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Fast-sintering of hydrothermally synthesized $BaTiO_3$ powders and their dielectric properties

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Hydrothermally synthesized barium titanate ($BaTiO_3$) powders with a submicrometre particle size have been fast-sintered with a heating rate of $\sim 200\,^{\circ}C\,min^{-1}$ at various temperatures (1250–1350 °C) for short times (5 and 15 min). The microstructures and dielectric properties of the sintered samples are studied and compared with those sintered conventionally. The sample fast-sintered at 1250 °C for 5 min had the highest dielectric constant value of approximately 3700 with an average grain size of about 1 μm. Both the dielectric constant and the Curie–Weiss temperature are found to be dependent on the grain size of the sintered samples, particularly when the average grain size is less than 5 μm. This has been attributed to the presence of internal stress in the fine-grained $BaTiO_3$.

1. Introduction

Barium titanate ($BaTiO_3$) is a well-known dielectric material with a dielectric constant of approximately 2000 at room temperature. It has been widely used in multilayer capacitors (MLC) [1, 2], thermistors [3–6], piezoelectric transducers [7, 8] and a variety of electro-optic devices [1, 9]. Recently, there has been renewed interests in thin film ferroelectrics for their possible applications as nonvolatile memories in the semiconductor industries [10–12].

Like other electronic ceramic materials, the electrical properties of $BaTiO_3$ are closely linked to its microstructural features, such as the porosity and grain size [13–15]. It is desirable to have a homogeneous microstructure for optimal properties. In principle, $BaTiO_3$ ceramics with a dense structure and fine grains possess better dielectric properties [14, 15]. This can be achieved by using high purity, stoichiometric $BaTiO_3$ powders composed of uniform particles, and subsequently controlling the grain growth during sintering. In this study, $BaTiO_3$ powders were prepared by the hydrothermal synthesis technique, and fired via a fast-sintering process, or so-called zone sintering. Hydrothermal synthesis, like other wet-chemical syntheses, is known to yield powders of submicrometre sized particles with maximum control over stoichiometry and purity [16]. The intimate atomic level contact between Ba and Ti precursors also allows much lower processing temperatures [17–22] and thus more uniform particle sizes. The fast-sintering process has been found to be capable of effectively restricting grain growth [24–31]. It has been successfully applied to the preparation of dense, fine-grained polycrystalline β-alumina [24], translucent aluminas [25–27], ferrites [28] as well as $BaTiO_3$ [29–31]. During fast-sintering, a powder compact undergoes a rapid high-temperature thermal treatment by being brought to a hot zone within a very short time. In this way, the densification process (e.g., lattice diffusion) can be enhanced while limiting the grain growth process (e.g., surface diffusion) [26, 27, 30]. With proper control of time and temperature, it can result in a high density ceramic with a fine grain size.

The goal of this study was to investigate the effect of fast-sintering on the microstructure and dielectric properties of $BaTiO_3$ ceramics using hydrothermally synthesized powders. The results are compared with those conventionally sintered.

2. Experimental procedure

The $BaTiO_3$ powders were hydrothermally synthesized at 95 °C. Details of the powder synthesis procedure can be found in an earlier publication [21]. The powders were uniaxially dry-pressed into disc-shaped pellets of 7.06 mm in diameter and approximately 2 mm in thickness under a pressure of about 170 MPa. No binders or additives were used for purity considerations.

Fast-sintering was performed under various conditions by adjusting the temperature of the hot zone and the dwell time (in the hot zone). A high purity alumina rod (99.99%) was used as a sample holder with one end cut flat. The sample was placed on the flat end of the rod, and then covered by a piece of alumina and bound to the sample holder by platinum wires. Two pieces of platinum foil were inserted between the sample and alumina surfaces to avoid possible high-temperature reactions. A high-temperature tube furnace (CM Inc. Rapid Temp Furnace) was used for the fast-sintering. A temperature profile of the furnace (i.e., temperature as a function of position in the tube) was measured for each sintering temperature. When the central hot zone of the furnace reached the desired temperature, the sample assembly lying at the outer (low-temperature) zone was pushed towards the central hot zone within a controlled period of time. This resulted in an estimated heating rate of about 200 °C min^{-1}. After a short dwell time (5 or 15 min), the assembly was removed from the hot zone to the low-temperature zone with a cooling rate of roughly 100 °C min^{-1}. For comparison, conventional sintering was also done in air at temperatures ranging between 1250–1350 °C with a dwell time of 2 h. The heating and cooling rates for the conventional sintering were maintained at 5 °C min^{-1} for all the runs. After the sintering, the apparent densities of the samples were determined by the Archimedes method.

The microstructures of the as-sintered samples were studied using a Hitachi S-400 scanning electron microscope (SEM). Prior to the SEM examination, the samples were ultrasonically cleaned in acetone, and the surfaces were then coated with a sputtered gold layer. The reported average grain size of a sintered sample corresponds to the mean diagonal values of about 30 individual grains.

The dielectric properties were measured at 1 kHz with an LCR meter (HP 4263A) at temperatures ranging from room temperature to 300 °C. Silver paste was applied on both sides of the sample which was cured at 700 °C for 1 h to form electrodes. Prior to applying the electrodes, the sample surfaces were polished, and the sample dimensions were obtained for use in the dielectric constant calculations. The electrical measurements were performed during the cooling cycle from 300 °C to room temperature with a cooling rate of 1 °C min^{-1}.

3. Results and discussions

The $BaTiO_3$ powder is composed of soft agglomerates with an ultimate particles size of about 0.06 μm. A more detailed discussion on the powder characteristics can be found elsewhere [21]. Table I summarizes the grain size, density and dielectric properties (i.e., dielectric constant, k', and loss tangent, tanδ) of the fast-sintered samples. The fast-sintering temperature varies between 1250–1350 °C, at which the samples were kept for 5 or 15 min. For comparison, the results of the conventionally sintered samples, previously reported [32], are also listed. Fig. 1(a–c) shows typical SEM micrographs of the $BaTiO_3$ samples fast-sintered for 5 min at 1250, 1300 and 1350 °C. All the fast-sintered samples show a limited grain growth, in contrast to those conventionally sintered. Also, the apparent density of all the fast-sintered samples is higher than 92% of the theoretical value, which is comparable to or higher than those obtained by conventional sintering (Table I). This suggests that the densification process is greatly enhanced (relative to the grain growth) by the fast-sintering process, which closely agrees with the results obtained by Mostaghaci and Brook [29–31]. It also indicates that the densification process is nearly completed during the first few minutes. As the dwell time is extended from 5 to 15 minutes, the grain growth process becomes prominent, resulting in an average grain size closer to those conventionally sintered (> 10 μm when sintered at 1300 °C for 15 min, for example). So, the dwell time in the fast-sintering process appears to have a dramatic effect on the microstructural development. This is different from what is commonly observed in conventional sintering, where the dwell time has only a minor effect on the microstructural development.

From Table I, it can be seen that the k' values are higher for samples with a smaller grain size. The sample fast-sintered at 1250 °C for 5 min, with an average grain size of about 1 μm, yields the highest dielectric constant of about 3700. The dielectric constant significantly decreases with an increase in the grain size until the grain size is above 5 μm. The observed increase in k' for fine-grained $BaTiO_3$ ceramics has been associated with the presence of a high internal stress in the fine-grained ceramics based on minimum free energy consideration [13–15]. The maximum dielectric constant is expected to occur at around a 1 μm grain size, which is achieved for the sample fast-sintered at 1250 °C for 5 min (Table I).

When the dielectric constant (k') is plotted against temperature (Figs 2 and 3), all the samples exhibit a ferroelectric Curie transition at $T_C \sim 130$ °C, which is consistent with the value reported in the literature [1]. The peak of the Curie transition, however, becomes

TABLE I Density, grain size, and dielectric properties of the sintered $BaTiO_3$ samples

Type of sintering	Sintering temperature (°C)	k' (30 °C)	tanδ (30 °C)	Grain Sizes$^{(a)}$ (μm)	Density$^{(b)}$ (g cm^{-1})	T_o (°C)	C (×10^5 K)
Conventional	1250	2814	0.038	~ 4	5.61 (93)	108	1.8
	1300	2663	0.039	~ 20	5.63 (93)	109	1.9
	1350	2558	0.037	~ 28	5.59 (94)	112	2.0
Fast-5 min	1250	3676	0.020	~ 1	5.53 (92)	84	2.1
	1300	3274	0.026	~ 2	5.65 (94)	97	1.7
	1350	2892	0.009	~ 4	5.71 (95)	110	1.8
Fast-15 min	1250	2947	0.009	~ 6	5.76 (96)	111	1.9
	1300	2721	0.006	~ 12	5.89 (98)	111	2.0

(a) Average grain size determined by taking the mean diagonal values of about 30 grains.

(b) Values in parentheses are the percentage relative densities compared to the theoretical density.

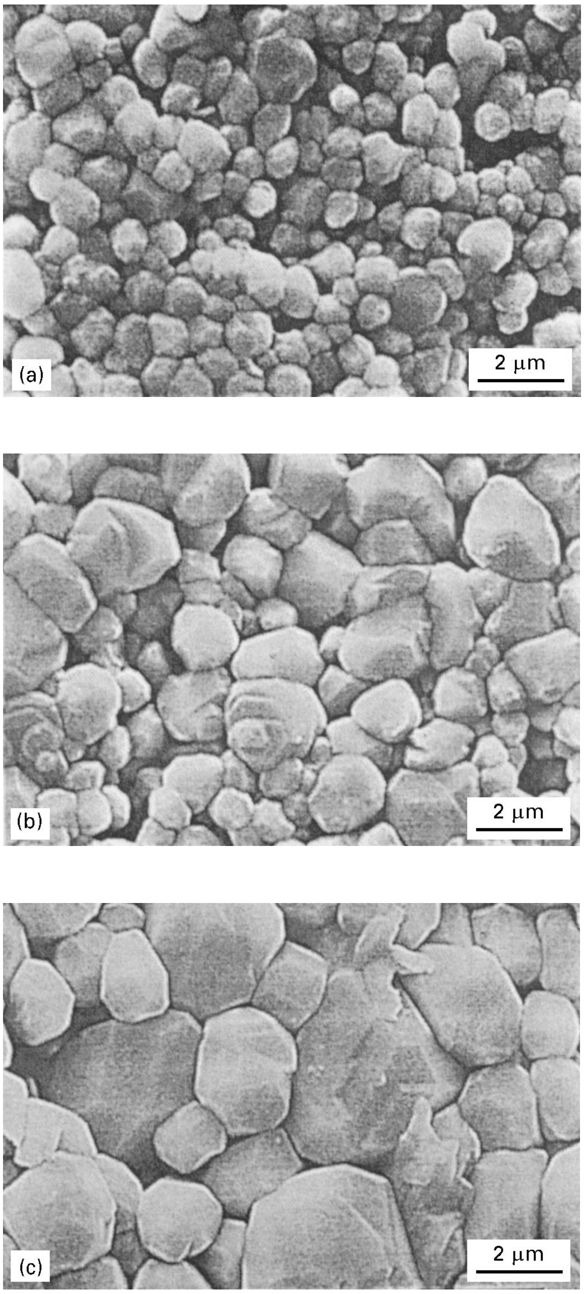

Figure 1 Typical SEM micrographs of the BaTiO$_3$ samples fast-sintered for 5 min at (a) 1250 °C, (b) 1300 °C, and (c) 1350 °C.

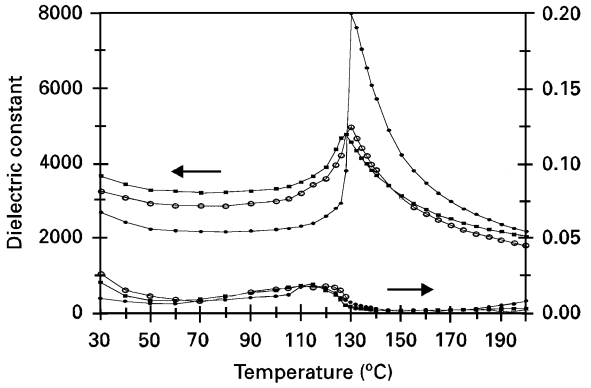

Figure 2 Temperature dependence of the dielectric properties (k' and tanδ) of the BaTiO$_3$ samples fast-sintered for 5 min at (■) 1250 °C, (○) 1300 °C and (●) 1350 °C.

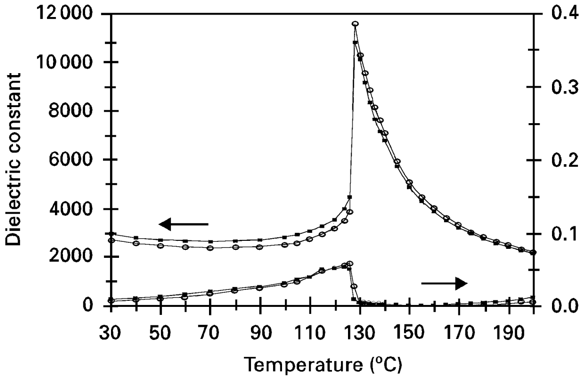

Figure 3 The plot of the dielectric properties (k' and tanδ) of the fast-sintered samples for 15 min at temperatures of: (■) 1250 °C, and (○) 1300 °C.

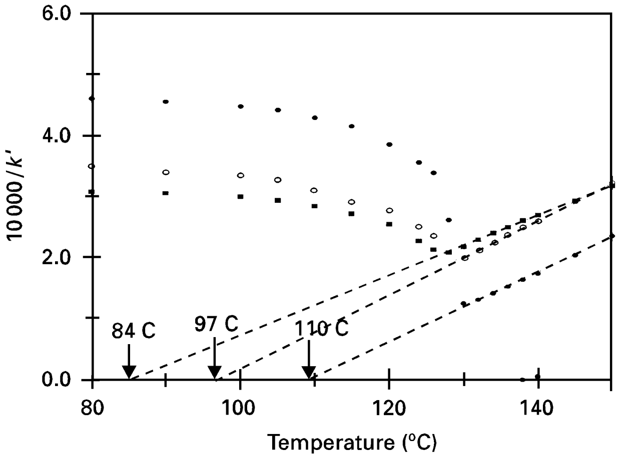

Figure 4 Plot of the inverse dielectric constant $(k')^{-1}$ of the samples fast-sintered for 5 min at temperatures of (■) 1250 °C, (○) 1300 °C and (●) 1350 °C. The Curie–Weiss temperature (T_o, listed in Table 1) is obtained by extrapolating the linear dependence to the x-axis.

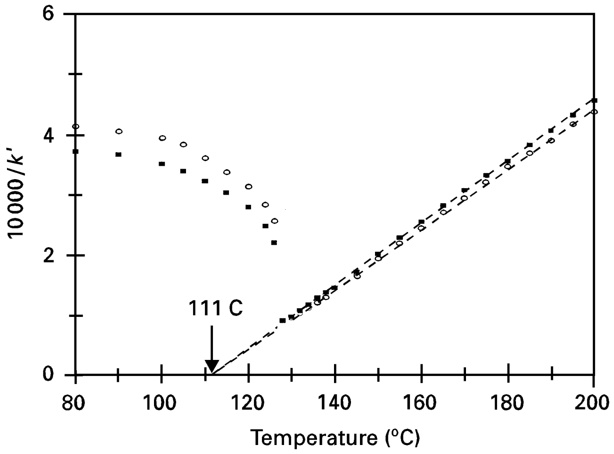

Figure 5 Plot of the inverse dielectric constant $(k')^{-1}$ of the samples fast-sintered for 15 min at temperatures of: (■) 1250 °C, and (○) 1300 °C.

broadened with a decrease in the grain size. On the other hand, by plotting $(k')^{-1}$ against temperature, a Curie–Weiss behaviour is revealed at temperatures above the Curie temperature (T_C), as is shown in Figs 4 and 5 for samples fast-sintered for 5 and 15 min, respectively. From the linear section of these

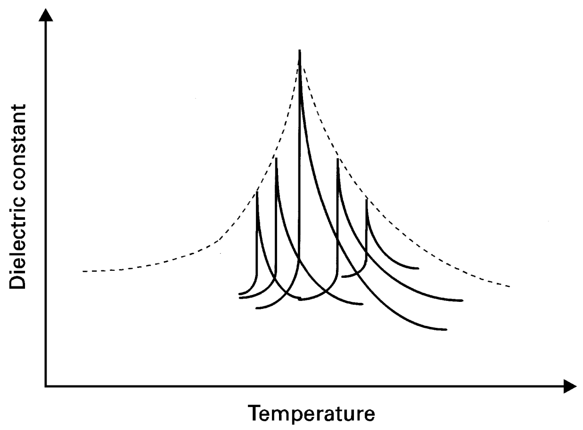

Figure 6 Schematic illustration of a diffused Curie transition as a result of the superimposition of multiple transitions.

plots, the Curie–Weiss temperature (T_o) and the Curie constant (C) were determined (also listed in Table I). The value of T_o appears to increase with an increasing grain size up to a value of 5 μm, above which the T_o value remains unchanged at a value ~110 °C. The Curie constant, however, having a value around 2×10^5 K for all the samples, does not show any systematic variation. This value is in reasonable agreement with those reported by Graham *et al.* [33]. The observed decrease of T_o in $BaTiO_3$ ceramics has been previously attributed to porosity [34], a depolarization effect [35] and structural disorder [33]. In our case, porosity seems unlikely to be the main factor affecting T_o, since the densities of all the samples are greater than 90% of the theoretical value (Table I). In addition neither the depolarization effect nor structural disorder can account for the differences in T_o, as they are only likely to be significant when the grain size is smaller than 1 μm [21]; note that all the samples investigated here have grain sizes about 1 μm or larger. A plausible explanation may come from consideration of the internal stress. The application of pressure has been shown to cause the Curie transition (T_C) to shift to either higher or lower temperatures, depending on the magnitude and the state of the induced stress (compressive or tensile) [36]. The presence of a large and non-uniform internal stress in fine-grained $BaTiO_3$ ceramics may result in the coexistence of different ferroelectric regions (having different stress states) and thus a distribution of T_C values. This means that the observed transition peak in the k'–T plot may be broadened as a result of the superimposition of the transition peaks created from various ferroelectric regions with different T_C values, this is schematically illustrated in Fig. 6. Such a broadened (or diffuse) phase transition has been commonly observed in Zr doped $BaTiO_3$ ceramics [37]. As the broadening of the transition peak becomes more significant, the Curie–Weiss temperature (T_o) becomes lower due to a smaller decrease in k' above T_C, as was observed in the samples fast-sintered at 1250 and 1300 °C for 5 min. However, the apparent T_C, which represents the temperature at which the transition is most likely to occur (i.e., the T_C corresponding to the maximum in k' value in the temperature distribution) appears not to be affected by the diffuse transition (~130 °C).

4. Conclusions

Hydrothermally prepared $BaTiO_3$ powders were fast-sintered at a heating rate of 200 °C min^{-1} at various temperatures for 5 and 15 min, and their microstructures and dielectric properties were compared with conventionally sintered samples (with a heating rate of 5 °C min^{-1}). The fast-sintered samples showed limited grain growth while achieving relatively high densities. The sample fast-sintered at 1250 °C for 5 min has an average grain size of about 1 μm and displays the highest dielectric constant (~3700). The increase of dielectric constant and a decrease in the Curie–Weiss temperature with decreasing grain size (< 5 μm) have been attributed to the presence of an internal stress in the fine-grained $BaTiO_3$ ceramics.

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