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Synthesis and Characterization of Dielectric Compositions in the BaO-rich Corner of the $BaO–Y_2O_3–TiO_2$ Ternary System

Ang Chen,[a] Yu Zhi,[b] V. M. Ferreira,[b] P. M. Vilarinho[b] & J. L. Baptista[b]*

[a]Department of Physics, Zhejiang University, Hangzhou 310027, People's Republic of China
[b]Department of Ceramic and Glass Engineering, University of Aveiro, 3800 Aveiro, Portugal

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Abstract

A single-phase $YBa_3Ti_2O_{8.5}$ ceramic located in the BaO-rich corner of the $BaO–Y_2O_3–TiO_2$ ternary system was synthesized. The dielectric properties of this material (permittivity $\epsilon = 29$, quality factor $Q = 1000$) are reported here for the first time. Compositions with the $BaO:Y_2O_3:TiO_2$ ratio equal to 6:1:5 and 5:1:4 were also synthesized. The Y615 ceramic consists of two phases ($YBa_3Ti_2O_{8.5}$ and $BaTiO_3$), and the Y514 ceramic consists of three phases ($YBa_3Ti_2O_{8.5}$, $BaTiO_3$, and Y_2TiO_5). They are dense ceramic composites. © 1996 Elsevier Science Limited.

1 Introduction

Dielectric compositions with high-performance dielectric properties at high frequency or/and microwave frequency were discovered in the TiO_2-rich corner of the $BaO–Re_2O_3–TiO_2$ system (Re = rare earth).[1] Figure 1 shows their positions in the ternary system. Compositions with the proportion of $BaO:Re_2O_3:TiO_2$ equal to 1:1:2, 1:1:3, 1:1:4, 1:1:5, and even 1:1:7 have been synthesized.[2] In the case of compositions around the proportion 1:1:4 ($BaRe_2Ti_4O_{12}$) or 1:1:5 ($BaRe_2Ti_5O_{14}$), excellent microwave ceramics have been obtained for a variety of microwave devices such as filters and oscillators.[2]

The new compound $YBa_3Ti_2O_{8.5}$ was reported to occur when the high transition temperature superconductor $YBa_2Cu_3O_{7-\delta}$ film was deposited in a $SrTiO_3$ single crystal matrix[3] or when $YBa_2Cu_3O_{7-\delta}$ was composed with a $BaTiO_3$ ceramic.[4] Although this compound has been reported, its electrical characteristics, e.g. the dielectric properties, have not yet been studied. Compared with $BaRe_2Ti_4O_{12}$ (Re = La, Nd, Sm, ...), which is located in the TiO_2-rich corner of the $BaO–Re_2O_3–TiO_2$ ternary system, the $YBa_3Ti_2O_{8.5}$ is located in the BaO-rich corner. In recent work, the authors synthesized a new series of dielectric ceramics having general composition $ReBa_3Ti_2O_{8+\delta}$ (Re = rare earth, such as, Y, Nd, Sm, ...); they are in the BaO-rich corner of the $BaO–Re_2O_3–TiO_2$ system (see Fig. 1). The primary experimental results indicated that this group of materials has permittivity $\epsilon > 25$, and quality factor $Q > 1000$ at 1 MHz.[5]

It is important to study the chemical reactions among the starting materials, the phase-forming process, the crystal structure and the ceramic microstructure of this new series of materials. The present paper is concerned with the synthesis and characterization of these compounds in the BaO-rich corner of the $BaO–Y_2O_3–TiO_2$ ternary system.

2 Experimental Procedure

The ceramics were prepared by the mixed oxide method. High purity starting materials, $BaCO_3$ (May & Baker Co.), TiO_2 (Johnson Matthey Co.) and Y_2O_3 (Fluka Chemie AG Co.), were weighed according to the $BaO:Y_2O_3:TiO_2$ ratios of 6:1:4, 6:1:5 and 5:1:4 (where the ratios 6:1:4, 6:1:5 and 5:1:4 are denoted as Y614, Y615 and Y514, respectively). The weighed batches were wet-mixed in agate pots by a planetary-type ball mill for 5 h. Then the powders were dried and calcined at 1200°C for 2 h. The calcined powders were milled again, dried, and isostatically pressed into discs at 300 MPa. Finally, the samples were sintered in air at 1515°C for 6 h.

Moreover, the powder mixture for each composition from the starting materials $BaCO_3$, Y_2O_3 and TiO_2 was calcined at 900, 1000, 1100, 1200, 1300 and 1400°C for 2 h, in order to study the phase-forming process.

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) (Netzsch STA 409C) were

* To whom correspondence should be addressed.

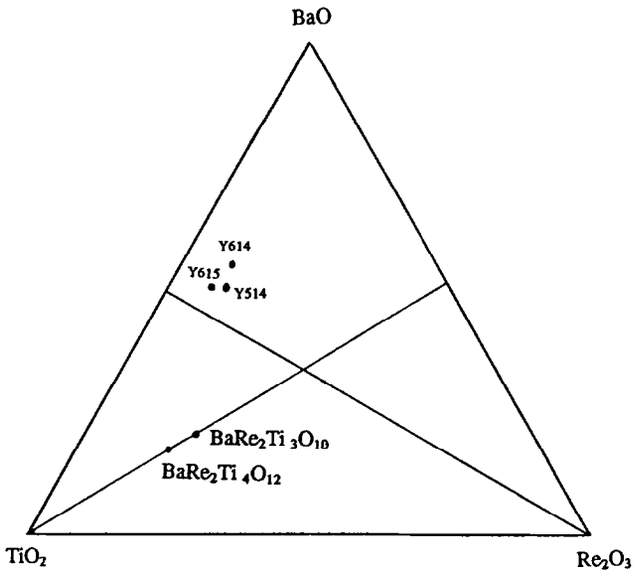

Fig. 1. Phase diagram of the $BaO–Re_2O_3–TiO_2$ ternary system (Re = Y, Nd, and Sm).

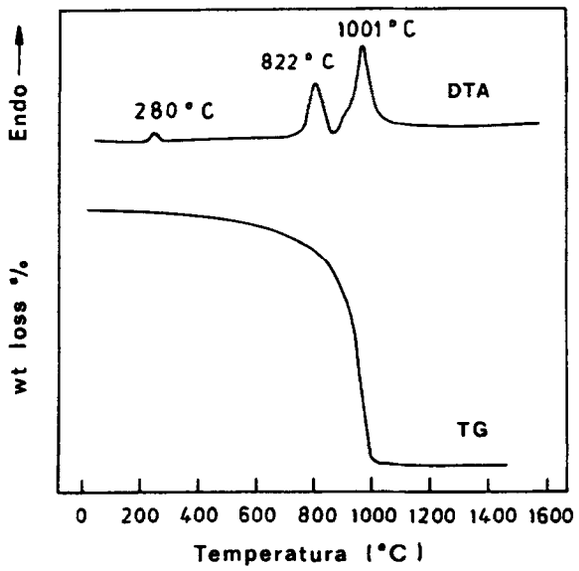

Fig. 2. Thermogravimetric and differential thermal analysis curves of the $6BaO–Y_2O_3–4TiO_2$ sample.

performed for the Y614 system with the heating rate of 10°C min^{-1}.

The calcinations at each calcining temperature and the final sintered samples were examined by X-ray powder diffraction (XRD) (Rigaku, Cu radiation) at room temperature to determine the phase assemblage. The microstructure of the sintered samples was observed by scanning electron microscopy (SEM) and electron probe microanalysis (EPMA) (Hitachi S4100 scanning electron microscope). The dielectric permittivity and dissipation factor of the samples were measured in the temperature range from 100 to 300 K at 1 kHz, 10 kHz, 100 kHz and 1 MHz (APD Cryogenics, Keithley 3330 LCZ, and HP4277A).

3 Results and Discussion

3.1 The phase-forming process in the BaO-rich corner of the $BaO–Y_2O_3–TiO_2$ system

3.1.1 $6BaO–Y_2O_3–4TiO_2$ ($YBa_3Ti_2O_{8.5}$) system

Figure 2 shows the TGA and DTA results for Y614. In the thermogravimetric curve, the small weight loss around 300°C is due to the evaporation of residual organic materials, caused by the manufacturing process, and absorbed water. A large weight loss occurring in the temperature range 850–1021°C corresponds to the release of CO_2. The DTA curve reveals two endothermic peaks in the range 801–850°C and 949–1045°C, which correspond to the phase transformation of $BaCO_3$. The first peak arose from the γ-$BaCO_3$ to β-$BaCO_3$ phase transformation,[6] while the second peak (949–1045°C) was attributed to the β-$BaCO_3$ to α-$BaCO_3$ phase transformation.[6] No peak in the DTA curve was observed above 1100°C.

The phases of powders calcined at various temperatures and of samples sintered at 1515°C were identified by XRD. The results are shown in Fig. 3.

It is assumed that the following chemical reactions occurred:

$$BaCO_3 + TiO_2 \rightarrow BaTiO_3 \quad (1)$$

$$BaCO_3 + TiO_2 \rightarrow Ba_2TiO_4 \quad (2)$$

$$BaTiO_3 + BaCO_3 \rightarrow Ba_2TiO_4 \quad (3)$$

$$BaTiO_3 + Ba_2TiO_4 + Y_2O_3 \rightarrow YBa_3Ti_2O_{8.5} \quad (4)$$

(1) The powder calcined at 900°C contains five phases: $BaCO_3$, Y_2O_3, $BaTiO_3$, Ba_2TiO_4 and $YBa_3Ti_2O_{8.5}$. The main phase is $BaTiO_3$, and only a small amount of the $YBa_3Ti_2O_{8.5}$ phase was formed. Some of the raw materials, $BaCO_3$ and Y_2O_3, remain. The TiO_2 phase has not been detected; this implies that TiO_2 has reacted completely. Reactions (1), (2) and (3) predominate at 900°C.

(2) The phases are $YBa_3Ti_2O_{8.5}$, Ba_2TiO_4, $BaTiO_3$, and Y_2O_3 for the powders calcined at 1000 and 1100°C.

(3) An increase in the $YBa_3Ti_2O_{8.5}$ takes place at 1200°C, with small amounts of the Ba_2TiO_4, $BaTiO_3$ and Y_2O_3 phases remaining. At 1300°C, the process is the same as that at 1200°C.

(4) Above 1400°C, only the single-phase $YBa_3Ti_2O_{8.5}$ is observed. The reaction predominating is illustrated by eqn (4).

Figure 4 shows the relative intensity of specific XRD peaks for each phase as a function of heating temperatures. It is clear that the relative intensity of the $YBa_3Ti_2O_{8.5}$ phase increases continuously

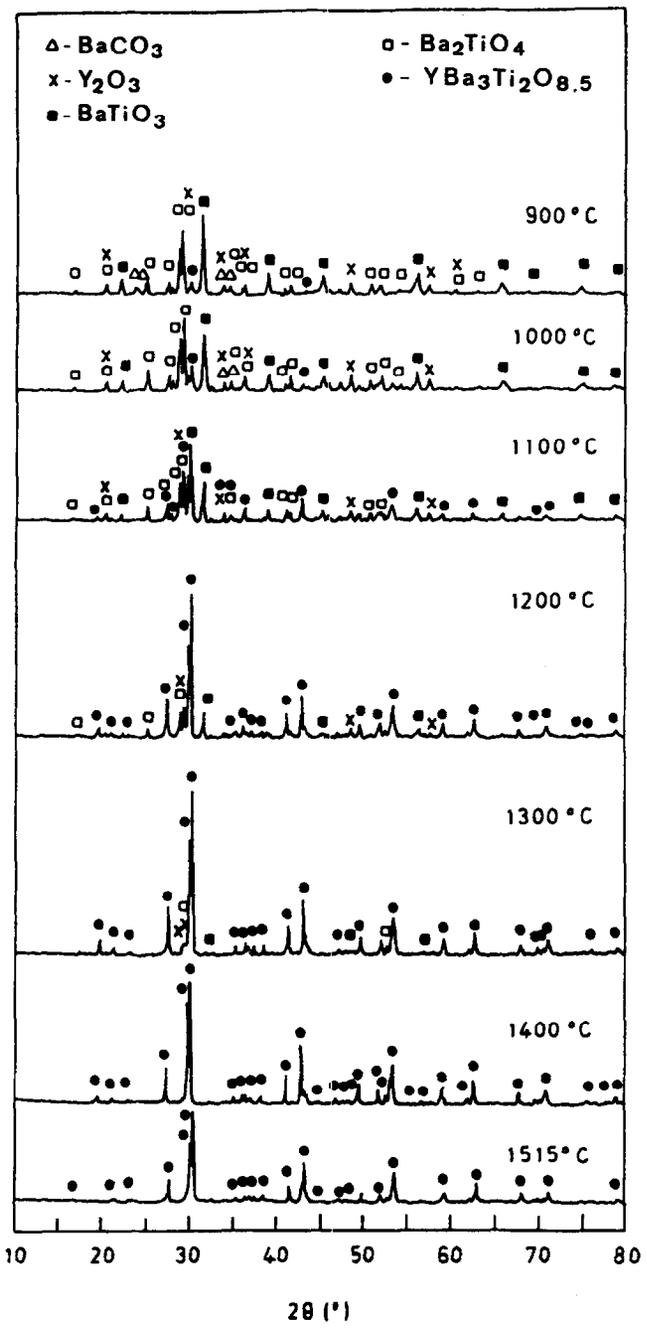

Fig. 3. X-ray powder diffraction patterns of $6BaO–Y_2O_3–4TiO_2$ powders calcined and sintered at various temperatures.

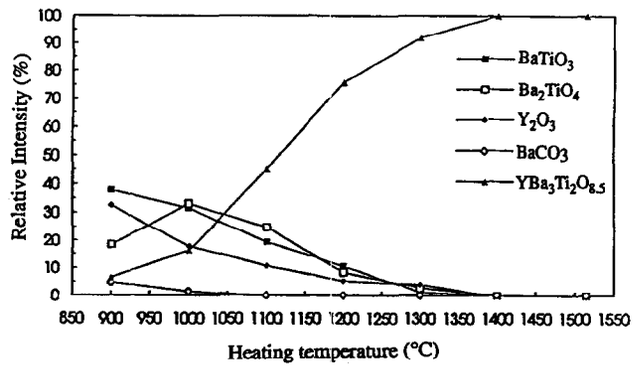

Fig. 4. Relative intensity of specific XRD peaks for each detected phase as a function of heating temperature for the Y614 sample.

and reaches nearly 100% in the high-temperature range (1400–1515°C), the relative intensities of the other phases decreasing with increasing temperature and becoming zero at 1400°C.

3.1.2 $6BaO–Y_2O_3–5TiO_2$ system

The typical composition of the TiO_2-rich phases of the $BaO–Re_2O_3–TiO_2$ ternary system is that with the $BaO:Re_2O_3:TiO_2$ ratio = 1:1:4 (written as $BaRe_2Ti_4O_{12}$). However, it is reported that the material with higher TiO_2 content, in which the ratio $BaO:Re_2O_3:TiO_2$ is 1:1:5, also exhibits excellent dielectric properties at microwave frequencies.[2] Correspondingly, it might be interesting to study the BaO-rich corner in the $BaO–Re_2O_3–TiO_2$ ternary system with high proportion of TiO_2. The

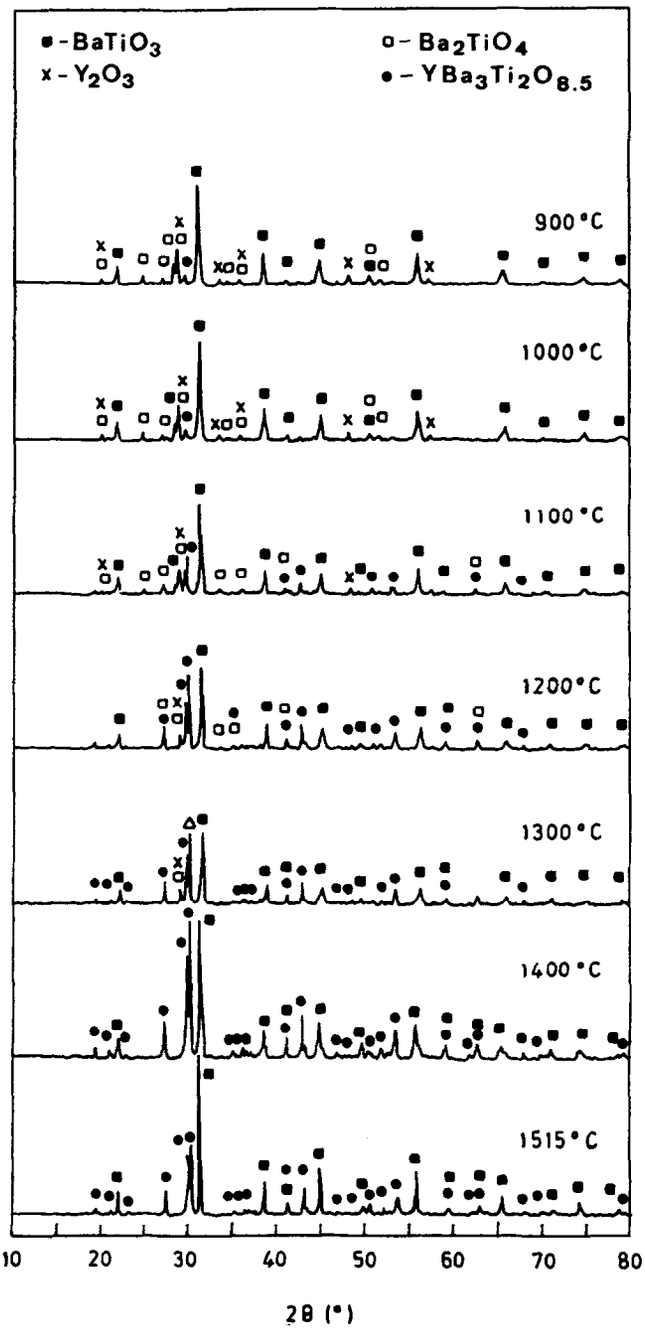

Fig. 5. X-ray powder diffraction patterns of $6BaO–Y_2O_3–5TiO_2$ powders calcined and sintered at various temperatures.

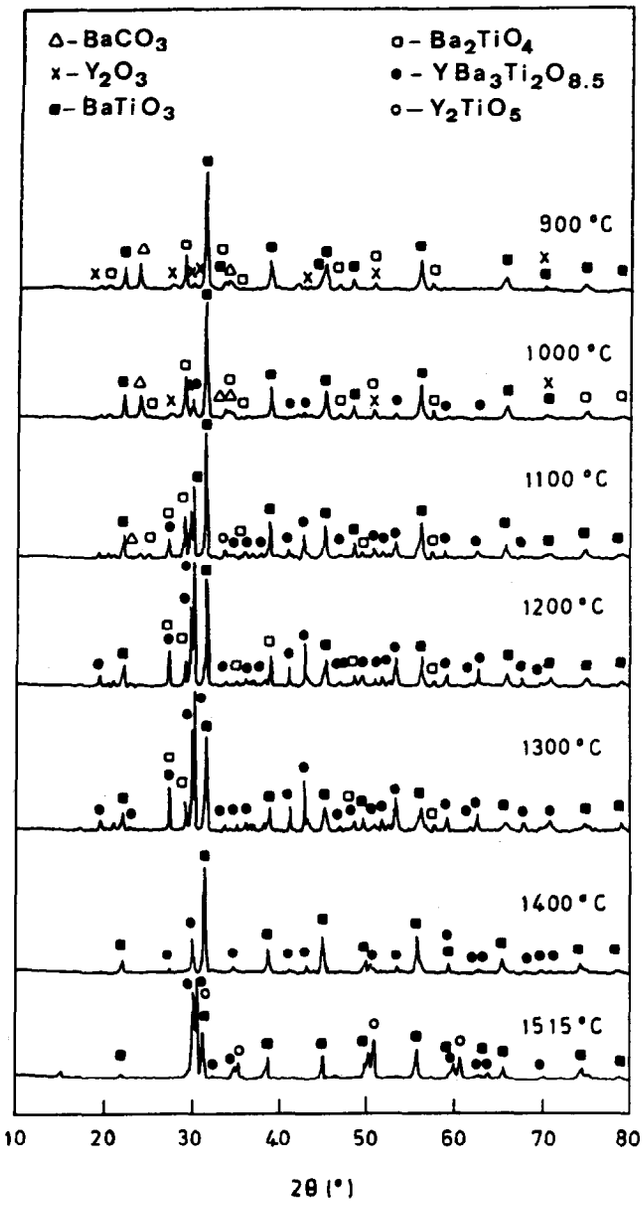

Fig. 6. X-ray powder diffraction patterns of $5BaO–Y_2O_3–4TiO_2$ powders calcined and sintered at various temperatures.

powder mixture with the $BaO:Y_2O_3:TiO_2$ ratio equal to 6:1:5 was calcined at 900, 1000, 1100, 1200, 1300 and 1400°C for 2 h and sintered at 1515°C for 6 h respectively. The X-ray powder diffraction results are shown in Fig. 5. The reactions can be also described by the eqns (1)–(4).

After calcining at 900°C for 2 h the powder contains four phases: $BaTiO_3$, Ba_2TiO_4, Y_2O_3 and a small amount of $YBa_3Ti_2O_{8.5}$. TiO_2 and $BaCO_3$ have not been observed; this implies that TiO_2 and $BaCO_3$ have reacted completely with each other and with Y_2O_3. After calcining at 1000°C for 2 h, and at 1100°C for 2 h, the results are the same as those at 900°C, and the amount of $YBa_3Ti_2O_{8.5}$ has increased. Three phases are observed: $BaTiO_3$, $YBa_3Ti_2O_{8.5}$ and a small amount of Y_2O_3, after calcining at 1200 and 1300°C for 2 h. Above 1400°C only two phases: $YBa_3Ti_2O_{8.5}$ and $BaTiO_3$, are observed by XRD. The sample sintered at 1515°C for 6 h also shows a two-phase structure consisting of $YBa_3Ti_2O_{8.5}$ and $BaTiO_3$ identified from the XRD results.

3.1.3 $5BaO–Y_2O_3–4TiO_2$ system

The phase-forming process of the ternary system $5BaO–Y_2O_3–4TiO_2$ was studied by the same method as used for the $6BaO–Y_2O_3–4TiO_2$ and $6BaO–Y_2O_3–5TiO_2$ systems. The XRD patterns of the $5BaO–Y_2O_3–4TiO_2$ powder calcined and sintered at various temperatures are shown in Fig. 6. The phase formation and chemical reactions for the Y514

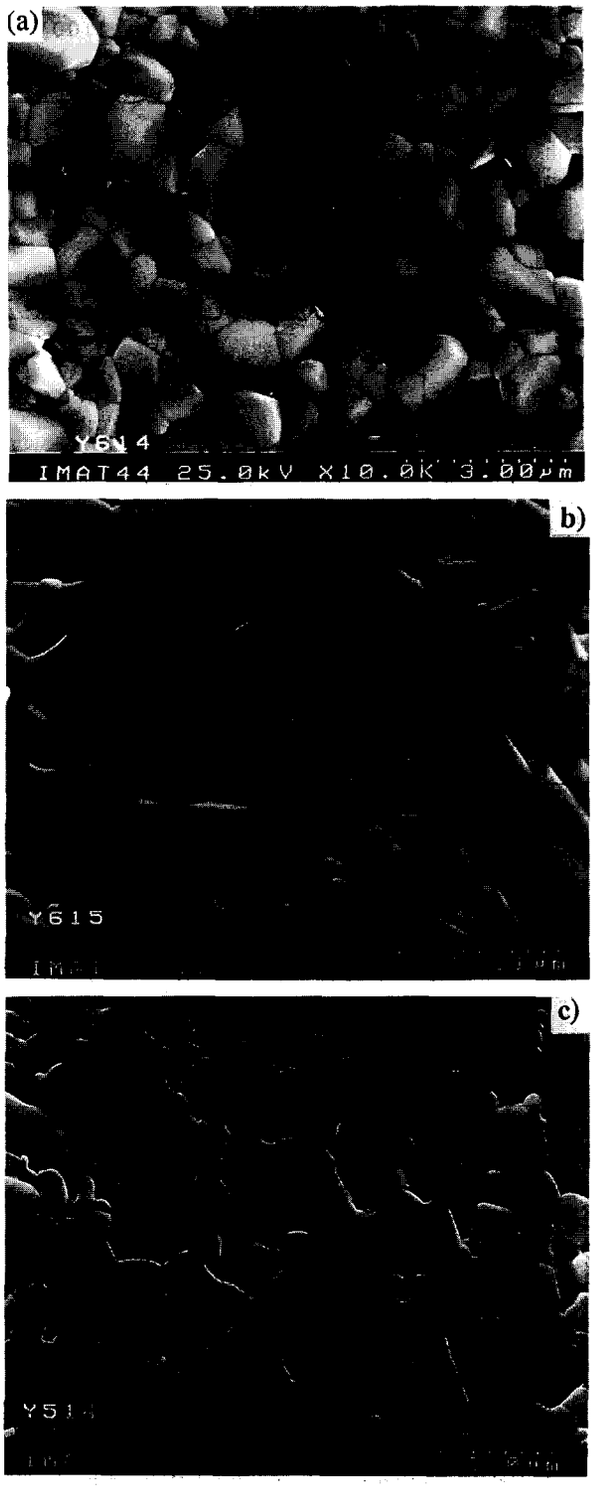

Fig. 7. SEM photomicrographs: (a) $YBa_3Ti_2O_{8.5}$, (b) Y615 and (c) Y514 sintered ceramics.

during calcining and sintering are similar to those of the Y615. However, besides the two main phases (Y614 and $BaTiO_3$), another phase was observed in the sintered samples which was identified as Y_2TiO_5. Here, another solid state reaction occurred:

$$TiO_2 + Y_2O_3 \rightarrow Y_2TiO_5 \quad (5)$$

3.2 Microstructure

Figure 7 shows photomicrographs of polished and thermally etched sections of Y614 ($YBa_3Ti_2O_{8.5}$), Y615 and Y514 samples sintered at 1515°C for 6 h. It can be seen that the $YBa_3Ti_2O_{8.5}$ ceramic sample shows a dense, single-phase microstructure with equiaxed grains. The Y615 ceramic sample shows a dense, but two-phase microstructure: one is the matrix phase with equiaxed grains, the other is the secondary phase with elongated grains. In the case of the Y514 ceramic, a small amount of a third (black) phase was observed besides the main two phases.

The phases were also microanalysed by EPMA. The results show that the composition of the matrix phase is near $YBa_3Ti_2O_{8.5}$; the elongated grains contain Ba and Ti in the case of the Y615 and Y514 ceramics; and the black grains contain Y and Ti in the case of the Y514 ceramics. By comparison with the XRD results, it is concluded that the matrix phase is $YBa_3Ti_2O_{8.5}$, the elongated phase is $BaTiO_3$ and the black grains, in the case of Y514 sample, are $Y_2Ti_2O_7$. In addition, it can also be seen that the grain size of the $YBa_3Ti_2O_{8.5}$ ceramic is small. The average grain size of the $YBa_3Ti_2O_{8.5}$ phase is less than 1 μm for single-phase Y614; and the grain size of the $YBa_3Ti_2O_{8.5}$ phase in the Y615 and Y514 compositions is about 2–3 μm.

3.3 Dielectric properties

The dielectric properties of this series of ceramics were measured and the results are shown in Table 1. It can be seen that all the samples are frequency-stable in the range 10 to 10^6 Hz. For the single-phase $YBa_3Ti_2O_{8.5}$, its relative permittivity is about 29 at 1 MHz, and dielectric dissipation factor is about 0·001; i.e. the quality factor is about 1000. For the Y615 and Y514 ceramics, the permittivity is about 100–120 and the dielectric dissipation factor is 0·0046–0·0066.

The temperature dependence of the permittivity of the $YBa_3Ti_2O_{8.5}$, Y615 and Y514 ceramics is shown in Fig. 8. The results indicate that no abnormal phenomenon occurred in the temperature interval from −173 to 127°C. The temperature coefficient in the temperature range −173 to 127°C is about +818 ppm $°C^{-1}$ for Y614, +132 ppm $°C^{-1}$ for Y615, and +222 ppm $°C^{-1}$ for Y514.

4 Conclusions

$YBa_3Ti_2O_{8.5}$ (Y614), a compound located in the BaO-rich corner of the $BaO–Y_2O_3–TiO_2$ ternary

Table 1. Dielectric properties of $BaO–Y_2O_3–TiO_2$ ceramics

	1 kHz		*10 kHz*		*100 kHz*		*1 MHz*	
Sample	ϵ	*tg*δ	ϵ	*tg*δ	ϵ	*tg*δ	ϵ	*tg*δ
Y614	30	0·005	29·5	0·0025	29·5	0·007	29	0·001
Y615	120	0·105	118	0·007	117	0·0074	115	0·0066
Y514	122	0·133	121	0·0085	117	0·008	115	0·0046

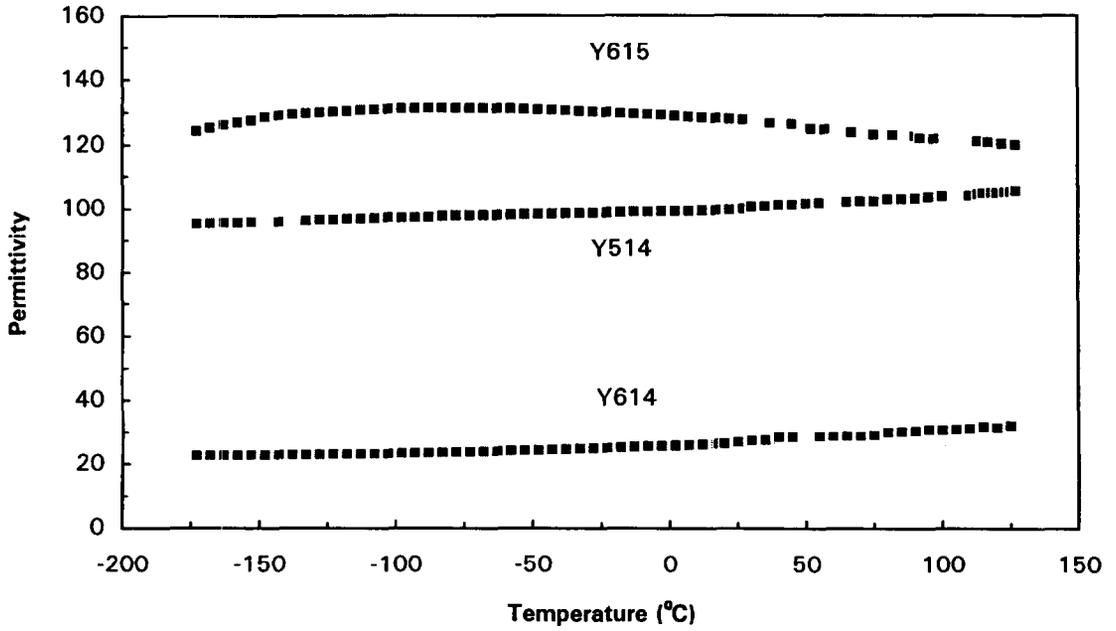

Fig. 8. Temperature dependence of permittivity of the Y614, Y615 and Y514 ceramics.

system, was synthesized and sintered as a single-phase ceramic. The dielectric properties of this material (permittivity $\epsilon = 29$, quality factor $Q = 1000$) are reported here for the first time.

Compositions with the ratio of $BaO:Y_2O_3:TiO_2$ equal to 6:1:5 and 5:1:4, were also synthesized. The Y615 ceramic consists of two phases ($YBa_3Ti_2O_{8.5}$ and $BaTiO_3$), and the Y514 ceramic consists of three phases ($YBa_3Ti_2O_{8.5}$, $BaTiO_3$ and Y_2TiO_5). They are dense ceramic composites.

This series of BaO-rich compositions in the $BaO–Y_2O_3–TiO_2$ ternary system with high-performance dielectric properties, are new kinds of ceramics. Their dielectric properties have not been reported before, to the authors' knowledge. The preliminary dielectric properties measurements indicate that this series of ceramic materials might be good candidate materials for high-voltage capacitors or electronic devices to be used at high frequency or even at microwave frequencies. Further work will be conducted to study the effect of doping with other elements (e.g. Pb, Bi) to promote their dielectric properties, and to understand the physical dielectric mechanisms responsible for the dielectric properties of the $YBa_3Ti_2O_{8.5}$ single-phase compound.

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