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Synthesis and Characterization of $Ba(Ti_{1-x}Ce_x)O_3$ Ceramics

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Abstract

A series of $Ba(Ti_{1-x}Ce_x)O_3$ dielectric ceramic materials was synthesized by the mixed oxide method with $x = 0{\cdot}1, 0{\cdot}2, 0{\cdot}3, 0{\cdot}33, 0{\cdot}4$ *and* $0{\cdot}5$. *The phase-forming process, the crystal structure of the main phase, the ceramic microstructure and the dielectric properties were studied. The results show that the compositions with* $x \leq 1/3$ *are mainly single-phase solid solutions of $BaTiO_3$ and $BaCeO_3$. The solubility limit is exceeded for* $x = 0{\cdot}4$. *Permittivity values ranging from 800 to 3700 with dissipation factors between 0·01 and 0·1 were measured at 1 MHz for the solid solutions, and a dielectric relaxation behaviour was observed. © 1997 Elsevier Science Limited.*

1 Introduction

In previous papers, a series of dielectric ceramics with the general composition $ReBa_3Ti_2O_{8{\cdot}5}$, which are in the BaO-rich corner of the $BaO–Re_2O_3–TiO_2$ (Re = Y, Nd, Sm, etc.) system, have been described by the authors.[1,2] The primary experimental results indicated that this group of materials has permittivity values (ε) > 25 and quality factor (Q) > 1000 at 1 MHz.

In the BaO-rich corner of the $BaO–Re_2O_3–TiO_2$ ternary system, single-phase compounds with the general composition $ReBa_3Ti_2O_{8+\delta}$ can only be formed when Re = Y, Nd, Sm; they belong to the hexagonal crystal system. When Re = La or Pr, a multiphase material is formed. When Re = Ce, the results of X-ray diffraction analysis indicated that the composition $CeBa_3Ti_2O_{8+\delta}$ belongs to the tetragonal system. In addition, it was observed that the composition $CeBa_3Ti_2O_{8+\delta}$ was formed by solid solution of $BaTiO_3$ with $BaCeO_3$.

Although some work has been done on the $BaO–CeO_2–TiO_2$ ternary system,[3-5] and much work on CeO_2-doped $BaTiO_3$,[6] the detailed phase-forming process and dielectric properties of $Ba(Ti_{1-x}Ce_x)O_3$ solid solution has been less reported. It seemed, therefore, meaningful to study the synthesis and dielectric properties of several $Ba(Ti_{1-x}Ce_x)O_3$ solid solutions.

The present paper reports the phase-forming process, crystal structure, microstructure and dielectric properties of $Ba(Ti_{1-x}Ce_x)O_3$ ceramics for $0 \leq x \leq 0{\cdot}5$.

2 Experimental Procedure

The ceramics were prepared by the mixed oxide method. The starting materials ($BaCO_3$, TiO_2 and CeO_2) were weighed according to the ratio of $Ba(Ti_{1-x}Ce_x)O_3$ where $x = 0, 0{\cdot}1, 0{\cdot}2, 0{\cdot}3, 0{\cdot}33, 0{\cdot}4$ and $0{\cdot}5$, respectively. Then they were wet mixed in an agate planetary mill with agate balls for 5 h. After drying, the powders were isostatically pressed at 300 MPa. Finally, the samples were sintered in air at 1540°C for 6 h.

X-ray powder diffraction analysis (XRD) was carried out, at room temperature, to determine the phase assemblage. The microstructure was observed by scanning electron microscopy (SEM). The dielectric properties were measured with a Keithley 3330 LCZ meter and Solartron 1260 Impedance Analyzer at different temperatures and different frequencies. Thermogravimetric (TG) and Differential Thermal Analysis (DTA) were used to evaluate the reactions occurring during heating.

3 Results and Discussion

3.1 Phases in the $Ba(Ti_{1-x}Ce_x)O_3$ system

3.1.1 Forming process of the phases in the $Ba(Ti_{1-x}Ce_x)O_3$ system

A series of compositions in the $Ba(Ti_{1-x}Ce_x)O_3$ system, with $x = 0{\cdot}1, 0{\cdot}2, 0{\cdot}3, 0{\cdot}33, 0{\cdot}4$ and $0{\cdot}5$, were synthesized. The phase present in samples calcined at different temperatures was identified by XRD. Data for the $x = 0{\cdot}2$ composition are

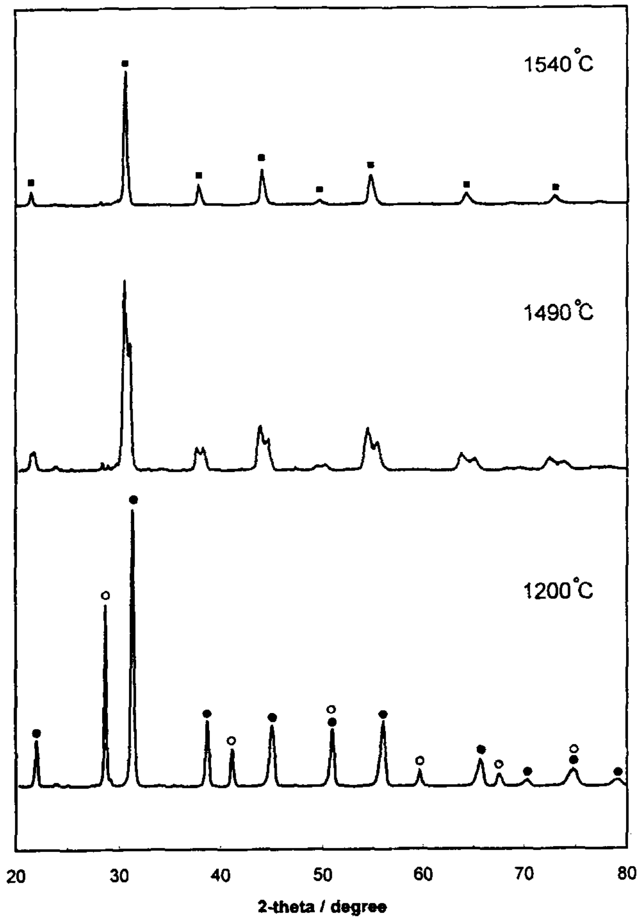


Fig. 1. X-ray powder diffraction patterns of the $Ba(Ti_{0·8}Ce_{0·2})O_3$ composition calcined and sintered at different temperatures. (■) $Ba(Ti_{1-x}Ce_x)O_3$ phase; (○) $BaCeO_3$ phase; (●) $BaTiO_3$ phase.

shown in Fig. 1; similar results were obtained for the other compositions. The results show the following:

(1) After calcination at 1200°C, it is observed that two phases, $BaCO_3$ and $BaCeO_3$, were formed by reaction between the $BaTiO_3$ and TiO_2 or CeO_2.

$$BaCO_3 + TiO_2 \rightarrow BaTiO_3 + CO_2\uparrow \quad (1)$$
$$BaCO_3 + CeO_2 \rightarrow BaCeO3 + CO_2\uparrow \quad (2)$$

(2) From Fig. 1, it can be seen that with the increase of the sintering temperature the diffraction peaks of the two phases move towards each other, overlapping for the highest temperature. This means that the crystal structure of each phase is modified by the incorporation of the other one, until a single solid solution phase is obtained.

After calcination at 1200°C, the distance between the strongest diffraction peaks (110) of the $BaTiO_3$ and $BaCeO_3$ phases is about 0·2596 Å. After sintering at 1490°C, this distance becomes smaller, about 0·0503 Å. Finally, after sintering at 1540°C, the group of the two individual peaks becomes one, indicating the presence of only one phase.

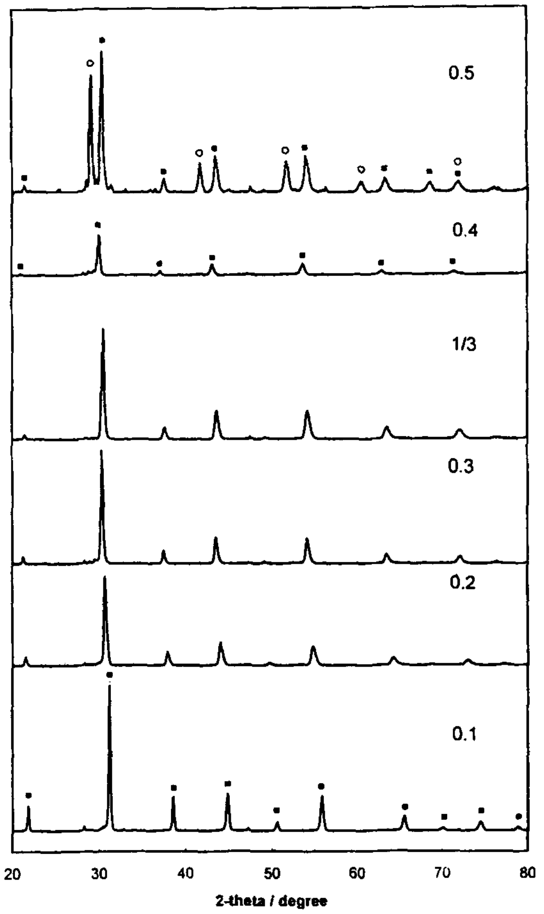


Fig. 2. X-ray powder diffraction patterns of the $Ba(Ti_{1-x}Ce_x)O_3$ (x = 0·1, 0·2, 0·3, 0·33, 0·4, 0·5) ceramics sintered at 1540°C for 6 h. (■) $Ba(Ti_{1-x}Ce_x)O_3$ phase; (○) $BaCeO_3$ phase.

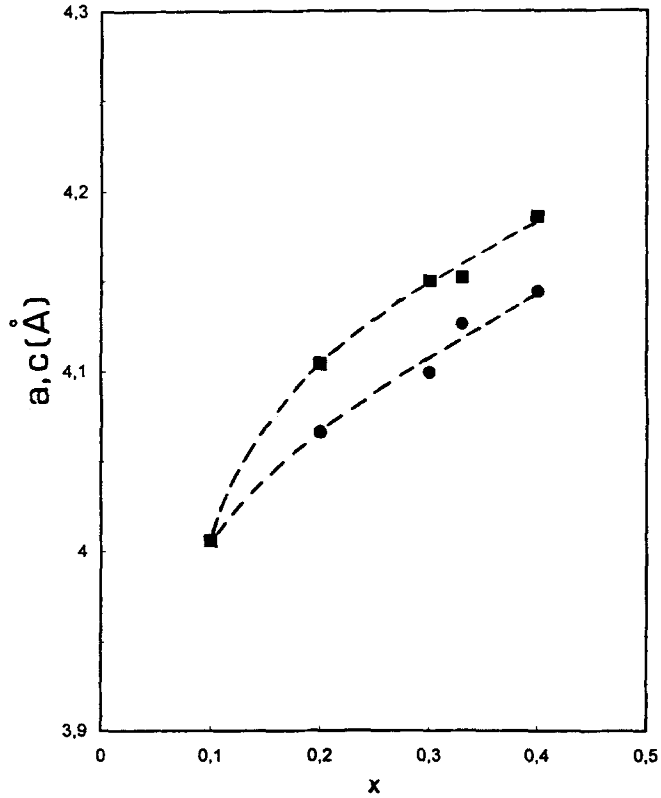
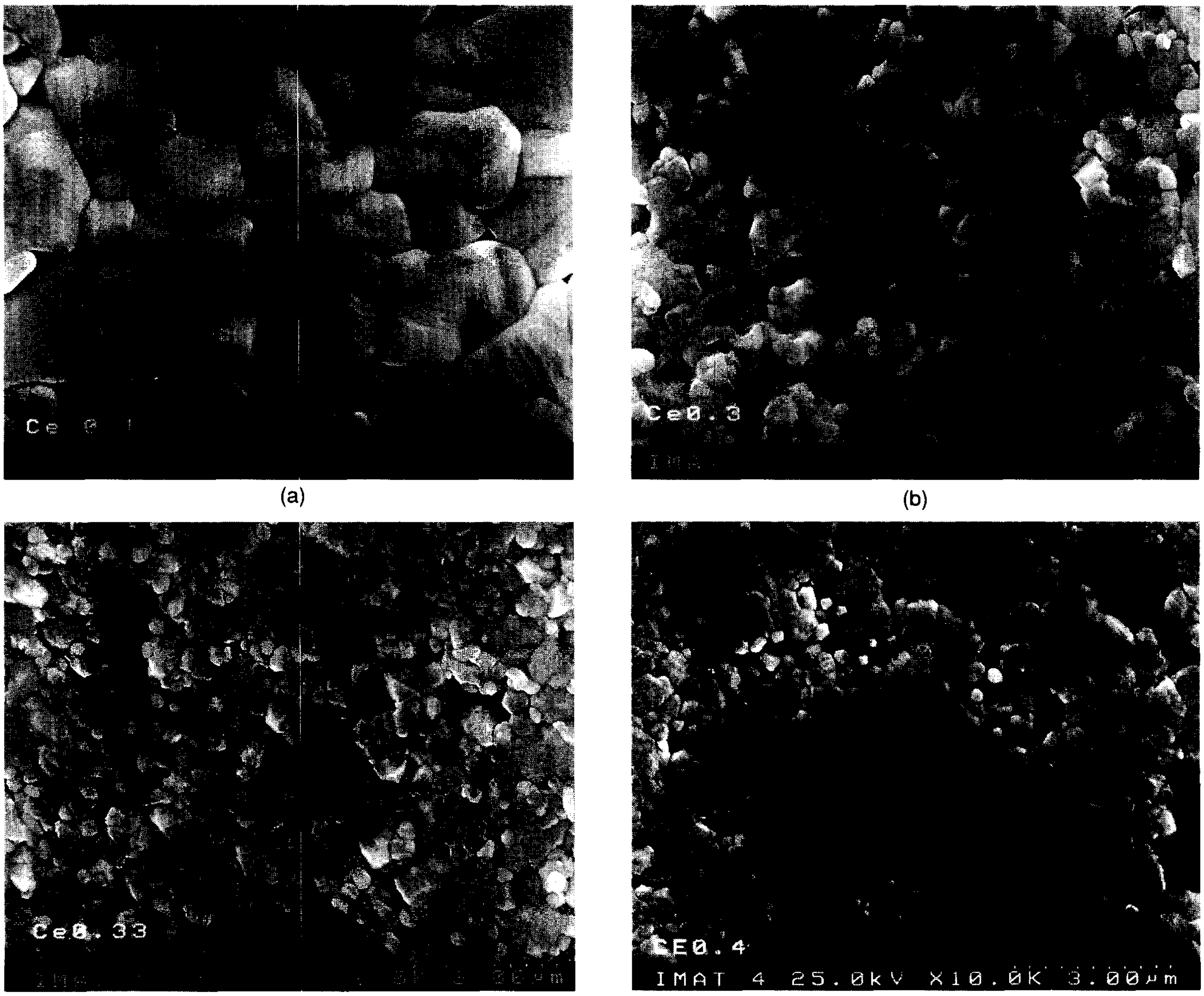


Fig. 3. The variation in the lattice parameter with the Ce content in the $Ba(Ti_{1-x}Ce_x)O_3$ ceramics. (●) lattice parameter a; (■) lattice parameter (c).



(a) (b)

(c) (d)

Fig. 4. Photomicrographs of polished sections (thermally etched) of $Ba(Ti_{1-x}Ce_x)O_3$ (x = 0·1, 0·3, 0·33 and 0·4) ceramics, sintered at 1540°C for 6 h.

The chemical reaction can be described by the equation:

$$(1\text{-}x)BaTiO_3 + xBaCeO_3 \rightarrow Ba(Ti_{1-x}Ce_x)O_3 \quad (3)$$

3.1.2 The phases and crystal structure in the $Ba(Ti_{1-x}Ce_x)O_3$ system

Figure 2 shows the X-ray powder diffraction patterns of the $Ba(Ti_{1-x}Ce_x)O_3$ ceramics, in which the Ce content changes from 0·1 to 0·5, sintered at 1540°C for 6 h. It can be seen that the samples with x = 0·1, 0·2, 0·3 and 0·33 are mainly single-phase, with a small amount of an identified second phase. For x = 0·4 and 0·5, the content of extra phases increases with one of them being identified as $BaCeO_3$, and another as CeO_2. This indicates that the solid solubility limit is about 0·33 in the $Ba(Ti_{1-x}Ce_x)O_3$ system when prepared by the mixed oxide method by sintering at 1540°C.

The results of XRD data show that the crystal structure can be well indexed to the cubic system for x = 0·1. But for x >0·1, it is better indexed to the tetragonal system. The variation in the lattice parameter with the Ce content is shown in Fig. 3. It indicates that the lattice parameter increases with the increase in Ce content for x <0·4.

3.2 Microstructure of the $Ba(Ti_{1-x}Ce_x)O_3$ ceramics

Figure 4 shows photomicrographs of polished sections (thermally etched) of $Ba(Ti_{1-x}Ce_x)O_3$ solid solutions (x = 0·1, 0·3, 0·33 and 0·4) samples, sintered at 1540°C for 6 h. It can be seen from the microstructures that the ceramics are dense. For compositions with $x \leq$ 0·33, a small amount of the second-phase particles can be seen dispersed in the main phase matrix. The microstructure of the x = 0·4 ceramic is clearly multiphase.

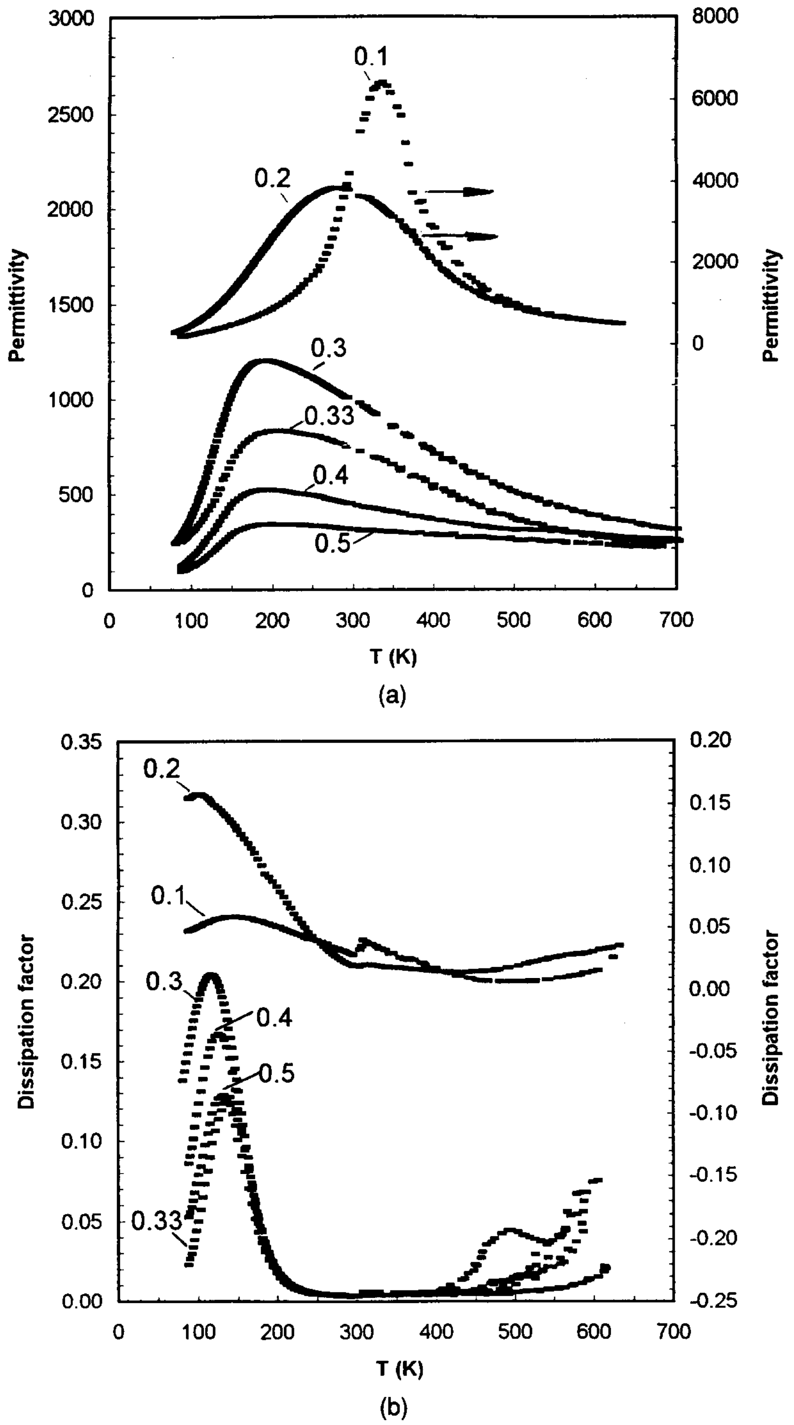


Fig. 5. Variation of the permittivity and dissipation factor with the temperature of the Ba($Ti_{1-x}Ce_x$)O_3 (x = 0·1, 0·2, 0·3, 0·33, 0·4 and 0·5) ceramics sintered at 1540°C for 6 h.

3.3 Dielectric properties of the Ba($Ti_{1-x}Ce_x$)O_3 ceramics

The temperature dependence of the dielectric properties of this series of ceramics has been measured. The variation of the permittivity and dissipation factor with the temperature is shown in Fig. 5. The results show that the dielectric permittivity, at any temperature, decreases as the Ce content increases. The same behaviour is observed for the temperature at which the dielectric permittivity and the loss factor reach a maximum.

The values of dielectric permittivity are 3700, 2120, 800 and of dissipation factor are 0·116, 0·02, 0·013 at 1 MHz at room temperature for the compositions with x = 0·1, x = 0·2 and x = 0·33, respectively. The dielectric properties indicate that this group of dielectric ceramics will probably be promising materials for capacitor applications.

4 Conclusions

A series of new perovskite-type structure solid-solution Ba($Ti_{1-x}Ce_x$)O_3 dielectric materials were synthesized. The compositions for $x \leq 0{\cdot}33$ are mainly single-phase, dense ceramics; for $x = 0{\cdot}4$ and 0·5, several phases are present, besides the solid solution, one of which is identified as $BaCeO_3$ and the other as CeO_2. The preliminary dielectric property measurements indicate that this series of ceramics could be candidates for capacitor applications.

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