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Composition driven ferroelectric transformations in lead-free $Ba(Ti_{1-x}Ce_x)O_3$ ($0.02 \le x \le 0.10$)

Vitaly Yu. Topolov [a], [*], Kumar Brajesh [b], Rajeev Ranjan [b]

[a] Department of Physics, Southern Federal University, 5 Zorge Street, 344090 Rostov-on-Don, Russia
[b] Department of Materials Engineering, Indian Institute of Science, Bangalore 560012, India

HIGHLIGHTS

- Dielectric and x-ray structural studies on heterophase $Ba(Ti_{1-x}Ce_x)O_3$ are performed.
- Phase contents are interpreted in terms of domains and stress-relief conditions.
- Role of domain types in complete stress relief at relatively small x is described.
- Key role of single-domain Amm2-phase interlayers in heterophases is first emphasized.
- Agreement between predicted and experimental phase contents at $0.02 \le x \le 0.10$ is stated.

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ABSTRACT

The Ce-modified lead-free $Ba(Ti_{1-x}Ce_x)O_3$ system is studied with regard to its dielectric and structural phase-transformation behaviour as a function of composition. Detailed Rietveld analysis of x-ray powder diffraction patterns revealed that the system exhibits orthorhombic (*Amm*2) + tetragonal (*P*4*mm*) phase coexistence for $x = 0.02$, pure orthorhombic (*Amm*2) for $0.02 < x < 0.07$ and orthorhombic (*Amm*2) + rhombohedral (*R*3*m*) phases for $0.07 \le x \le 0.10$. Heterophase states of the $Ba(Ti_{1-x}Ce_x)O_3$ system are analyzed taking into account domain (twin) types and stress-relief conditions at interphase boundaries. This analysis enables us to consider the role of specific domain types in a complete stress relief even at relatively small values of x. Volume fractions of the ferroelectric phases coexisting in samples are found using the volume fractions of some domain types in these phases at $0.02 \le x \le 0.10$. Results of our calculations and experimental studies on the volume fractions of the coexisting phases are consistent.

1. Introduction

The overwhelming majority of high-effective piezoelectric ceramics belong to ferroelectrics of the perovskite type and contain lead that is the key chemical element in ferroelectric $PbTiO_3$ and related solid solutions [1,2]. Heterophase states and elastic effects near the morphotropic phase boundary were studied in such systems of perovskite-type lead-containing solid solutions as $Pb(Zr_{1-x}Ti_x)O_3$, $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3 - xPbTiO_3$, $(1-x)Pb(Zn_{1/3}Nb_{2/3})O_3 - xPbTiO_3$, $(1-x)Pb(Fe_{1/2}Nb_{1/2})O_3 - xPbTiO_3$, $(1-x)BiFeO_3 - xPbTiO_3$, and $(1-x)BiScO_3 - xPbTiO_3$ (see, for instance, Refs. 3, 4). Lead-containing compounds may pollute and destroy the environment because of toxic characteristics of Pb. Undoubtedly one of the important challenges in modern materials science [5] is to find an high-effective alternative to lead-containing ferroelectric ceramics. In the last decade, lead-free ferroelectric, piezoelectric and related materials have been in the focus of research and development. As follows from recent studies, a few parameters of novel lead-free ferroelectrics [4–6] become comparable to the parameters of the well-known lead-based solid solutions.

$BaTiO_3$-based lead-free ferroelectric solid solutions have shown promising piezoelectric response [7–11] in the poled state. Recently, Kumar et al. have shown that Ce-modification of $BaTiO_3$ enhances the direct piezoelectric response as well as the high-field piezoelectric strain [12]. This system is therefore interesting as a potential lead-free piezoelectric since its properties are comparable with widespread ferroelectric ceramics such as PZT [1], ZTS, PCR [13], etc. In this paper we report the detailed structural

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[*] Corresponding author.
E-mail address: vutopolov@sfedu.ru (V.Yu. Topolov).

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characterization of the ferroelectric Ba(Ti$_{1-x}$Ce$_x$)O$_3$ (BCTx) solid-solution system as a function of composition. We also analyze the heterophase states and domain structures using the crystallographic approach [3,4] to reveal an influence of some domain types on the phase contents in BCTx.

2. Experimental

BCTx at $0.01 \le x \le 0.10$ was synthesized by the solid state method. High-purity grade powders of BaCO$_3$, TiO$_2$, CeO$_2$ were weighed according to their stoichometric ratios, which was followed by drying at 200 °C for 2 h in a hot air oven. These powders were thoroughly ball milled using a planetary ball mill (Fritsch P5) with zirconia jars and balls. Acetone was used as the mixing medium. Calcination was carried out at 1100 °C for 4 h. Sintering was carried out in two steps: first at 1300 °C for 4 h and then 1500 °C for 6 h. Scanning electron microscopy images (Fig. 1) revealed the specimens to be dense with the average grain size ~10^{-6} m. X-ray diffraction studies were carried out using Bruker, D8 Advance. Structural refinement was carried out by Rietveld refinement technique using FULLPROF software [14].

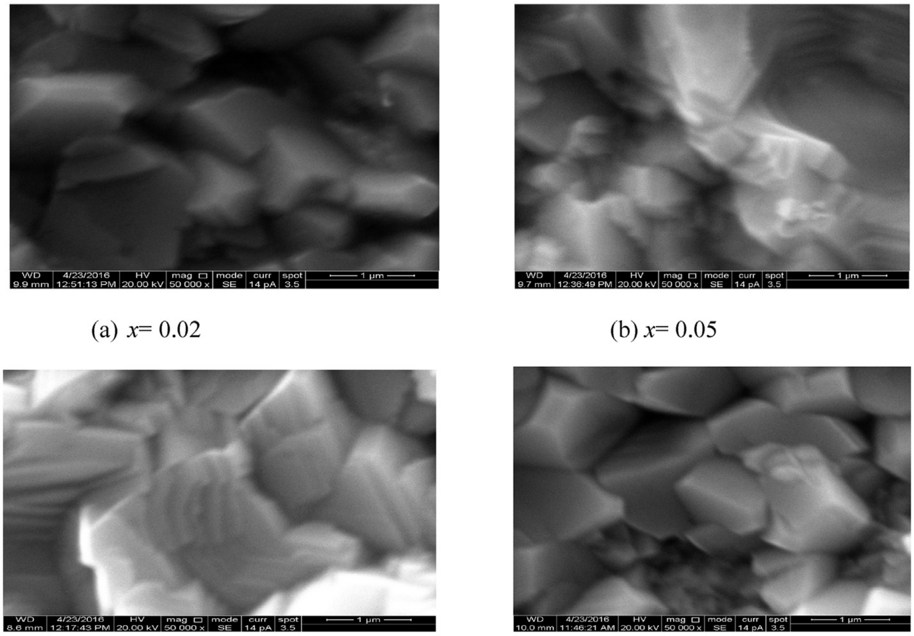
3. Results

3.1. Dielectric study

Fig. 2a–c shows the temperature dependence of relative dielectric permittivity ε and loss tangent tanδ of three representative compositions of BCTx. While the real part of ε shows one sharp maximum for $x = 0.02$ which becomes diffuse for higher compositions $x = 0.08$ and 0.12, the loss tangent revealed more information regarding the phase transitions. For example, a weak anomaly can be seen at ~35 °C in the loss tangent plot for $x = 0.02$. In analogy with the Zr-modified BaTiO$_3$, reported before [9,10], this transition is most likely to be orthorhombic–tetragonal (O–T in our further abbreviations). The proximity of this transition to room temperature suggests that both the phases may coexist at room temperature for this composition. The O–T phase boundary near room temperature is, therefore, be the most likely reason for the enhancement in the piezoelectric properties of the studied system, shown in Fig. 2a. The loss tangent at $x = 0.08$ shows three anomalies above room temperature. In analogy with a similar situation in Zr- and Sn-modified BaTiO$_3$ [9,10], the three anomalies can be attributed to rhombohedral (R) – O ($T_{R\text{-}O}$), O–T ($T_{O\text{-}T}$) and T–cubic (T_C) in the order of increasing temperature. For $x = 0.12$, the $T_{R\text{-}O}$ and $T_{O\text{-}T}$ are not detected. The loss tangent of this composition peaks at a significantly lower temperature than the permittivity peak. This is one of the physical characteristics of a relaxor ferroelectric, and such behaviour suggests that with increasing Ce content, the studied system tends to evolve from a regular ferroelectric state to a relaxor ferroelectric state. The phase diagram built on the basis of the dielectric study of different compositions is shown in Fig. 2e. As is shown in Fig. 2e, T_C decreases with increasing x. The O–T and R–O phase boundaries gradually increasing with increasing x, similar to what has been reported for the Sn-, Zr- and Hf-modified BaTiO$_3$ systems [10].

3.2. Structural study

Since, as shown in Section 3.1, the dielectric anomaly corresponding to the O–T phase transition occurs at 35 °C for $x = 0.02$, this composition is therefore expected to show O ($Amm2$ symmetry) phase at 27 °C. However, Rietveld analysis of the XRD data with the pure O structural model ($Amm2$) did not give satisfactory fit. The pattern was rather satisfactorily fitted with the T + O coexistence model as shown in the insets of Fig 3a. The XRD pattern of $x = 0.05$, on the other hand, could be fitted satisfactorily with a single phase ($Amm2$) model, see Fig. 3b. The XRD pattern of $x = 0.08$ and $x = 0.10$ looked very similar to each other at the visual level. Since the dielectric anomalies corresponding to the $Amm2 + R3m$ phase transition of these compositions are very close to room temperature. So, we considered the possibility of coexistence of



(a) $x = 0.02$ (b) $x = 0.05$

(c) $x = 0.07$ (d) $x = 0.10$

Fig. 1. Scanning electron microscope (SEM) images of sintered specimens of Ba(Ti$_{1-x}$Ce$_x$)O$_3$ for different compositions.