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Understanding the mechanism of large dielectric response in Pb-free $(1-x)Ba(Zr_{0.2}Ti_{0.8})O_3-x(Ba_{0.7}Ca_{0.3})TiO_3$ ferroelectric ceramics

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ABSTRACT

(1-*x*)Ba($Zr_{0.2}Ti_{0.8}$)O_3-*x*($Ba_{0.7}Ca_{0.3}$)TiO_3 (BZT-*x*BCT) ceramics have been reported to exhibit large dielectric response in the vicinity of the multi-phase-coexisting point (i.e. triple point). However, the reason for large dielectric response in such a material system is still unclear and thus awaits explanation. In this paper, we investigate the reason for large dielectric response by studying the phase transition behavior around the triple point of BZT-*x*BCT ceramics. Our results show that the transition enthalpy nearly vanishes and the associated specific heat shows discontinuity on the triple point, which suggest tricritical behavior (i.e. crossover point from first to second order phase transition) for such a triple point. Further Rayleigh analysis indicates that strong dielectric response is due to large reversible contribution which may be caused by phase transition. Moreover, TEM study shows a mottled domain structure with numerous nanodomains close to tricritical triple point, which reveals a polarization isotropic state. In addition, a six-order Landau free energy modeling demonstrates that the energy barrier between paraelectric and ferroelectric phases nearly vanishes on the tricritical triple point, which facilitates large polarizability in the presence of external electric field and is thus responsible for large dielectric permittivity in BZT-*x*BCT.

1. Introduction

Dielectric material, due to its functionality of storing and controlling charges and electrical energies, has been found a variety of applications on modern electronic and electric power equipments [1,2]. And the capability for the storage of charges can be scaled by dielectric permittivity, which quantifies how easily material becomes polarized in the presence of electric field. With the ongoing demand for the power-capacitive and compact electronic and electric power systems, developing materials with large dielectric permittivity has been becoming an urgent need for device design and manufacture.

Barium titanate ferroelectric materials have been found the application as a promising ceramic capacitor system with large permittivity, utilizing their high dielectric response around the para-ferro transition point (Curie temperature T_C) [3]. During practical application, $BaTiO_3$ ceramics always employ different categories of additives to modify dielectric properties according to application requirement [4,5]. For example, in order to develop high-permittivity capacitance materials, a group of additives called "T_C shifters" (such as $SrTiO_3$, $BaSnO_3$ etc.) have been doped in the $BaTiO_3$-based ceramics. The dielectric permittivity is enhanced

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through shifting the Curie temperature to lower temperature region near room temperature (e.g. in Z5U-type capacitors) [5]. On the other hand, a so-called "T_C depressors" (e.g. $CaTiO_3$, $MgZrO_3$ etc.) have also been added in $BaTiO_3$ materials with the purpose of making the dielectric permittivity peak broaden so that better temperature-stability can be achieved (e.g. X7R-type capacitors) [6–8]. Regardless of the type for additives, the dielectric response around Curie temperature determines the upper limitation for dielectric permittivity in material system, and thus plays a crucial role on designing high permittivity dielectric materials.

Recently, a strong dielectric response has been reported in the (1-x)$Ba(Zr_{0.2}Ti_{0.8})O_3$-$x(Ba_{0.7}Ca_{0.3})TiO_3$ (BZT-xBCT) ceramic material [9], which may find potential application as the high permittivity dielectric material. Originally, such a material system has been designed as a promising Pb-free piezoelectric ceramic, which exhibits large piezoelectric response (with d_{33} = 560–620pC/N) comparable with soft PZT [9–17]. The optimal piezoelectric response occurs at a so-called morphtropic phase boundary (MPB) [18–20], which starts from a multi-phase coexisting point known as "triple point". It has also been reported that such a triple point shows a tricritical behavior, which refers to a special thermodynamic condition with the crossover of first and second order transition [9,21]. It should be noted that the tricritical phenomenon in ferroelectrics was firstly reported in the phase transitions under external pressure [22–24]. Later, such an effect was also found in the composition-temperature phase diagram of Pb-based ferroelectric materials [25–28]. Recent studies on the Pb-free BZT-xBCT ceramic uncovered the relevance of such a thermodynamically special point to large piezoelectric response [9,21]. Although this issue is still controversial [10,21], several material systems were designed based-on the tricritical point idea similar to BZT-xBCT [19,29,30]. Very recent studies even reported enhanced electrocaloric effect due to the critical phenomenon in ferroelectric materials [35–37]. Moreover, strong dielectric response was found in BZT-xBCT ceramic in the vicinity of triple point that shows tricriticality, and the highest dielectric permittivity can reach up to $\varepsilon_r > 20000$ [9]. Despite of its poor temperature stability, large dielectric response around the Curie temperature of BZT-xBCT ceramic can still be utilized after further modification, and can thus have the potential applications for high permittivity ceramic capacitors. However, although the above-mentioned dielectric, piezoelectric, electrocaloric properties have been discovered in systems containing tricritical point, it is still lack of the deep understanding on the tricriticality and its role on enhancing the relevant properties. In particular, the mechanism underneath strong dielectric response in BZT-xBCT is still blur, which may hinder the design of new high permittivity material based on it.

In the present work, we systematically investigate the mechanism for large dielectric response in BZT-xBCT ceramics through studying the phase transition behavior around the triple point of such a material system. In order to clarify the contributions for each dielectric activity, we have measured the polarization (P)-electric field (E) curves for various compositions across the triple point. With the purpose of monitoring phase transition behaviors, we have further performed systematic thermal analysis for BZT-xBCT ceramics. Moreover, the microstructure origin has been characterized by means of transmission electron microscope (TEM) study. A sixth-order Landau free energy modeling has been proposed based on our experimental results. Beyond our earlier paper [21] only regarding the phase transition behavior of triple point, the present work not only investigates thermodynamic origin and microstructure characteristics for large dielectric response in BZT-xBCT system, but also provides a new approach on achieving large dielectric response and making design for high-permittivity materials.

2. Experimental

2.1. Specimen preparation

The (1-x)$Ba(Zr_{0.2}Ti_{0.8})O_3$-$x(Ba_{0.7}Ca_{0.3})TiO_3$ (x = 0.2–0.8) ceramics were fabricated by using the conventional solid-solution method. The raw chemicals of $BaCO_3$, TiO_2, $BaZrO_3$, $CaCO_3$ were weighed according to their stoichiometric ratios. We then mixed the powder via ball milling method with the medium of ethyl alcohol. After drying, the mixtures were calcinated at 1350 °C for 3 h in air. The products were grinded into powder again, followed by adding binders of 10 wt % aqueous solution for polyvinyl alcohol (PVA). And we further shaped the powder into pellets. Finally, the pellets were put into oven to perform the sintering procedure at 1450 °C for 3 h in air, and high-quality BZT-xBCT ceramic specimens were obtained.

The ceramic specimens for further microstructure observation were prepared following the TEM sample preparation procedure. The BZT-xBCT ceramic samples were mechanically grinded into thin pellets with the thickness of 80 μm. We then cut the specimens into disks with the diameter of 3 mm by using the ultrasonic cutter in order to fulfill the specimen dimension requirement for TEM holders. The disks were then dimpled so that the middle part thickness was reduced to around 20 μm. The specimens were transferred onto supporters, and further thinned until it is penetrated by using precision ion polishing system. Thin foils exhibiting good electron transparency can be observed by TEM.

2.2. Characterizations

In order to characterize the dielectric property for BZT-xBCT ceramics, the parameters (e.g. permittivity, loss tangent) were detected by a LCR impedance analyzer equipped with a temperature chamber. We then measured the polarization(P)-electric field(E) curves by ferroelectric workstation (Radiant technology), and Rayleigh analysis has been conducted for these P-E curves to clarify the contributions for each dielectric activity. With the purpose of monitoring phase transition behavior, a differential scanning calorimeter (DSC, TA Instruments Q2000) was used to detect transition enthalpy at Curie temperature. And the heat capacity changes during phase transitions were detected by a physical property measurement system (PPMS, Quantum Design). Moreover, the microstructure origin for the specimens was investigated by means of transmission electron microscope (TEM JEM 2100F, JOEL) equipped with a hot specimen stage (Gatan 636).

3. Results and discussion

3.1. Dielectric measurement

The ferro-para transition is always accompanied with a dielectric permittivity peak (known as dielectric anomaly), which can be monitored by measuring the dielectric thermal spectrum for the BZT-xBCT ceramics. Therefore, we measured the temperature-dependence of dielectric permittivity at 1 kHz for a series of compositions with x = 0.24, 0.3, 0.325, 0.5, 0.7. Among these specimens, x = 0.325 is a very special composition. In our previous work, we found that such a composition exhibits a multi-phase coexisting point (i.e. triple point) at its Curie temperature by detecting the phase transition sequence for each composition [21].

Fig. 1(a)-(e) show the temperature-dependence of dielectric permittivity for each composition. It can be seen that the relative permittivity value (ε_r) for ferroelectric or paraelectric phase is low ($\varepsilon_r < 2000$). But the permittivity curve for each specimen around Curie temperature is enhanced, and it exhibits a peak at Curie