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Study on barium titanate ceramics prepared by various methods

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Barium titanate ($BaTiO_3$) ceramics have been fabricated using powders prepared by sol-gel, coprecipitation and mixed oxide methods. The powders prepared by sol-gel and coprecipitation have average crystallite diameters of 100 nm and 300 nm, respectively while the diameter of the mixed oxide powder is ∼1–3 μm. When sintered at the same temperature of 1320°C, the three $BaTiO_3$ ceramics have very different grain size, with the one prepared by the mixed oxide method having the largest grain size of 20 μm. The dielectric permitivity increases as the grain size of the ceramic becomes smaller. The room temperature (25°C) dielectric permittivity, pyroelectric and piezoelectric properties of these ceramics have been measured as functions of the poling field. The $BaTiO_3$ ceramic fabricated from nanosized powder derived from the coprecipitation method is found to have the smallest grain size and better properties than prepared from the sol-gel route, and is thus a good candidate for use in devices that required thick (10 to 20 μm) ferroelectric films. © *2001 Kluwer Academic Publishers*

1. Introduction

Since the discovery of barium titanate ($BaTiO_3$) in the early 1940's, there has been a continuous development of using it in new industrial and commercial applications. $BaTiO_3$ is widely used as capacitors, ultrasonic transducers, pyroelectric infrared sensors and positive temperature coefficient (PTC) resistors [1–4]. Being a lead-free ferroelectric ceramic, $BaTiO_3$ is an environmentally friendly material, thus making it a good candidate for various applications.

In order to prepare $BaTiO_3$ ceramic thick films (10–20 μm) for use in various devices, the ceramic is required to have small grain size and reasonably good properties. $BaTiO_3$ ceramic prepared from the conventional mixed oxide route has too large (>10 μm) a grain size for thick film applications. In the present study, $BaTiO_3$ powders prepared by the sol-gel process [5] and the coprecipitation method [6] are sintered at various temperatures to give ceramics with small grain size, the properties of which are then compared with those of $BaTiO_3$ ceramics prepared by the mixed oxide route [7]. In the following sections, $BaTiO_3$ (sol-gel), $BaTiO_3$ (coprecipitation) and $BaTiO_3$ (oxide) denote the ceramic samples prepared by sintering powder obtained from the sol-gel process, coprecipitation method and mixed oxide method, respectively. The dielectric permittivity, pyroelectric and piezoelectric properties of $BaTiO_3$ ceramics prepared by various methods are investigated.

2. Sample preparation and experiments

Nanosized $BaTiO_3$ powder was prepared either by the sol-gel process or by the coprecipitation method. In the sol-gel process (Fig. 1), barium acetate and titanium isopropoxide were dissolved in deionized water and then mixed under continuous stirring at room temperature (25 °C). The amounts of barium acetate and titanium isopropoxide were in a molar ratio of 1 : 1. In order to avoid precipitation, small amounts of acetic acid and acetylacetone were added. The sol was relatively stable and became a gel in a few days. The $BaTiO_3$ gel was dried at 100 °C for 24 h and then annealed at 800 °C for 24 h to give $BaTiO_3$ powder. The average crystallite size of the annealed powder was about 100 nm as determined by X-ray diffraction.

The $BaTiO_3$ powder prepared by coprecipitation method was supplied by the Shanghai Institute of Ceramics. In the coprecipitation process, a mixed solution of barium chloride and titanium tetrachloride was added drop by drop into oxalic acid while being vigorously stirred. The amounts of barium chloride and titanium tetrachloride were in a molar ratio of 1 : 1. The amount of oxalic acid used was 20% in excess of the stoichiometric amount required to give precipitates. The resulting $BaTiO_3$ precipitates were washed repeatedly in deionized water and then dried at 80 °C. The crystallite size of the powder was about 300 nm.

The $BaTiO_3$ powder prepared by the mixed oxide route was provided by Zhongshan University in Guangzhou. The $BaTiO_3$ powder was prepared by reacting $BaCO_3$ and TiO_2 in air. $BaTiO_3$ was initially formed at the $BaCO_3$-TiO_2 grain boundaries. Then $BaTiO_3$ reacted with $BaCO_3$ to form Ba_2TiO_4 until all the $BaCO_3$ was exhausted. Finally Ba_2TiO_4 reacted with the remaining TiO_2 to form $BaTiO_3$. The size of the powder was between 1 to 3 μm.

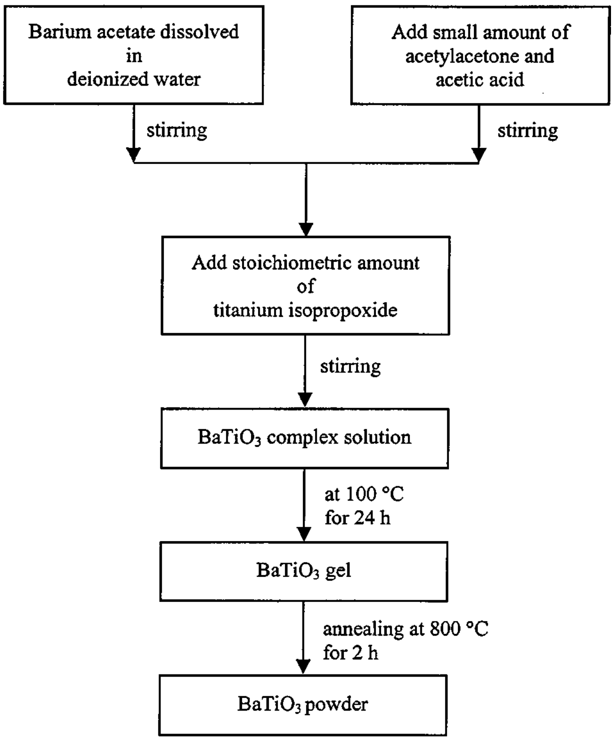

Figure 1 Flowchart showing the procedures for preparing $BaTiO_3$ powder by a sol-gel process.

The $BaTiO_3$ powders prepared by the above three methods were pressed into discs and sintered at various temperatures for 1 h to give the ceramic samples.

The structures of the samples were studied by scanning electron microscopy (Leica Steroscan 440) and X-ray diffraction (Philips X'pert XRD System). For electrical measurements, air-dried silver paint was applied to both sides of each sample to serve as electrodes. The relative permittivity ε' and dielectric loss $\tan\delta$ at 1 kHz were measured using a HP4194A impedance analyzer. After the $BaTiO_3$ samples had been poled at various d.c. fields, the pyroelectric coefficient p was measured using the digital integration method [8] and the piezoelectric coefficient d_{33} was measured by a Pennebaker model 8000 piezo d_{33} tester (American Piezo- Ceramic Inc.). A HP4194A impedance analyzer was used to measure the thickness electromechanical coupling coefficient k_t by a resonance technique following the IEEE standard [9].

3. Experimental results

3.1. Structures and microstructures

Figs 2–4 show the SEM micrographs of $BaTiO_3$ (sol-gel), $BaTiO_3$ (coprecipitation) and $BaTiO_3$ (oxide), respectively. For the SEM measurements, the

TABLE I Showing the variations of grain size, tetragonality (c/a) and density with sintering temperature for $BaTiO_3$ ceramics prepared by different methods

Synthesis method	Sintering temperature (°C)	Average grain size (μm)	c/a ratio	Density (kg/m^3)
Sol-gel	1150	2	1.009	5574
	1200	5	1.010	5649
	1320	10	1.010	5685
Coprecipitation	1250	0.60	1.006	5250
	1280	0.72	1.007	5400
	1300	0.90	1.008	5510
	1320	1.13	1.009	5706
Mixed oxide	1320	20	1.010	5702

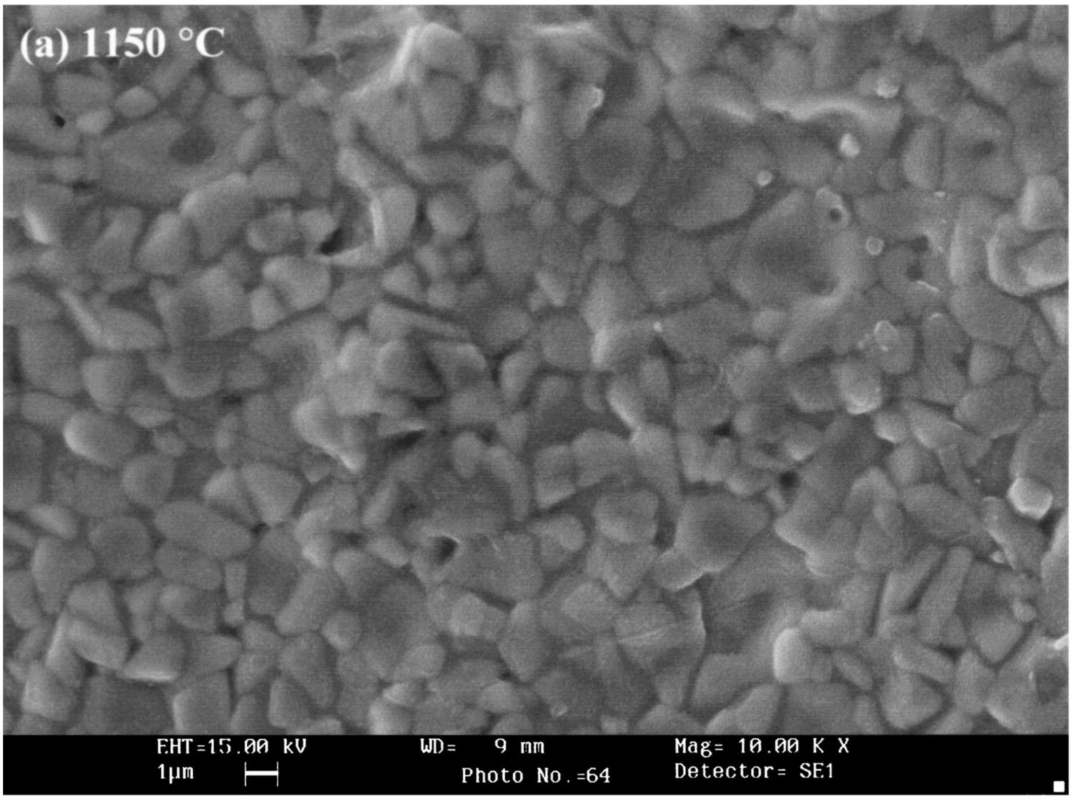

Figure 2 SEM micrographs of $BaTiO_3$ (sol-gel) ceramic sintered at (a) 1150°C, (b) 1200°C and (c) 1320°C. *(Continued.)*

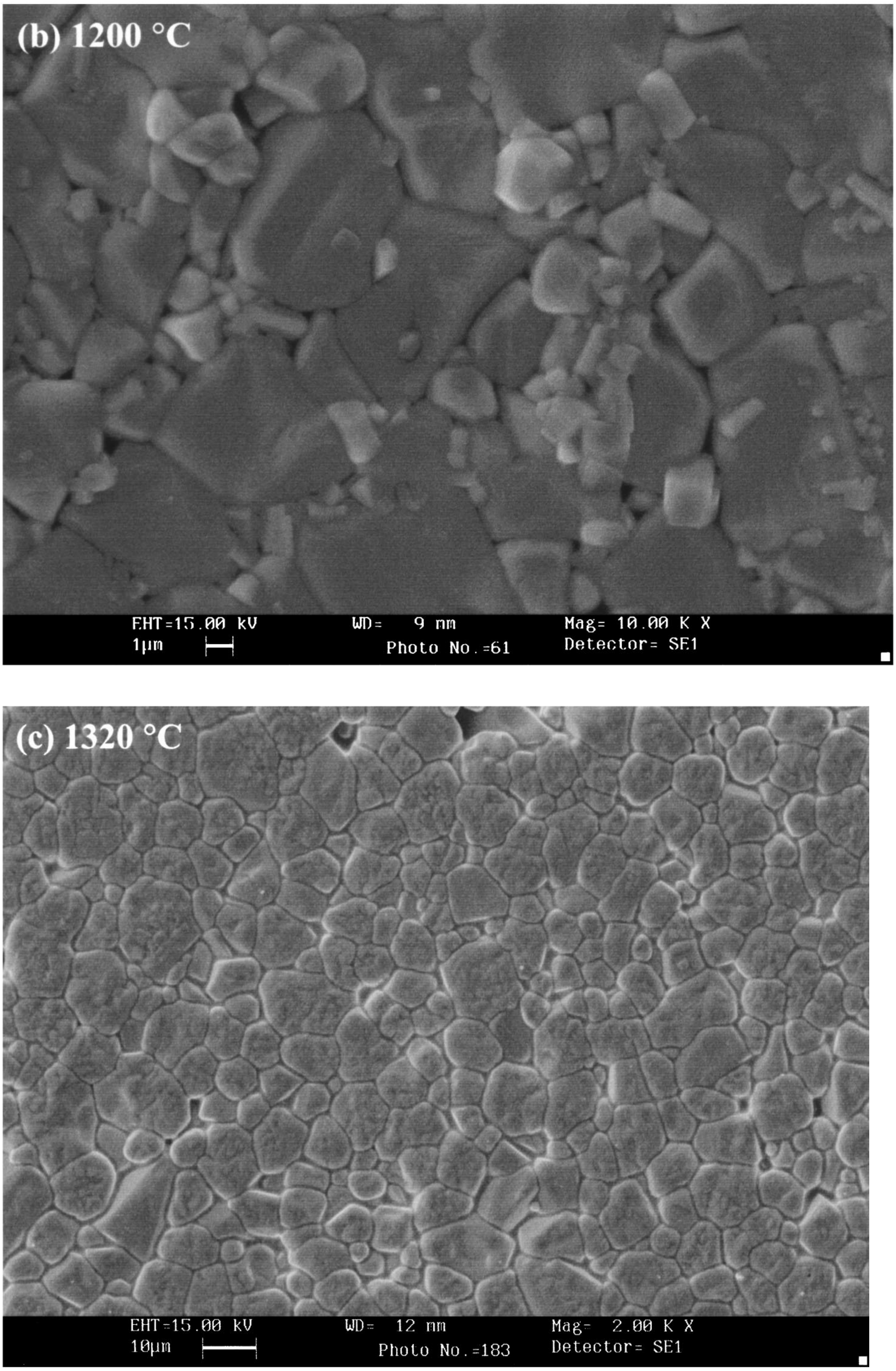

Figure 2 (Continued).

ceramics were polished and thermally etched at a temperature 50 °C below the sintering temperature. The average grain size was determined from the SEM micrographs and shown in Table I. For $BaTiO_3$ (sol-gel), the grain size of the ceramic increases rapidly as the sintering temperature T_s increases, reaching 10 μm at $T_\mathrm{s} = 1320$°C (Fig. 2). However, the grain size of $BaTiO_3$ (coprecipitation) is very small and shows a much slower increase with sintering temperature, reaching only 1.13 μm at $T_\mathrm{s} = 1320$°C (Fig. 3). Following the conventional procedure, $BaTiO_3$ (oxide) was sintered only at 1320°C. This results in a grain size much larger than those in $BaTiO_3$ (sol-gel) and $BaTiO_3$ (coprecipitation) (Fig. 4).

Fig. 5 shows the XRD patterns of $BaTiO_3$ (coprecipitation) sintered at 1320 °C. Although not shown,

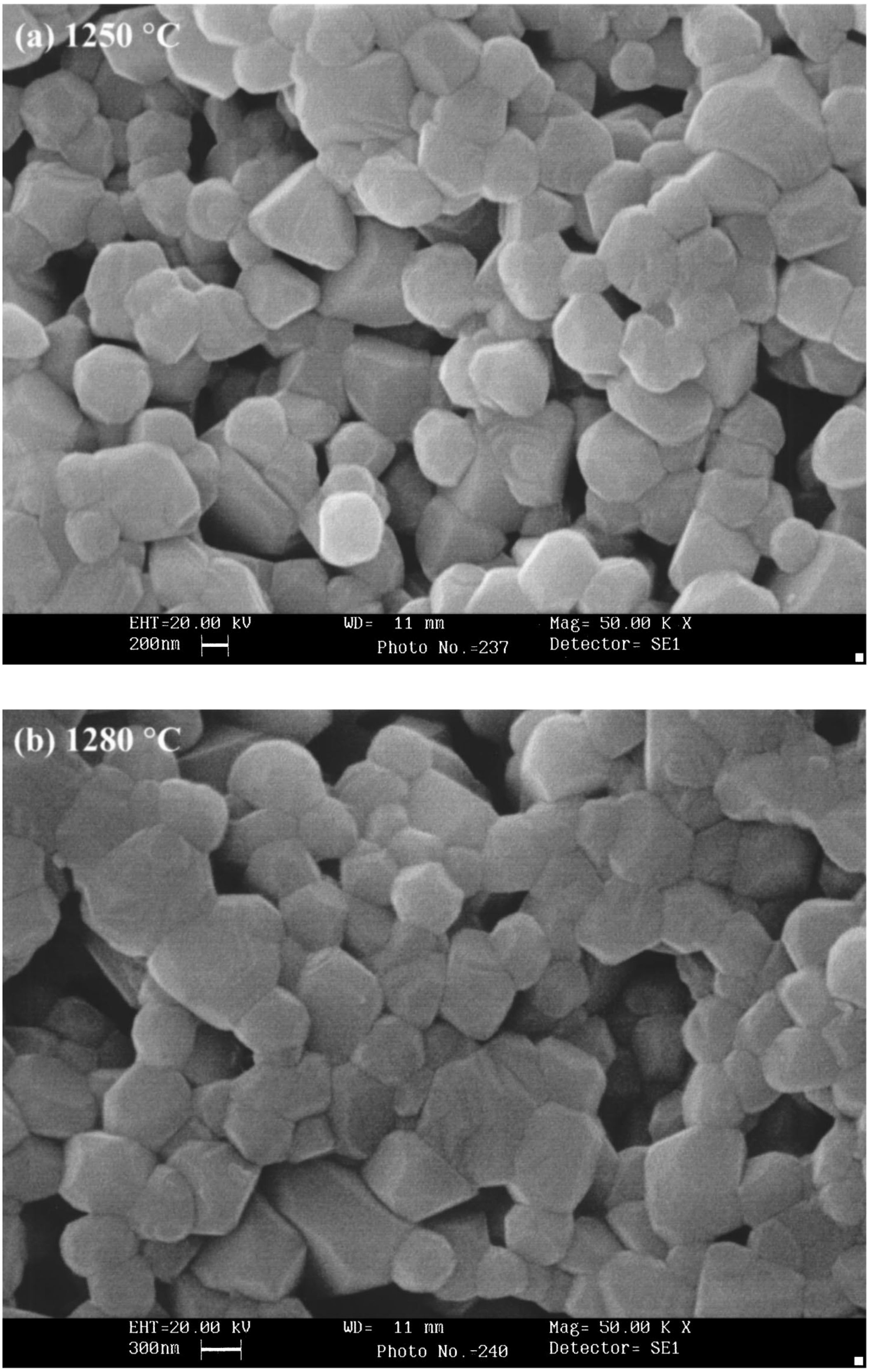

Figure 3 SEM micrographs of $BaTiO_3$ (coprecipitation) ceramic sintered at (a) 1250°C, (b) 1280°C and (c) 1300°C and (d) 1320°C. *(Continued.)*

the XRD patterns of $BaTiO_3$ (sol-gel) and $BaTiO_3$ (oxide) are very similar to that shown in Fig. 5 showing that perovskite structure has been formed. The tetragonality (c/a ratio) are obtained from the XRD patterns and shown in Table I. The tetragonality of both $BaTiO_3$ (sol-gel) and $BaTiO_3$ (coprecipitation) increases as T_s increases and saturates at 1.010, a value closed to the reported value [10–12]. The densities of the ceramic samples are also given in Table I. In subsequent work, properties of $BaTiO_3$ (sol-gel), $BaTiO_3$ (coprecipitation) and $BaTiO_3$ (oxide) sintered at 1320 °C are reported and compared.

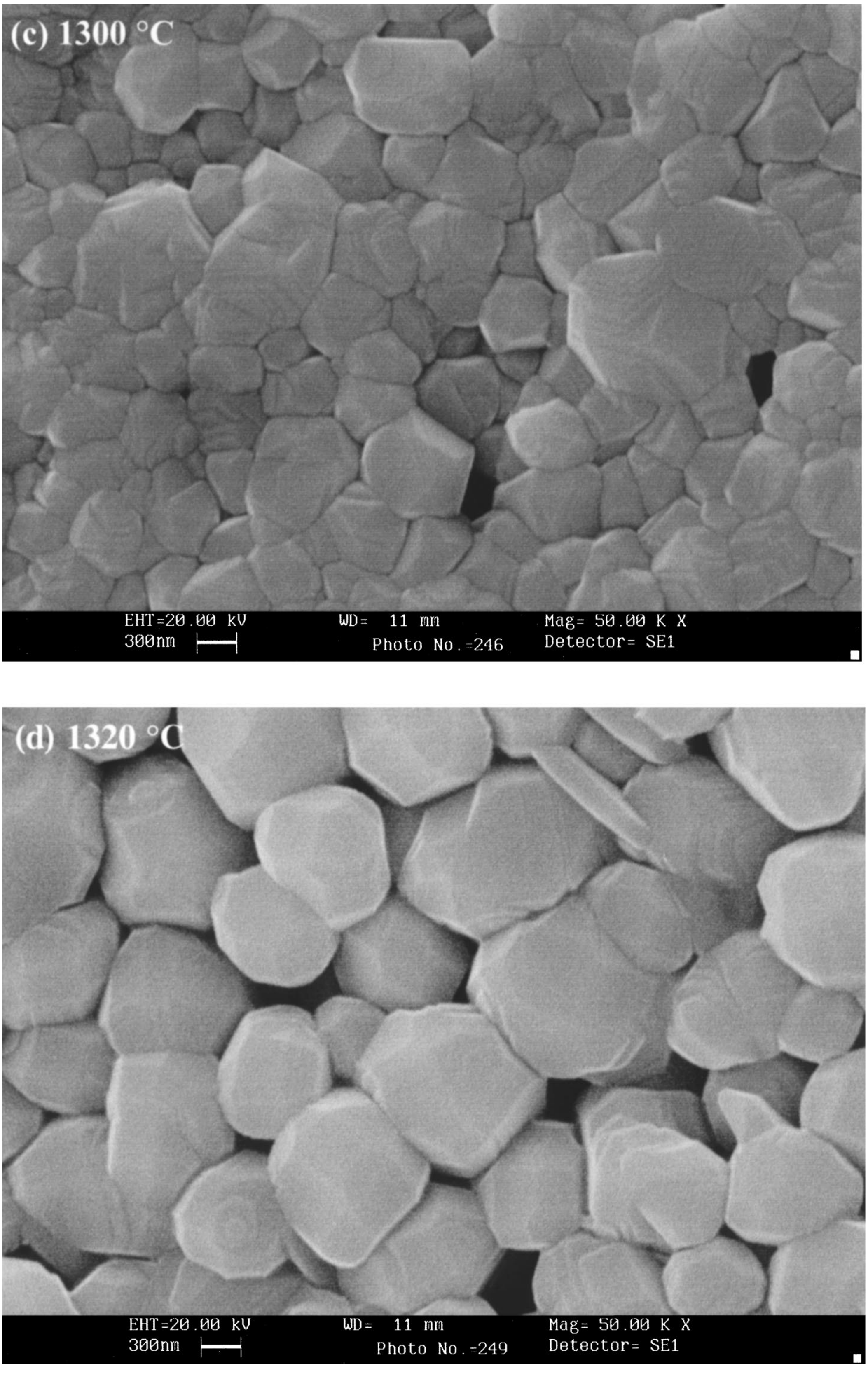

Figure 3 *(Continued).*

3.2. Dielectric, pyroelectric and piezoelectric properties

All $BaTiO_3$ samples were poled at 90 °C in an oil bath by applying various d.c. fields. After poling, the samples were annealed in a short-circuited condition at 50 °C for 3 h before measurements. This process can eliminate the contribution of thermally stimulated current in subsequent measurements. The dielectric permittivity ε and loss tan δ of the samples were measured before poling. The samples were poled using different poling fields and as the poling field increases, ε' decrease (Fig. 6) which may be due to the domain orientation after poling. As the grain size of the ceramic decreases (Table I), ε' increases (Table II). which exhibit a grain size effect similar to that reported in the literature [10, 11].

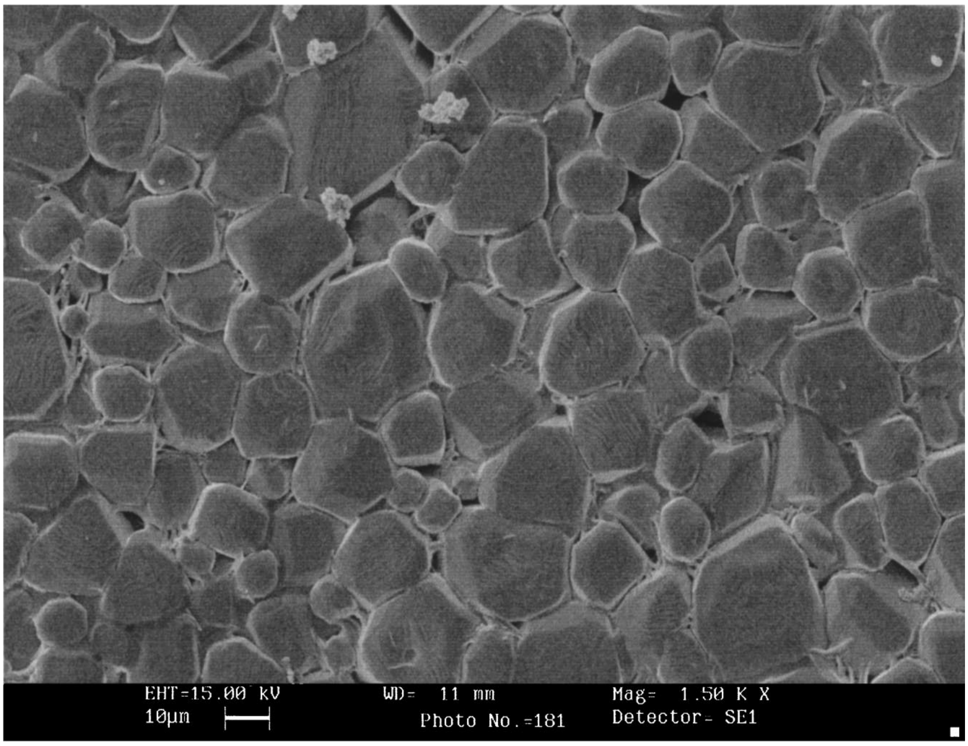

Figure 4 SEM micrograph of $BaTiO_3$ (oxide) ceramic sintered at 1320°C.

TABLE II Properties of $BaTiO_3$ ceramics after being poled with $E = 5$ kV/mm at 90 °C

Synthesis method	Sol-gel	Coprecipitation	Mixed oxide
Sintering temperature (°C)	1320	1320	1320
Pyroelectric coefficient p (μC/m^{2}K)	121	157	235
Piezoelectric coefficient d_{33} (PC/N)	117	143	175
Thickness electromechanical coupling coefficient k_t	0.16	0.22	0.25
Dielectric permittivity ε' (1 kHz, before poling)	1825	1941	1160
Dielectric loss tan δ (1 kHz, before poling)	0.04	0.04	0.02

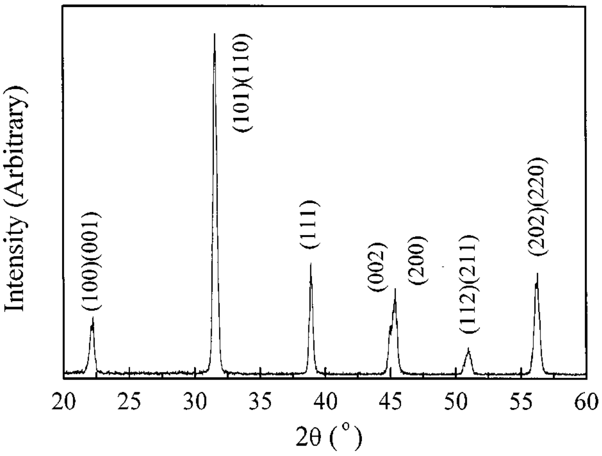

Figure 5 XRD patterns of $BaTiO_3$ (coprecipitation) ceramic sintered at 1320°C.

The pyroelectric coefficient p and piezoelectric coefficient d_{33} of the $BaTiO_3$ ceramics were measured at 25 °C as functions of the poling field in Figs 7 and 8, respectively. Both p and d_{33} increase as the poling field increases and tend to saturate when the poling field is above 3 kV/mm. The maximum attainable p and d_{33} are given in Table II. $BaTiO_3$ (oxide) has the maximum p and d_{33} which are closed to the reported values of $p = 200$ μC/m^{2}K and $d_{33} = 190$ pC/N [7, 12]. Fig. 9 shows the relationship between the thickness electromechanical coupling coefficient k_t and the poling field. Similar to p and d_{33}, k_t increases as the poling field increases and tends to saturate when the samples is poled above $E = 3$ kV/mm. The maximum attainable k_t are also given in Table II. However, the measured k_t of the $BaTiO_3$ ceramics is smaller than the reported value ($k_t \sim 0.35$ [1, 7]). $BaTiO_3$ (coprecipitation) has k_t close to $BaTiO_3$ (oxide) and is higher than that of $BaTiO_3$ (sol-gel).

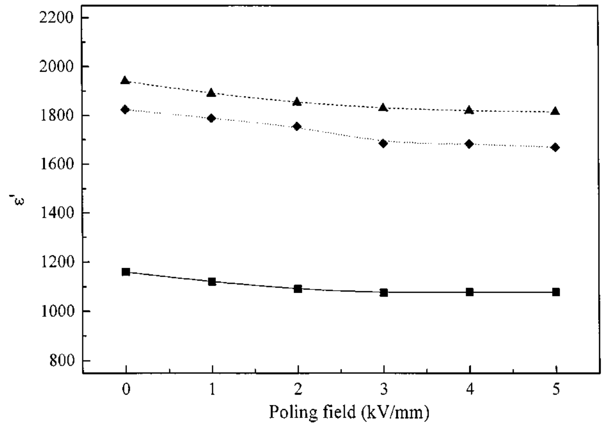

Figure 6 Room temperature dielectric permittivity ε' of $BaTiO_3$ sintered at 1320°C versus poling field.

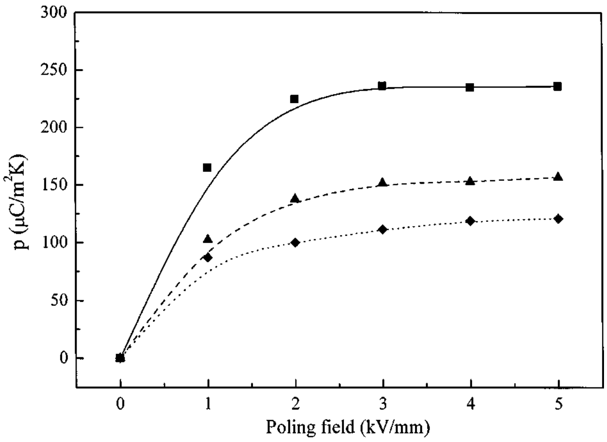

Figure 7 Pyroelectric coefficient p of $BaTiO_3$ sintered at 1320°C versus poling field.

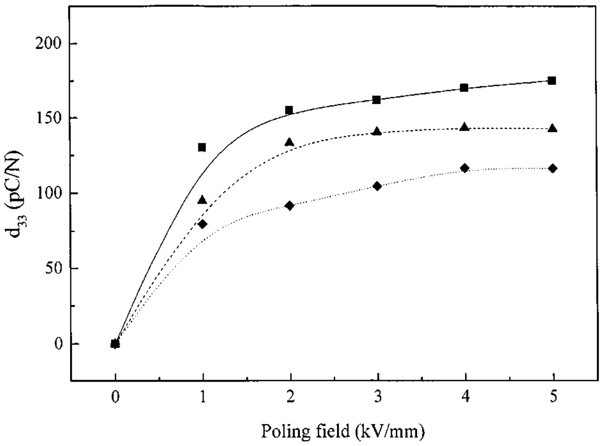

Figure 8 Piezoelectric coefficient d_{33} of $BaTiO_3$ sintered at 1320°C versus poling field.

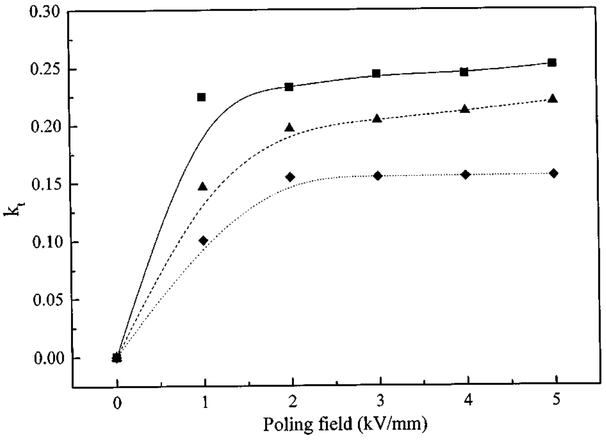

Figure 9 Thickness electromechanical coupling coefficient k_t of $BaTiO_3$ sintered at 1320°C versus poling field.

4. Conclusion and discussion

$BaTiO_3$ ceramics have been fabricated using powder prepared by the sol-gel, coprecipitation and conventional mixed oxide methods. Characteristics of $BaTiO_3$ ceramics prepared by these methods have been investigated. As expected, $BaTiO_3$ (oxide) has the largest grain size (20 μm) and the best properties. The average grain size of $BaTiO_3$ (sol-gel) sintered at 1320 °C is about 10 μm which is too large for thick film applications and it also breaks down easily upon poling. After poling with d.c. field higher than 3 kV/mm, the pyroelectric coefficient p, piezoelectric coefficient d_{33} and the thickness electromechanical coupling coefficient k_t of $BaTiO_3$ (sol-gel) tend to saturate. Although not shown in detail, we found that if $BaTiO_3$ (sol-gel) was sintered at 1200°C, except for having a smaller grain size (5 μm) and a higher dielectric permittivity, the measured values of p, d_{33} and k_t are almost identical to $BaTiO_3$ (sol-gel) sintered at 1320°C showing that there is an upper limit of materials properties which cannot be improved by the grain growth. For $BaTiO_3$ (coprecipitation), as the sintering temperature increases, the grain grow is very slow. The $BaTiO_3$ (coprecipitation) sample sintered at 1320°C has an average grain size of 1.13 μm which is much smaller than $BaTiO_3$ (sol-gel) and $BaTiO_3$ (oxide).

In conclusion, it is found that $BaTiO_3$ ceramic sintered by using nanosized powder derived from the coprecipitation method has good potential to be used in thick film device applications. $BaTiO_3$ (coprecipitation) has a smaller grain size, its p and d_{33} are higher than those of $BaTiO_3$ (sol-gel) and its k_t is comparable to that of $BaTiO_3$ (oxide).

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