicinity of the Curie point temperature, where measurements were taken every 2 or 3° C.

3. Results

The results of the initial investigation, using mixtures of $BaTiO_3 + BaZrO_3$ as precursors to solid solution, are illustrated in Figs 3–5. The dependence of the Curie point temperature on sintering parameters for two of these compositions ($x = 0.10$ and $x = 0.20$) is shown in Figs 3 and 4, respectively. For a given composition, the Curie point temperature is lowered with increased sintering temperature. This is illustrated by Fig. 5, which sums up the data by showing the change in Curie point temperature from a 16 h, 1250° C to a 2 h, 1400° C firing for each mixture composition.

Figs 6 and 7 demonstrate the effect of sintering temperature on the Curie point temperature of $Ba(Ti_{1-x}Zr_x)O_3$ ($x = 0.10$ and 0.20, respectively) solid solutions made from homogeneous powder. The data for all of the homogeneous powder compositions are shown in Fig. 5.

Although each curve in Figs 3, 4, 6 and 7 represents data for only one sample, it was observed that for each material and firing schedule there was very little piece-to-piece variation in Curie point temperature.

4. Discussion

This investigation began as a practical matter, to determine the composition of a $BaTiO_3$–$BaZrO_3$ solid solution with maximum permittivity at 20° C. It became apparent, however, that the composition could not be generally stated, but was a function of processing variables. This led to the question — "Was the Curie point temperature variation for a given composition due to variation in grain size or chemical homogeneity?" The use of chemically homogeneous powder allowed the variables to be separated and the question to be resolved.

Consider the $Ba(Ti_{0.80}Zr_{0.20})O_3$ solid solution. With

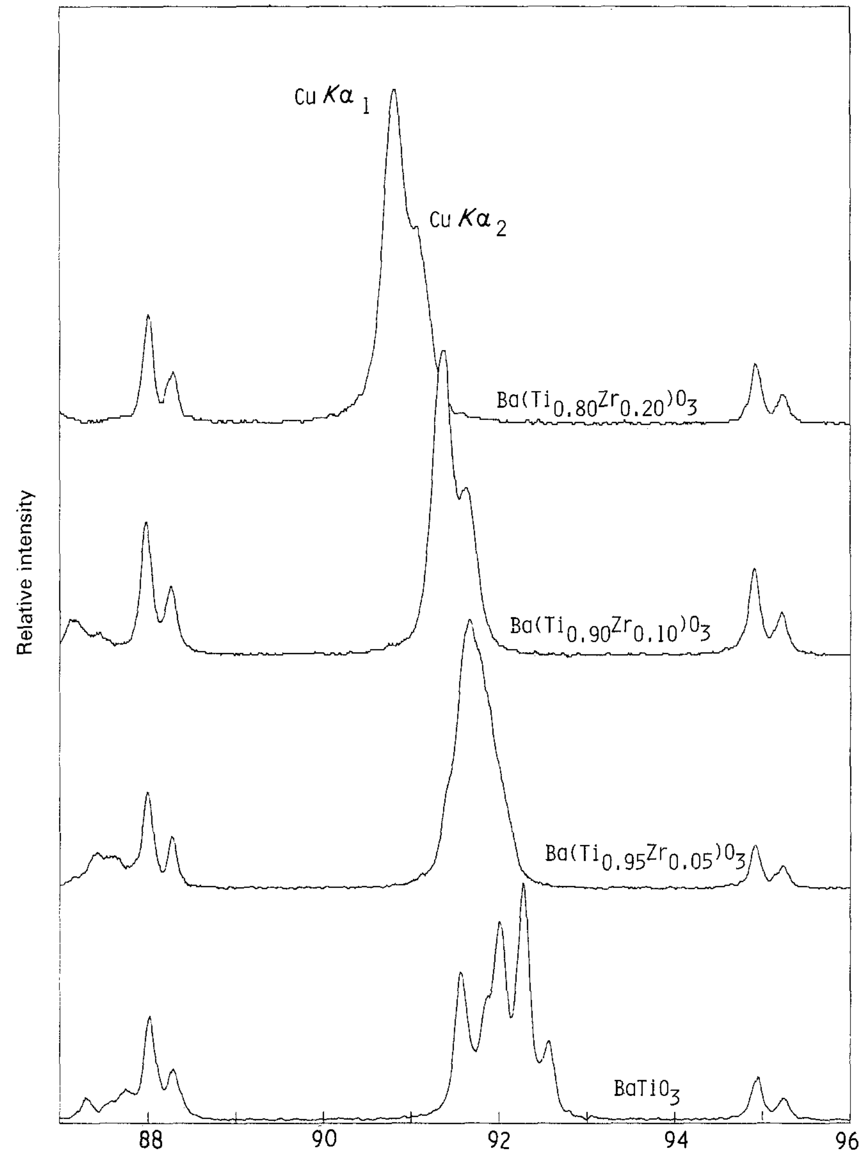

Figure 2 321 reflection of $Ba(Ti_{1-x}Zr_x)O_3$ ($x = 0$, 0.05, 0.10 and 0.20) powders after being heated to 1100°C for 1 h (silicon standard at $2\theta \sim 88°$ and $\sim 95°$).

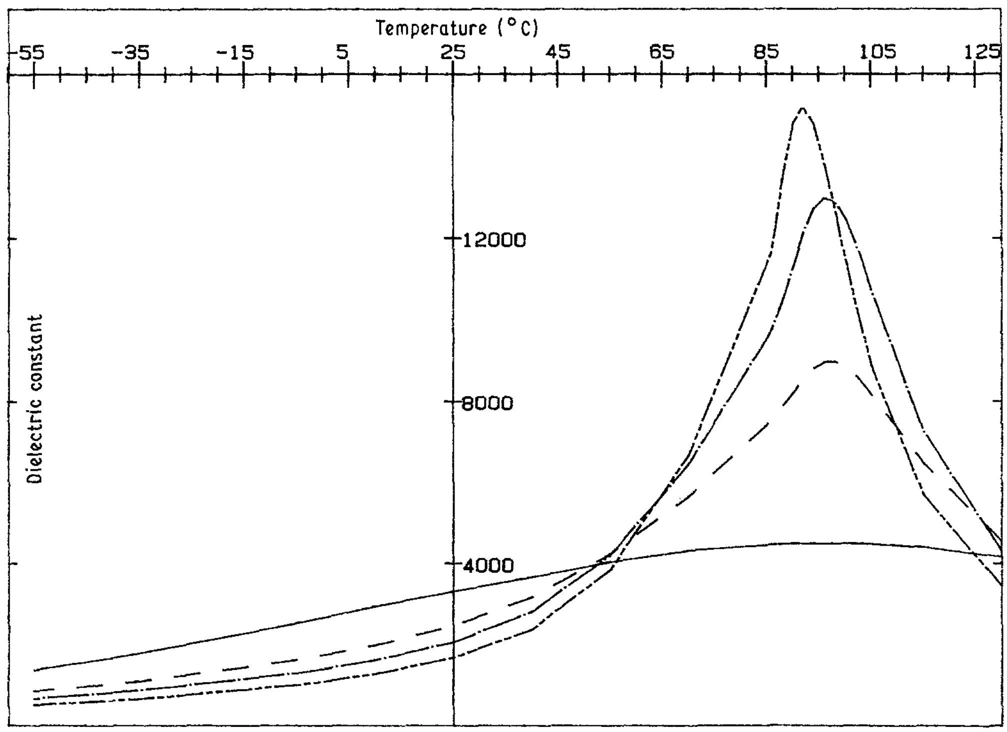

Figure 3 Dielectric constant – temperature curve dependence on sintering conditions for mixed powder composition 0.90 $BaTiO_3$–0.10 $BaZrO_3$. (—— 1250°C 2 h, – – 1250°C 16 h, –·–·– 1300°C 2 h --------- 1400°C 2 h).

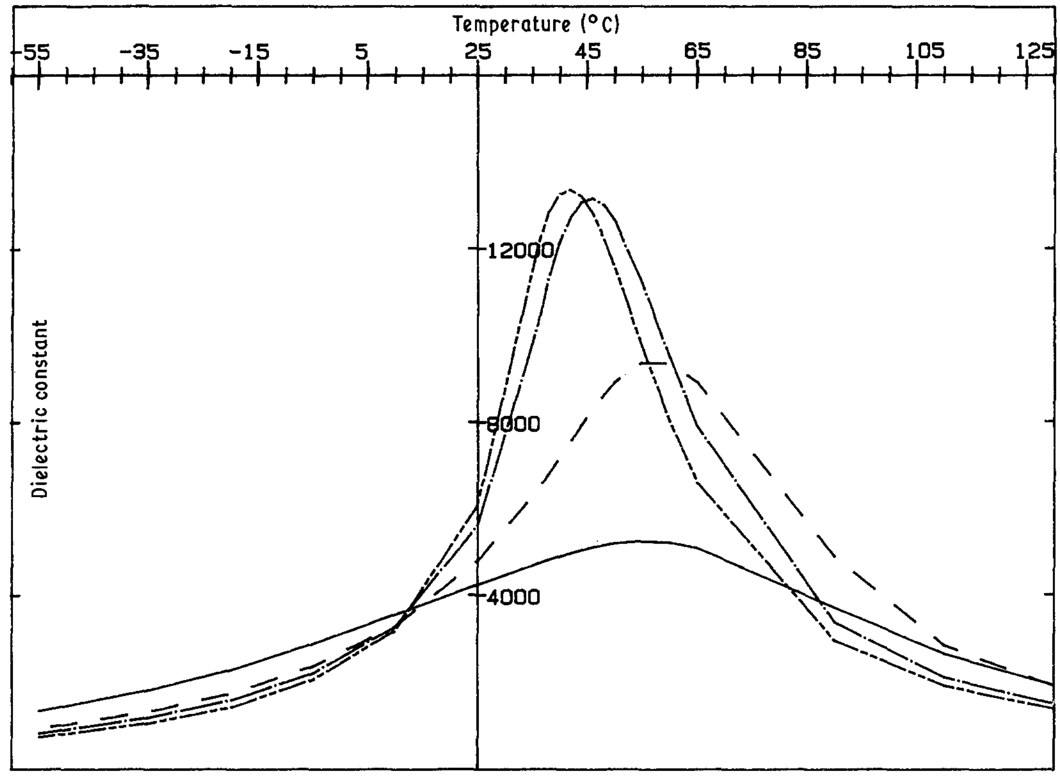

Figure 4 As Fig. 3 for 0.80 $BaTiO_3$–0.20 $BaZrO_3$.

homogeneous powders, the Curie point temperature changes from ~ 34° C for a 1250° C sinter to ~ 30° C for a 1400° C firing (Fig. 7). If made from a mixture of $BaTiO_3$ and $BaZrO_3$ powders, the Curie point temperature varies from ~ 57° C to ~ 42° C (Fig. 4). This comparison, along with observations of grain size (Fig. 8), indicates that the Curie point temperature variation with firing temperature of the mixed powder samples is primarily caused by differences in chemical homogeneity. Further evidence is provided by noting that most of the change in Curie point temperature for the mixed powder samples is between the 1250° C and 1300° C curves and observing the large line-broadening (indicative of chemical inhomogeneity) difference in the X-ray diffraction pattern of units fired at these temperatures. This is illustrated for the 321 reflection by Fig. 9, curves a and b. In addition, there appears to be some variation of the Curie point temperature with microstructure, as illustrated by the homogeneous powder units fired at different temperatures.

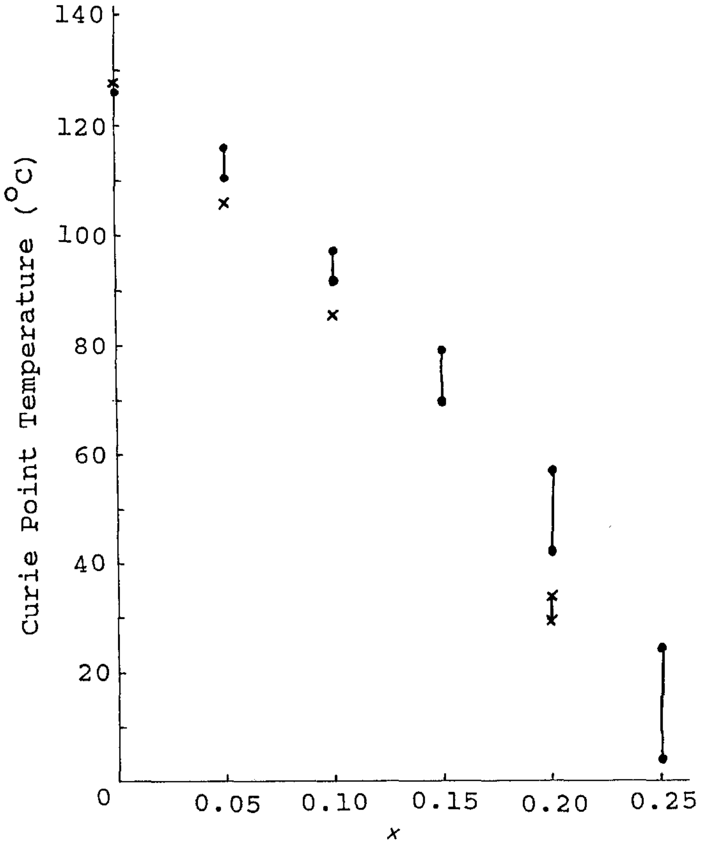

Figure 5 Curie point temperature range with firing conditions as a function of composition for mixed (●—●) and homogeneous (x—x) powder units for $Ba(Ti_{1-x}Zr_x)O_3$.

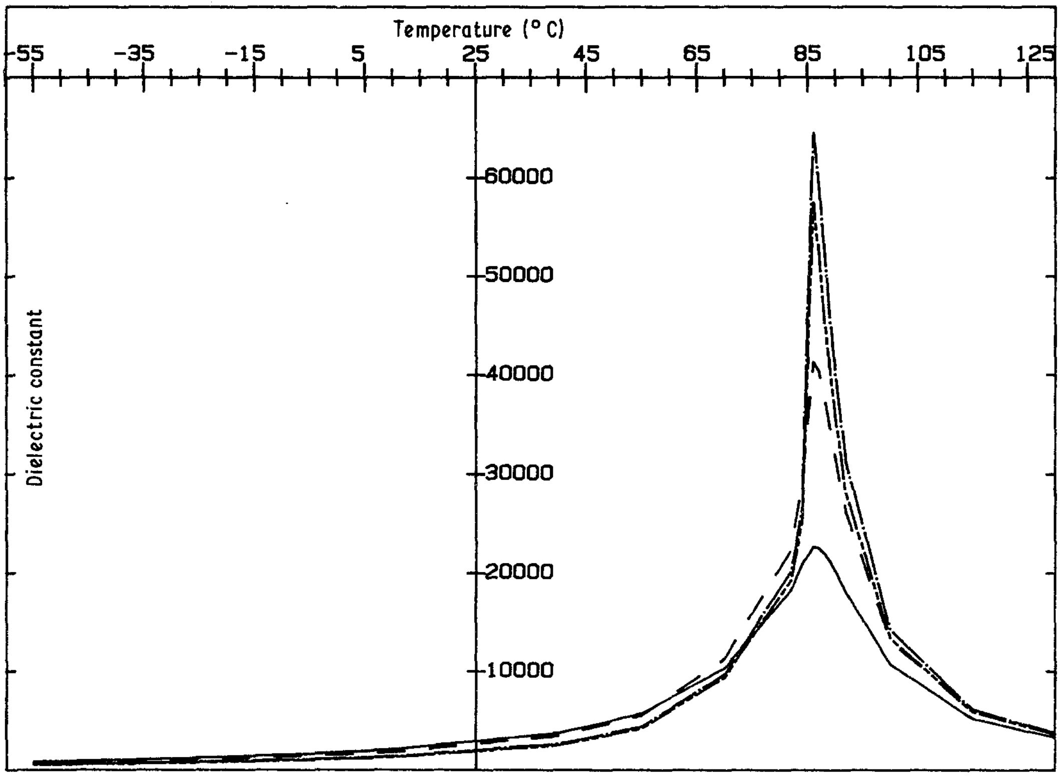

Figure 6 Dielectric constant–temperature curve dependence on sintering conditions for homogeneous powder composition $Ba(Ti_{0.90}Zr_{0.10})O_3$. Symbols as in Fig. 3.

Interestingly, the 1250° C sintered homogeneous powder unit shows a sharper peaked diffraction pattern than the 1400° C mixed powder sample (Fig. 9, curves c and d), indicating that even a 1400° C, 2 h sinter was insufficient for the mixed powder units to reach chemical equilibrium. The 12° C Curie point temperature difference between homogeneous and mixed powder samples can be attributed to both samples not actually having the same overall composition, as well as to homogeneity and microstructural differences.

The data of this investigation clearly indicate that equilibrium, or homogeneous solid solutions of $Ba(Ti_{1-x}Zr_x)O_3$ have lower Curie point temperatures than non-equilibrium, inhomogeneous solid solutions of the same composition. However, it is not immediately apparent why this should be so. A simple model

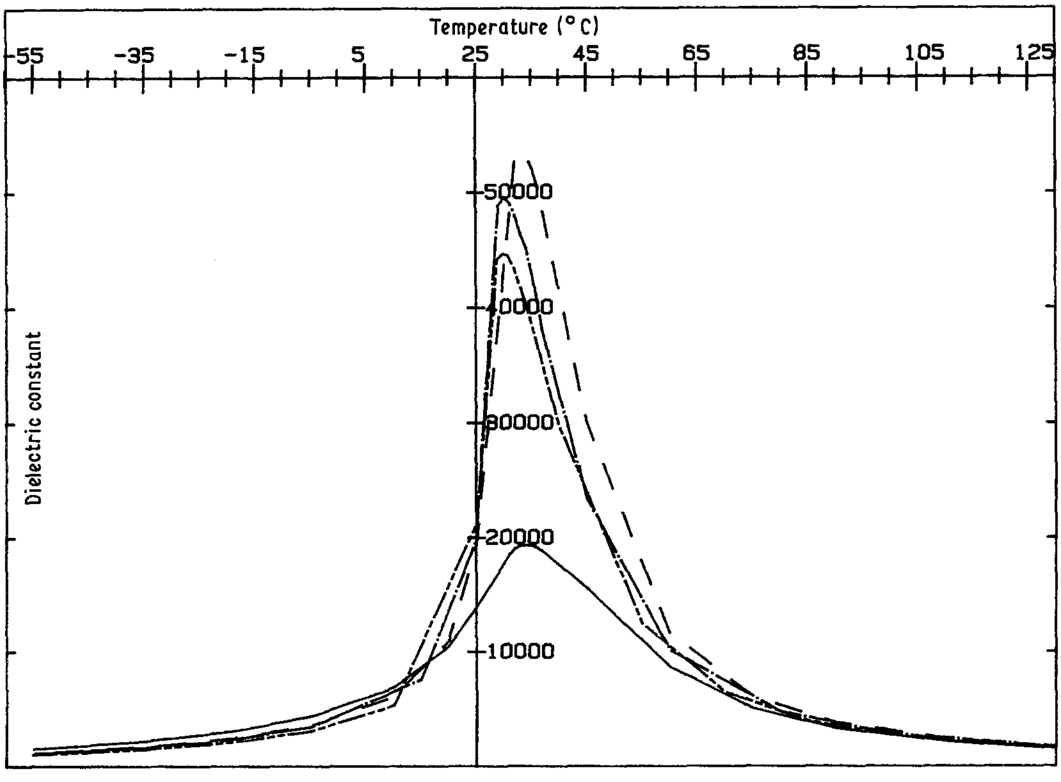

Figure 7 As Fig. 6 for $Ba(Ti_{0.80}Zr_{0.20})O_3$.

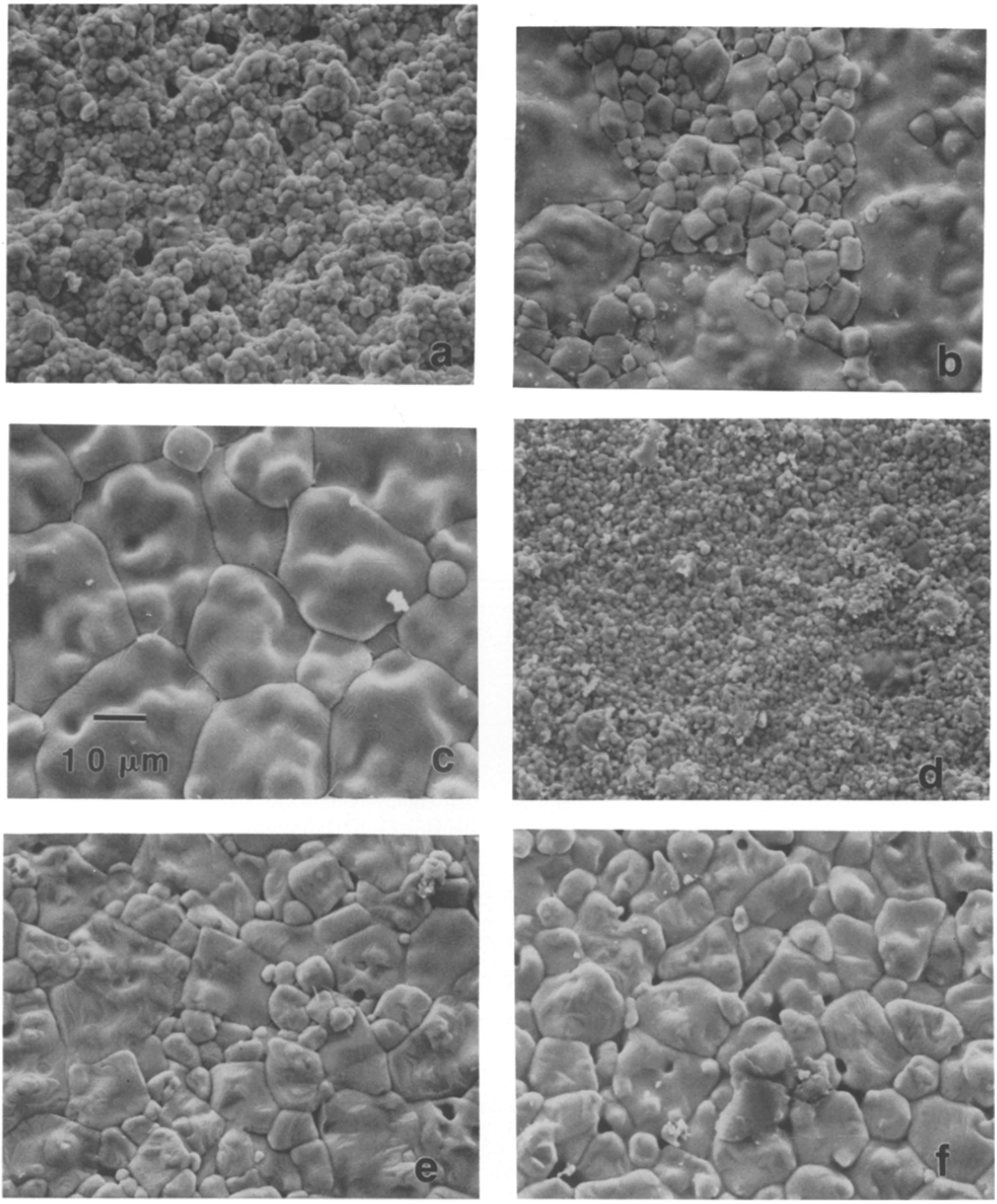

Figure 8 SEM micrographs of the surface of $Ba(Ti_{0.80}Zr_{0.20})O_3$ units after (a) 1250° C, (b) 1300° C, (c) 1400° C; and 0.80 $BaTiO_3$–0.20 $BaZrO_3$ units after (d) 1250° C, (e) 1300° C, (f) 1400° C. All firings were for 2 h.

of the inhomogeneous ceramic is that it consists of a symmetric compositional distribution of volume elements, each having a Curie point temperature characteristic of its composition. The width of the distribution is an indication of the homogeneity of the sample. The dielectric properties of the piece are a summation over the individual volume elements. It is evident that the compositional homogeneity would determine the sharpness of the permittivity maximum at the Curie point temperature of the sample. However since any volume element on one side of the compositional distribution curve is balanced by an element on the other side, it would seem at first glance that the Curie point temperature of the overall ceramic would not be affected by the distribution width. However, careful analysis of the situation reveals that in drawing this conclusion one has tacitly assumed an averaging of symmetric volume element permittivity curves. The permittivity of each ferroelectric volume elements is more accurately given by

$$\varepsilon = k \qquad \text{for } T < T_c$$

$$\varepsilon = C/(T - T_0) \quad \text{for } T \geqslant T_c$$

where k and C are constants, T_0 is the Curie tem-

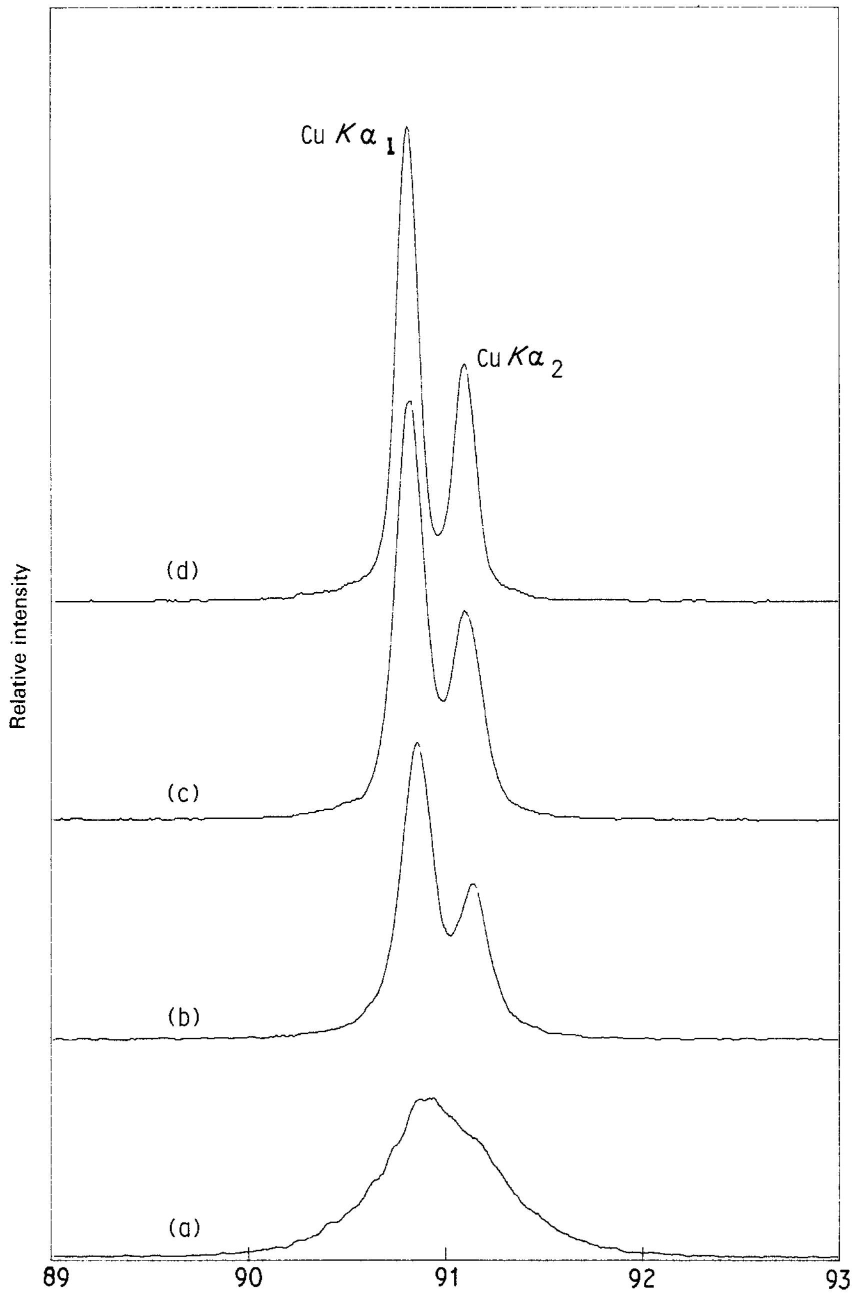

Figure 9 321 reflection of various fired pieces: 0.80 $BaTiO_3$–0.20 $BaZrO_3$ (a) 1250° C, (b) 1300° C, (c) 1400° C; and $Ba(Ti_{0.80}Zr_{0.20})O_3$ (d) 1250° C. All firings were for 2 h. Full width at half maximum for Cu$K\alpha_1$ 2θ are (a) 0.461° (b) 0.192° (c) 0.173° and (d) 0.134°.

perature, and T_c is the Curie point temperature. If one averages over volume elements with this permittivity as a function of temperature characteristic then one finds that indeed the compositional distribution width does affect the temperature of maximum permittivity for the sample [9, 10]. The more homogeneous composition sample has a lower Curie point temperature.

The magnitude of the permittivity of the homogeneous powder compositions should be noted. It was observed that dielectric constants in excess of 40 000 for the $Ba(Ti_{0.80}Zr_{0.20})O_3$ compositions coincided with the growth of large grains (Fig. 8) [11]. An explanation for the exceptionally large permittivities shown by both $Ba(Ti_{0.90}Zr_{0.10})O_3$ and $Ba(Ti_{0.80}Zr_{0.20})O_3$ is not offered at this time.

5. Conclusions

Solid solutions formed by sintering mixtures of $BaTiO_3$ and $BaZrO_3$ are often chemically inhomogeneous. Permittivity measurements of these non-equilibrium systems indicate higher Curie point temperatures than would be attained if the sintering were sufficient to reach chemical equilibrium.

The Curie point temperatures of homogeneous solid solutions of $Ba(Ti_{1-x}Zr_x)O_3$ ($x = 0, 0.05, 0.10, 0.20$) were determined. The shift in the Curie point temperature from that of $BaTiO_3$ was found to be −21° C for $x = 0.05$, −41° C for $x = 0.10$, and ~ -95° C for $x = 0.20$. Thus, with respect to Curie point temperature, $Ba(Ti_{1-x}Zr_x)O_3$ solid solutions exhibit Henrian behaviour in the compositional range from $x = 0$ to $x \sim 0.10$.

Acknowledgements

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