JOURNAL OF MATERIALS SCIENCE 28 (1993) 6617–6621

Study on the dielectric properties of oxide-doped Ba(Ti, Sn)O_3 ceramics prepared from ultrafine powder

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Ultrafine $BaTiO_3$ and $BaSnO_3$ powders were prepared by thermal decomposition of oxalates through synthesis by the method of co-precipitation; Dy_2O_3, Nb_2O_5 and ZnO, used as dopants, were added to the main constituents, known as the tailor-made Ba(Ti, Sn)O_3, according to the indicated compositions, then the batches were mixed until they became homogeneous. Careful treatment was necessary in later stages of the process of ceramic making. The dielectric properties of the ceramics were measured. It was found that high ε, low $\tan\delta$ and low $d\varepsilon/dt$ were characteristics of these ceramics. The results could be explained by the effects of peak shifting, broadening and grain-size inhibition. The relationship between composition, structure and properties is discussed.

1. Introduction

The development of various special ceramics with excellent properties has been realized to be dependent on the characters of the raw material, including the chemical impurity content, particle size, morphology of particles, etc., which are important factors having decisive influence on the preparation of modern fine ceramics. High-temperature calcined $BaTiO_3$ and $BaSnO_3$ chemical reagents showed some shortcomings, such as too large a particle size, higher impurity content and lower chemical activity, and therefore are not suitable for enhancing the dielectric properties of ceramics for high technical uses.

In the present work, we attempted to approach the $BaTiO_3$–$BaSnO_3$ system ceramics which possess high dielectric constants and other satisfactory electrical properties. They are expected to find application in making capacitors with small-sized specifications. Hence, the work may be of practical significance.

2. Experimental procedure

2.1. Processing

The preparation process started from chemical precipitation reactions of oxalate in order to obtain $BaTiO_3$ ultrafine powders through decomposition, which will be used as the precursors for making the ceramics. The chemical reaction equations are as follows.

$$BaCl_2 + TiCl_4 + 2H_2C_2O_4 + 5H_2O \xrightarrow{\sim 80\,^{\circ}C} BaTiO(C_2O_4)_2\cdot 4H_2O + 6HCl \qquad (1)$$

$$BaTiO(C_2O_4)_2\cdot 4H_2O \xrightarrow{\sim 800\,^{\circ}C} BaTiO_3 + 4H_2O + 2CO_2 + 2CO \qquad (2)$$

$$BaCl_2 + SnCl_2 + 2H_2C_2O_4 + \tfrac{1}{2}H_2O \xrightarrow{\sim 80\,^{\circ}C} BaSn(C_2O_4)\cdot\tfrac{1}{2}H_2O + 4HCl \qquad (3)$$

$$BaSn(C_2O_4)_2\cdot\tfrac{1}{2}H_2O \xrightarrow{\sim 1000\,^{\circ}C} BaSnO_3 + 2CO_2 + 2CO + \tfrac{1}{2}H_2O \qquad (4)$$

The batches were then prepared through weighing and mixing. Technological operations were continuously carried out by drying, grinding, granulating, and moulding, and finally, the sintered ceramic samples were obtained by firing. The chemical compositions of the ceramics are given in Table I.

2.2. Measurement of structure and properties

The particle size of $BaTiO_3$ and $BaSnO_3$ powders were separately measured by SEM. It was found that the maximum size of these particles did not exceed 0.20 μm, even when there were agglomerates. At the same time, the phase-transformation temperatures completed at 800 °C for $BaTiO_3$ and 1000 °C for $BaSnO_3$ were determined by DTA. Scanning electron micrographs of $Ba(TiO)(C_2O_4)_2\cdot 4H_2O$ and $BaSn(C_2O_4)_2\cdot\frac{1}{2}H_2O$ are shown in Figs 1 and 2.

The precursor powders prepared by chemical precipitation were identified by X-ray diffraction (XRD)

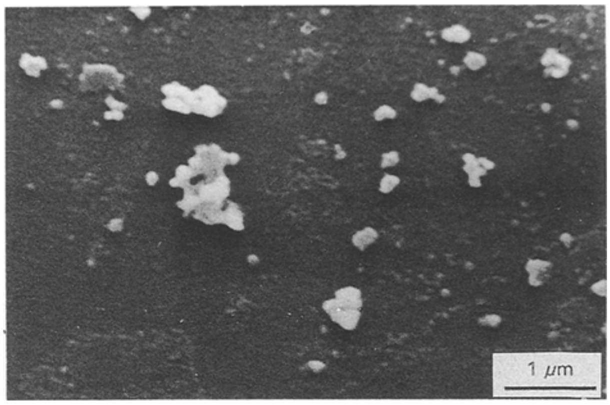

Figure 1 Scanning electron micrograph of $BaTiO_3$ ultrafine powder (×11 300).

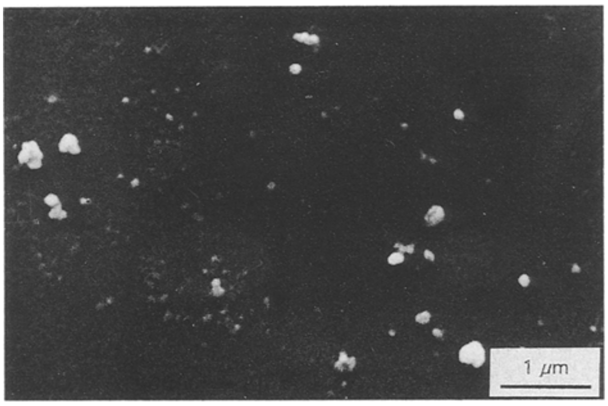

Figure 2 Scanning electron micrograph of $BaSnO_3$ ultrafine powder (×11 300).

analysis. The results indicated that the characteristic data are comparable with data given in the JCPDS card. It was found that the powders were tetragonal $BaTiO_3$ and cubic $BaSnO_3$; the lattice constants agreed well with theoretical data. XRD curves are shown in Figs 3 and 4.

Dielectric properties of ceramic samples were measured on a precise capacitance-conductance bridge, Model CD-7A; the resistivities of these samples were measured using a ZC-36 high resistometer. The ε and tan δ versus temperature curves for representative samples 1, 1′, 4, 5, 6, 6′ are shown in Figs 5–10, respectively.

The elementary data derived from the above measurements of the dielectric properties of different samples are summarized in Table II. The microstructure of ceramic samples is shown in Fig. 11.

3. Discussion

It has been noted that the preparation of $BaTiO_3$ and $BaSnO_3$ ultrafine powders through chemical precipitation reactions and calcination had been investigated and found to be successful. The particle sizes generally lay within the range 0.08–0.14 μm. Such powders, not only exhibit reliable purity, but also have some beneficial properties including better fluidity and chemical activity. They can thus be regarded as the ideal tailor-made ultrafine raw materials for ceramic making.

TABLE I Chemical composition of the ceramics

Code number of sample[a]	Composition (wt%)				
	$BaTiO_3$	$BaSnO_3$	Nb_2O_5	ZnO	Dy_2O_3
1	100				
1′	100				
2	88.0	12.0			
3	85.0	15.0			
3′	85.0	15.0			
4	85.0	12.0	1.3	0.4	0.8
5	79.5	18.0	1.3	0.4	0.8
6	97.5		1.3	0.4	0.8
6′	97.5		1.2	0.3	1.0

[a] Samples 1′, 3′, 6′ prepared from common raw materials.

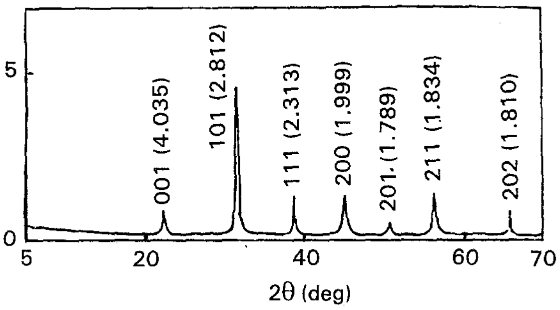

Figure 3 XRD curve of $BaTiO_3$ ultrafine powder.

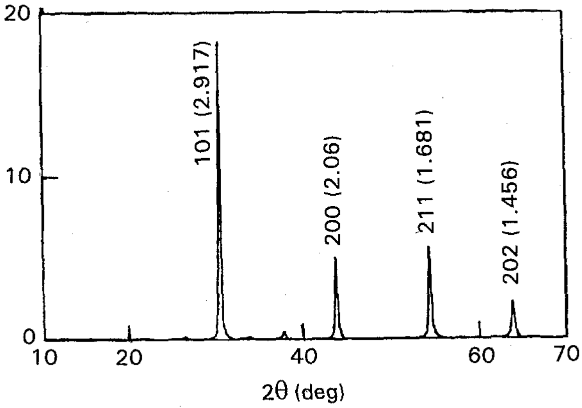

Figure 4 XRD curve of $BaSnO_3$ ultrafine powder.

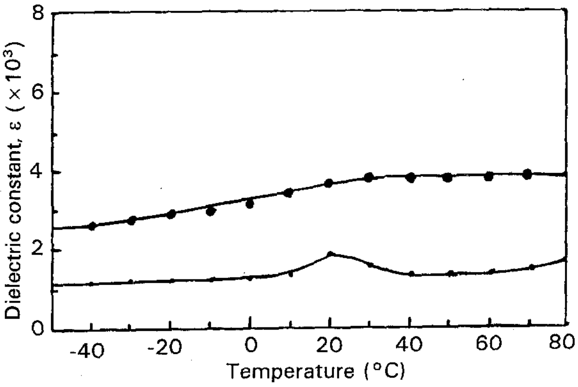

Figure 5 Dielectric constant versus temperature for samples (○) 1, and (●) 1′.

TABLE II Dielectric properties of the ceramic samples

Sample number	ε	Tan δ	ΔC/C (%)		ρ_v (Ω mm)	E (kV mm^{-1})	Grain size (μm)	Firing temperature (°C)
			− 20 °C	+ 80 °C				
1	3213	3.71	− 9.6	+ 8.4	1.97	2.54	3–5	1300
1′	1800	1.82	− 33	+ 13				1340
2	7000	2.90	− 81	− 66	2.52	2.83	15–25	1320
3	7900	2.80	− 77	− 76	2.11	2.97	18–25	1320
3′	8200		− 96	+ 50				1340
4	5930	1.31	− 26	− 19	3.20	2.80	1.4–1.8	1320
5	10371	1.24	− 20	− 38	2.87	3.98	1.5–2.0	1330
6	4600	1.32	− 15	0.61	2.53	2.12	1.5–2.0	1300
6′	3500	0.46	− 15	+ 18				1340

[a]Samples 1′, 3′, 6′ prepared from common raw materials.

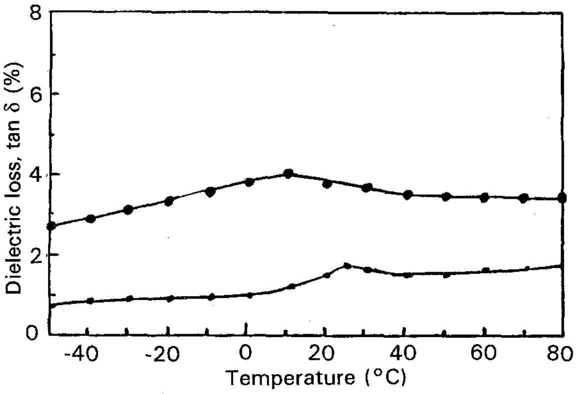

Figure 6 Dielectric loss versus temperature for samples (○) 1 and (●) 1′.

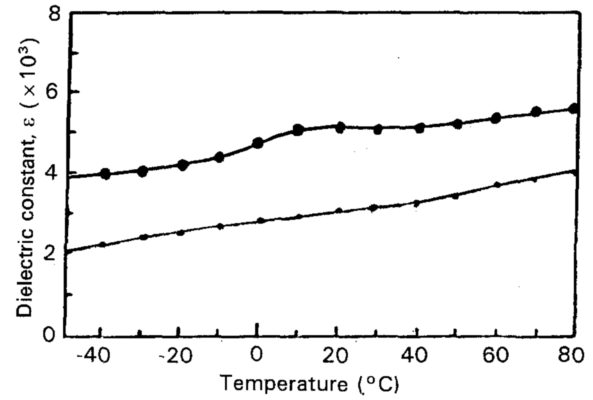

Figure 9 Dielectric constant versus temperature for samples (○) 6 and (●) 6′.

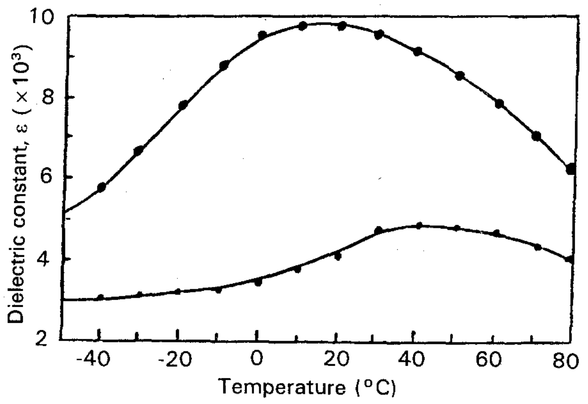

Figure 7 Dielectric constant versus temperature for samples (○) 4 and (●) 5.

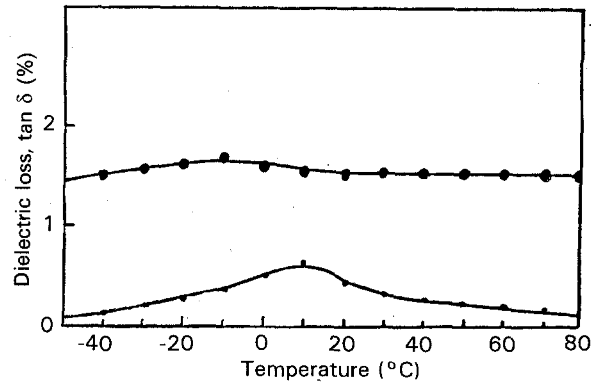

Figure 10 Dielectric loss versus temperature for samples (○) 6 and (●) 6′.

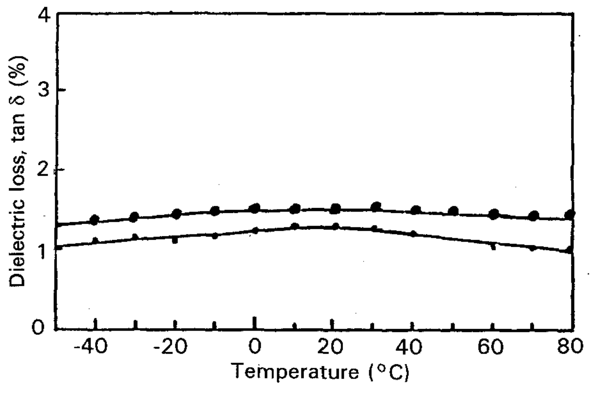

Figure 8 Dielectric loss versus temperature for samples (○) 4 and (●) 5.

From the measured dielectric properties, it could be seen that the ceramic Sample 1, made from pure $BaTiO_3$ ultrafine powder, was always characterized by better dielectric properties than that of those Samples 1′, made from industrial chemicals ($BaTiO_3$). Because of the high ε (up to 3000 at room temperature), an appreciable tan δ and the relatively lower temperature coefficient of ε, the pure $BaTiO_3$ ceramic may be expected to find use as a dielectrics of a low-frequency capacitor.

When $BaTiO_3$ ceramic was modified by $BaSnO_3$, we obtained stronger dielectric ceramics such as Samples 2 and 3, and their values of ε may reach more than 7000 and the Curie point rose to very near room

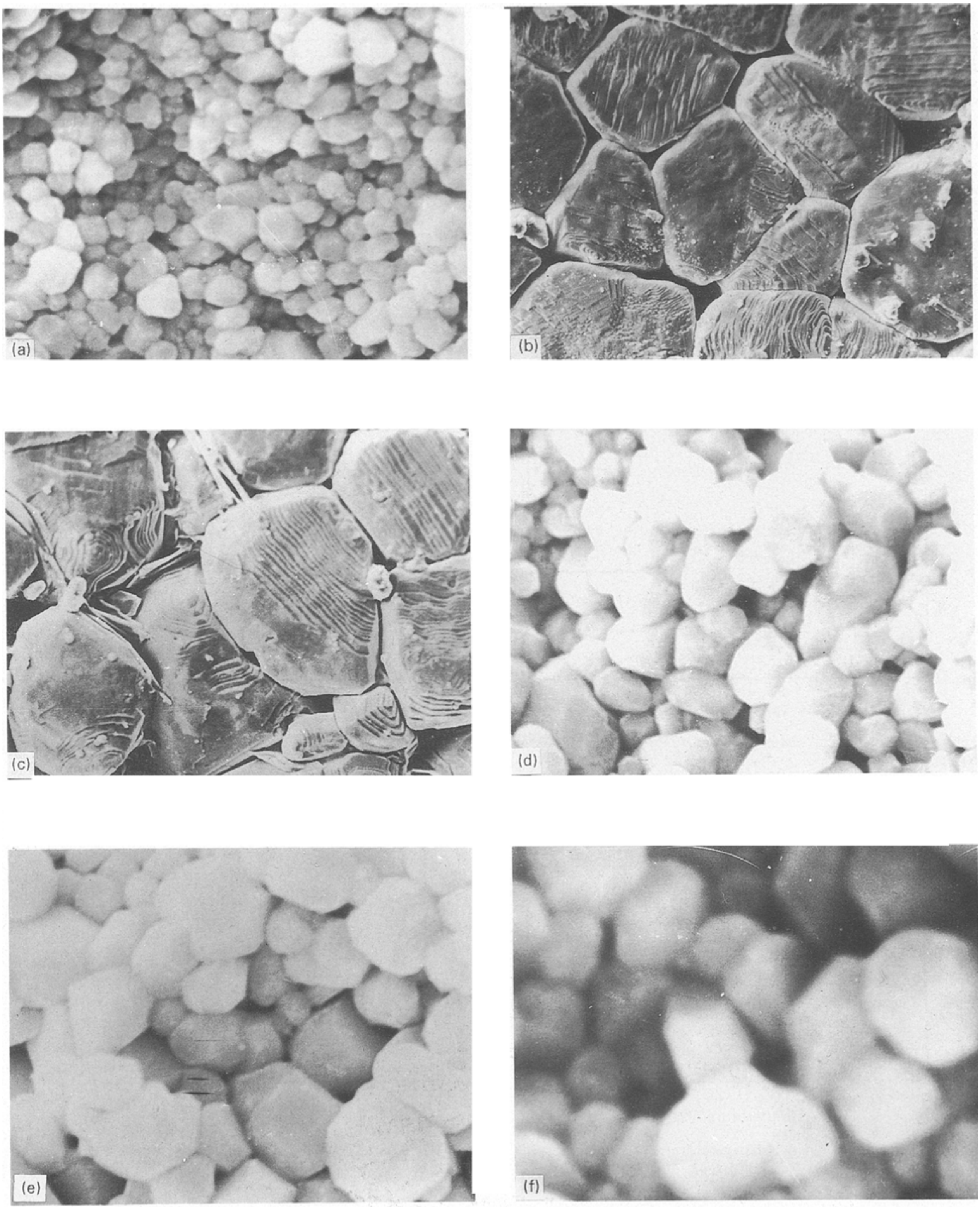

Figure 11 Microstructure of different $BaTiO_3$–$BaSnO_3$ ceramics. (a) Sample 1, SEM, ×2000; (b) Sample 2, SEM, ×1600; (c) Sample 3, SEM, ×1600; (d) Sample 4, SEM, ×8100; (e) Sample 5, SEM, ×11 000; (f) Sample 6, SEM, ×11 000.

temperature. However, the dielectric loss of these ceramics is still a little high. According to their high-temperature coefficient of ε, these ceramics may be expected to find use as non-linear dielectrics.

In order to improve the dielectric properties of the $BaTiO_3$–$BaSnO_3$ system ceramics, Dy_2O_3, Nb_2O_5 and ZnO were selected for use as additives. It was found that for such ceramics, a series of samples could be obtained with quite high ε, low $\tan\delta$ and low temperature coefficient of ε (in the range -20 to $+80\,^{\circ}C$). Therefore, these ceramics may be expected to find application in low-frequency alternating capacitors and will be suitable for fabricating small-sized devices.

On comparing with the properties of the above ceramics, ε of those samples prepared with ultrafine powders is generally higher than that of powder prepared using chemical reagents. Unfortunately, $\tan\delta$ for the latter powders is slightly higher than that of the former. But when complex additives were introduced, the dielectric properties of the samples became satisfactory.

According to the dielectric behaviour shown above, some explanation can be given from the view point of crystal chemistry. The atomic structure of $BaTiO_3$ is perovskite-type crystal. For pure $BaTiO_3$ we can see that the coordination states of different ions in $BaTiO_3$ form a ferroelectric crystal in which the Ti^{4+} is placed in octahedral positions and the crystal appears to undergo spontaneous polarization. In such a case, there will be some stress and strain between the ions, so the coordinated polyhedra will appear deformed causing the crystal to have certain dielectric properties. If we substitute some ions into the structure, as mentioned above, where Sn^{4+} substitutes for Ti^{4+}, or to form a solid solution, Zn^{2+} and Dy^{3+} substitute for Ba^{2+} ($BaSnO_3$ is a nonferroelectric crystal), then the deformation will change and some ions will be relaxed. The subsequent dielectric properties behaviour will also change. As a result, we see that there are two types of characteristic behaviour which may be found, the first is a shift of the Curie point, and the second is an overlapping effect which is indicated in the dielectric properties. For example, when Zn^{2+}, Dy^{3+}, Sn^{4+}, and Nb^{5+}, were added only in small amounts, the polarizing peak appears to be widened. At the same time, ε also increases, $\tan \delta$ decreases, and the ratio $d\varepsilon/dT$ becomes lower. All these phenomena indicate that in the complex system the overlapping effect may be appreciably noted. Therefore, in order to improve the dielectric properties for such ceramics, the additives may be changed, if necessary, and the rule of crystal chemistry may provide some inspiration in advance.

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Received 23 June 1992
and accepted 27 April 1993