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Different microstructure and dielectric properties of $Ba_{1-x}Ca_xTiO_3$ ceramics and pulsed-laser-ablated films

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Abstract

A comparative study of the microstructure and dielectric properties between $Ba_{1-x}Ca_xTiO_3$ (BCT) ceramics and films were performed in the whole Ca concentration range of x = 0-1. The ceramics were prepared by conventional solid-state reaction technique and the films by the method of pulsed-laser deposition. X-ray diffraction (XRD) study of the BCT ceramics exhibited a pure tetragonal phase for x = 0-0.25, a tetragonal–orthorhombic diphase for x = 0.25-0.85 and a pure orthorhombic phase for x = 0.90-1.00. And the dielectric phase transition temperature from tetragonal to cubic was marginally affected by the Ca doping into BaTiO₃. However, BCT films deposited on Pt/Si/SiO₂/Si substrates showed a different microstructure and dielectric properties. Tetragonal–orthorhombic diphase was not found in the BCT films for x = 0.25-0.85, and a large decrease of the Curie point and diffuse phase transition were observed in the BCT films. Based on the compositional analysis, such phenomena were ascribed to the occupancy of some Ca²⁺ to the Ti⁴⁺ sites in the BCT films. © 2006 Elsevier Ltd. All rights reserved.

Keywords: A. Ceramics; A. Thin films; B. Laser deposition

1. Introduction

Ferroelectric materials have been applied to many electronic and optical devices, utilizing their excellent dielectric, piezoelectric and optical properties. Specially, BaTiO₃ and isovalent-substituted BaTiO₃ are the promising candidates and have been actively studied. Among them, Ca doped BaTiO₃ (Ba_{1-x}Ca_xTiO₃, BCT) crystals are considered to be one of the foremost potential candidates for the lead-free electro-optic modulators and memory devices [1]. And the BCT ceramics near the solubility limit of x = 0.23 have shown high electrostrictive strain of 0.22% at an electric field of 50 kV/cm [2].

Microstructure and dielectric properties of BCT ceramics prepared by conventional solid-state reaction technique have been reported by several workers [2–8]. It has been found that Ca^{2+} replaces Ba^{2+} in $BaTiO_3$ to form tetragonal BCT solid solutions when *x* is less than 0.23. Above the solubility limit of x = 0.23, the ceramics are in diphasic coexistence and composed of tetragonal $Ba_{0.8}Ca_{0.2}TiO_3$ solid solution and orthorhombic $Ba_{0.07}Ca_{0.93}TiO_3$ solid solution. This insolubility region extended to x = 0.90, and above this limit orthorhombic $CaTiO_3$ -based solid solutions were formed. This effect is quite puzzling, since other similar elements, like Sr^{2+} and Pb^{2+} , can replace Ba^{2+} in $BaTiO_3$ to form solid solutions without insolubility limitation.

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Modern micro-devices require high-performance materials in the form of films with thickness in the range of a few hundred and even tens of nanometers. However, the reports on the BCT films are lack in open literature. Victor et al. [9] reported the microstructure and dielectric properties of the BCT thin film with *x* between 0.05 and 0.17, and found that the films showed quite different dielectric behaviors from those of the corresponding ceramics. To the best of our knowledge, no detailed structural and dielectric studies have been reported for the BCT films in the whole Ca concentration (x = 0-1). In this paper, we report on a comparative study of the microstructure and dielectric properties between BCT ceramics and films in the whole Ca concentration range of x = 0-1.

2. Experiment

BCT ceramics with x between 0 and 1 were prepared by conventional solid-state reaction technique. High-purity starting powders of BaCO₃, TiO₂ and CaCO₃ were mixed with addition of alcohol, ball-milled for 10 h, then dried and heated at 900 °C for 4 h in air. After that, they were remixed and pressed into disk-shaped pellets with 10 mm in diameter, and finally sintered at 1400 °C for 4 h. The sintered pellets were polished to near 0.7 mm in thickness and the silver paste was coated on both sides as electrodes. BCT films were deposited onto the Pt/Si/SiO₂/Si substrates by a 248 nm KrF excimer pulsed laser (Lambda Physik 105i) with an energy density of 1.6 J/cm² using the above ceramics as targets. During the deposition, the substrate temperature was maintained at 700 °C and the laser frequency was 5 Hz. The base pressure was initially pumped down to 2.0×10^{-3} Pa and then high-purity oxygen gas was introduced into the chamber to a pressure of 20 Pa prior to the deposition. The thicknesses of all the BCT films were about 450 nm as measured by an ET350 Talysurf profilometer (Kosaka Laboratory Ltd.). For carrying out the electrical measurement, Pt dots of 0.28 mm in diameter were deposited onto the films at room temperature through a shadow mask by a radio-frequency sputtering technique. The temperature-dependence of the dielectric properties was measured by a HP4284 LCR meter in a computer-controlled Delta 9023 oven. The frequency dependence of the dielectric properties was measured by a HP4294A impedance analyzer. The ceramics and films were structurally characterized by a Rigaku D/MAX 3C X-ray diffraction (XRD). Scanning electron microscopy (SEM) of Hitachi S-4700 was used for the observation of the microstructure of the film surface. The composition of the element in targets and films were identified using energy-dispersive spectrometry (EDS) attached to a SEM of Hitachi S-4700 and X-ray photoelectron spectroscopy (PHI-550 Photoelectric Spectrometer, XPS).

3. Results and discussions

The typical microstructure of the BCT ceramics (x = 0, 0.5 and 1.0) is shown in Fig. 1(a). All the patterns show a polycrystalline perovskite nature without impurity phases. The pure BaTiO₃ ceramic shows a tetragonal phase with a distinct tetragonal splitting at (0 0 2)/(2 0 0), while the pure CaTiO₃ ceramic is an orthorhombic phase, as identified and indexed using the standard XRD data of the corresponding powder. In Ba_{0.5}Ca_{0.5}TiO₃ ceramic, the tetragonal and orthorhombic phases were coexisted. The peaks marked "*" in Fig. 1(a) are related to the tetragonal Ba-rich phase and the ones marked "#" to the orthorhombic Ca-rich phase. Fig. 1(b) shows the refined XRD patterns of BCT ceramics with different *x* from 0 to 1 near the tetragonal strongest peak (1 1 0) and orthorhombic strongest peak (1 2 1). The structures of the ceramics were determined to be a pure tetragonal phase for *x* from 0 up to 0.25, tetragonal and orthorhombic phase coexistence for x = 0.30-0.85, and a pure orthorhombic phase for x = 0.90-1.00. The results are similar to those reported [2]. However, the solubility limit for Ca addition in BaTiO₃, which is between 0.25 and 0.3, increased a little, and that within 0.85 and 0.9 for Ba addition in CaTiO₃ decreased a little, comparing with those reported (x = 0.23 and 0.93, respectively). This may be due to the different processes in the fabrication of the ceramics.

The XRD patterns for the BCT films (x = 0, 0.5 and 1.0) are presented in Fig. 2(a). It can be seen that the XRD results for the BCT films are different from those of the corresponding ceramics. The BCT films did not show a distinct tetragonal splitting when x is equal to 0 or 0.5. For pure BaTiO₃ film the lattice parameters were determined to be a = b = 3.995 Å and c = 4.034 Å, which are in agreement with the PDF card, and compare well with a = b = 3.995 Å and c = 4.034 Å as measured by Mitsui and Westphal [6]. So the pure BaTiO₃ film is still in tetragonal phase at room temperature, although the tetragonal splitting was not observed in the XRD pattern, which can be due to the grain size or substrate–film interface effect.

From Fig. 2(a), we also found that the double peaks near 32.3° corresponding to the tetragonal Ba-rich (1 1 0) peak and orthorhombic Ca-rich (1 2 1) peak in the BCT ceramics were not observed in the corresponding films with x



Fig. 1. (a) XRD patterns of the BCT ceramics for x = 0, 0.5 and 1.0; (b) refined XRD patterns of BCT ceramics for x from 0 to 1 near the tetragonal strongest peak (1 1 0) and orthorhombic strongest peak (1 2 1).

between 0.30 and 0.85. And, the evolution of the secondary phase was not observed in the BCT films. This characteristic is shown more clearly in Fig. 2(b), where the (1 1 0) peak is enlarged for *x* changing from 0 to 1. It is shown that the two peaks of (1 1 0) and (1 2 1) in Fig. 1(b) merge into one peak in Fig. 2(b), when *x* is between 0.3 and 0.85. When further comparing Figs. 2(b) and 1(b), we found that the position of this peak is between the ones of (1 1 0) and (1 2 1). Table 1 listed the detailed (1 1 0) and/or (1 2 1) peak positions (2θ values) of the BCT films and ceramics for *x* = 0–1. From the table, we can get that: (1) for *x* = 0–0.25, the 2θ values of the (1 1 0) peak for the BCT films are a little smaller than those of the corresponding ceramics. However, for *x* = 0.9–1, the 2θ values are a little larger than those of the 2 θ values for (1 1 0) and (1 2 1) peaks of the corresponding ceramics. Above results indicates that lattice distortion appeared in the BCT films. This could be happened due to the occupancy of Ca²⁺ in the Ti⁴⁺ site and the compositional deviation in the films, which will be discussed in detail in the following paragraph.

Fig. 3(a) shows the dielectric constant of BCT ceramics for x = 0 and 0.25 at elevated temperature from 40 to 160 °C under 1, 10 and 100 kHz. We found that Ca addition in BCT ceramics causes a slight change of the Curie point, which lines at about 125 °C for x = 0, and at 115 °C for x = 0.25. In addition, Ca addition causes a slight decrease in peak height, but an increase in width. It was previously reported that [9], for BCT ceramics, the Curie point (cubic–tetragonal phase transition point) was not sensitive to the Ca concentration when x is less than 0.5. Present study is consistent with this point. However, for BCT films, Ca addition in BaTiO₃ film decreases the Curie point drastically. Fig. 3(b) is the corresponding dielectric constant of BCT films for x = 0 and 0.25. For pure BaTiO₃ film, a Curie point can be observed from the figure, which is about 112 °C and close to that of the corresponding target, although the



Fig. 2. (a) XRD patterns of the BCT films for x = 0, 0.5 and 1.0; (b) refined XRD patterns of BCT films for x from 0 to 1 near the tetragonal strongest peak (1 1 0).

transition peak is broadened and the peak height is lowered significantly. However, for BCT film with x = 0.25, the dielectric constant shows a monotonic decrease when the temperature increases from 40 to 160 °C, indicating the Curie temperature is lower than 40 °C in this case. Thus, there was a large decrease for the Curie point for Ba_{0.75}Ca_{0.25}TiO₃ film comparing with the corresponding target and the pure BaTiO₃ film.

Table 1		
The detailed (1,1,0) and/or (1,2,1) neak positions (2 θ values) of the BCT ceramics and films for	x = 0 - 1	

<i>x</i> (mole fraction)	2θ of ceramic (1 1 0) peak (°)	2θ of ceramic (1 2 1) peak (°)	Average 2θ value of ceramic (1 1 0) and (1 2 1) peak (°)	2θ of the corresponding
				film peak (°)
0	31.49	_	_	31.44
0.10	31.60	-	_	31.48
0.20	31.64	-	_	31.56
0.25	31.76	-	_	31.67
0.30	31.77	32.76	32.27	32.18
0.40	31.78	32.82	32.30	32.22
0.50	31.80	32.83	32.32	32.26
0.60	31.82	32.85	32.34	32.31
0.70	31.86	32.87	32.37	32.35
0.80	31.98	32.96	32.47	32.65
0.90	-	32.82	_	32.88
1.00	-	33.04	_	33.12



Fig. 3. Dielectric constant of BCT (a) ceramics and (b) films for x = 0 and 0.25 at elevated temperature from 40 to 160 °C under 1, 10 and 100 kHz.

As pointed out in Section 1, it has been established that the dielectric phase transition temperature near 120 °C from tetragonal to cubic phase is marginally affected by the substitution of the Ca²⁺ in Ba²⁺ site in the Ba_{1-x}Ca_xTiO3 ceramics. However, several groups [10,11] suggested that there is a probability of Ca²⁺ occupying the Ti⁴⁺ site in BaTiO₃ lattice, provided the atomic concentration ratio of (Ba + Ca)/Ti is larger than unity. This ratio leads to excess barium and thus forcing Ca²⁺ to occupy the Ti⁴⁺ site. The occupancy will cause a drastic decrease in the dielectric phase transition temperature, acting in the same manner as a hydrostatic pressure [12]. In addition, Zhuang et al. suggested that the occupancy of Ca²⁺ in the Ti⁴⁺ site will create a compressional stress and lead to the distortion of the lattice in BaTiO₃ [13]. We also note that Victor et al. [9] also observed an anomalous decrease of dielectric phase transition temperature in BCT films with *x* = 0.05 and 0.12, which was ascribed to the occupancy of the Ca²⁺ in the Ti⁴⁺ site.

In order to examine whether the shifting of the Curie point and lattice distortion of the BCT films in this study are due to the occupancy of the Ca^{2+} in the Ti^{4+} site, we performed the compositional analysis on both the BCT ceramics and films by EDS and the results were shown in Table 2. It can be seen that the atomic concentration ratios of

Table 2 The EDS compositional analysis results of BCT ceramics and films

(note fraction) (Da + Ca)/ If value of certaines (Da	(Ba + Ca)/Ti value of films	
0.20 1.00 1.18	8	
0.25 1.00 1.11	1	
0.40 1.00 1.25	5	
0.60 1.00 1.27	7	
0.90 1.00 1.25	5	

For ferroelectric films, the decrease in the dielectric phase transition temperature and the appearance of the relaxorlike dielectric behavior may also attribute to several other reasons, such as grain size effect and the stress existed between the film and substrate [9,14]. Fig. 4 shows the SEM micrographs of some BCT films. The dense and uniform micrographs are clearly seen in all samples, and the grain size was quite large (about 50–100 nm). So in our case the grain size effect can be ignored. In addition, the film–substrate stress effect is also not the main reason for the shifting of the Curie point, since the Curie point did not move significantly for pure BaTiO₃ film, comparing with that of the BaTiO₃ ceramic. However, the film–substrate dead layer effect will result in a relaxor-like behavior in the film, as pointed out in our previous study about (Pb,Sr)TiO₃ films [15].

Based on above discussion, we ascribed the lattice distortion and the decrease in the Curie temperature of the BCT films mainly to the occupancy of some Ca²⁺ in the Ti⁴⁺ site. Since the ion radius for Ca²⁺ is much larger than that of Ti⁴⁺, Ca²⁺ replacing Ti⁴⁺ in the octahedral sites of the perovskite structure will cause a localized expansion of the unit cell, and result in a lattice distortion. This lattice distortion makes the tetragonal Ba-rich phase and orthorhombic Ca-rich phase in the BCT films for x = 0.3 and 0.8 to be undiscerning through the XRD. The occupancy of Ca²⁺ in the Ti⁴⁺ sites also introduces the compressional stress in the lattice, resulting in a drastic decrease in the phase transition temperature. In addition, it will result in a compositional and structural disorder due to the symmetry breaking, due to the difference in valences (4+ versus 2+) and ionic radii (0.69 Å versus 0.99 Å) between the Ti⁴⁺ and Ca²⁺ ions on the B site of the ABO₃ perovskite structure [9]. This is believed to be responsible for the diffused phase transition observed in the Ca doped BaTiO₃ films, as the same manner happened in typical relaxors, such as Pb(Zn_{1/3}Nb_{2/3})O₃ [16].



Fig. 4. SEM micrograph of the BCT films: (a) x = 0.20; (b) x = 0.40; (c) x = 0.60; (d) x = 0.80.

1668

4. Conclusions

We have observed quite different microstructure and dielectric behaviors between the pulsed-laser-deposited BCT films and the corresponding ceramics. The BCT ceramics exhibit a pure tetragonal phase for *x* from 0.00 up to 0.25, tetragonal and orthorhombic phase coexistence for x = 0.30-0.85, and a pure orthorhombic phase for x = 0.90-1.00, along with a small change of the Curie point with *x* up to 0.5. However, BCT films deposited on Pt/Si/SiO₂/Si substrates tetragonal–orthorhombic diphase was not found in the BCT films for x = 0.25-0.85, and a large decrease of the Curie point and diffuse phase transition were observed in the BCT films. Such phenomena were ascribed to the occupancy of some Ca²⁺ to the Ti⁴⁺ sites in the BCT films.

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