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Piezoelectric and ferroelectric properties in $Ba(Zr,Ti)O_3$ and CuO-Ba(Zr, Ti)O_3 ceramics

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ABSTRACT

In this paper, we have investigated the piezoelectric and ferroelectric properties of $Ba(Zr_{0.04}Ti_{0.96})O_3$ and CuO-$Ba(Zr_{0.04}Ti_{0.96})O_3$ ceramics prepared by the conventional solid solution method. $Ba(Zr_{0.04}Ti_{0.94})O_3$ ceramics were sintered at 1400, 1450, and 1500 °C to optimize the sintering temperature of pure BZT. BZT ceramics with 1 mol% of CuO added were sintered at 1300, 1350, 1400, 1450, and 1500 °C. It was found that the optimal sintering temperature was decreased by 50 °C, while the piezoelectric properties were enhanced, compared to those of pure BZT ceramics. The ceramics showed excellent piezoelectric properties with d_{33} 302 pC/N and ferroelectric properties with dielectric constant 2135. The piezoelectric CuO-BZT ceramics were investigated according to the change of sintering temperature by considering the microstructure and the piezoelectric and ferroelectric properties compared with those of pure BZT.

1. Introduction

For the past decade, $(K,Na)NbO_3$-(KNN) based ceramics have been regarded as a promising piezoelectric and ferroelectric material to replace $Pb(Zr,Ti)O_3$-(PZT). However, KNN ceramics have several disadvantages such as the need for special handling of the starting powders, sensitivity of properties to non-stoichiometry, and a complex densification process [1]. The $BaTiO_3$ (BT) system has also attracted much attention as a replacement for the Pb-based systems. In fact, BT had been widely researched as a piezoelectric material before the discovery of PZT [2]. BT has previously been used in a number of application fields such as actuating, sensing, and multilayer ceramic capacitors [3–6]. BT ceramics have been known to show high level piezoelectric properties (d_{33} = 191 pC/N) [2]. However, since BT has a very low Curie temperature of 130 °C, its use should be limited. In recent years, many researchers have attempted to modify the performance of BT ceramics by synthetic process, low sintering technology, and doping materials [6–11]. Among the BT based systems, $Ba(Zr,Ti)O_3$ (BZT) ceramics show their special characteristics through modifying the Ti/Zr ratio in the BZT material. Therefore, the piezoelectricity, dielectric relaxation, and tunability can be improved with the specific zirconium content for the material because of its better chemical stability [12]. In this paper, $Ba(Zr_{0.04}Ti_{0.96})O_3$ was selected as the matrix system because it shows a tetragonal phase [13] and promising performances [14]. We found that the piezoelectric stability can be significantly enhanced by the proper combination of partially substituted Ti with Zr and by adding a small amount (1 mol%) of CuO additive. 1 mol% CuO-added $Ba(Zr_{0.04}Ti_{0.96})O_3$ ceramics show excellent piezoelectric performance of high piezoelectric coefficients and relatively high Curie temperature. It is reasonable to assume that copper oxide play a role as a low sintering aid in BZT ceramics to enhance the densification during the sintering process due to low melting point and liquid-phase effect [14]. The properties of pure $Ba(Zr_{0.04}Ti_{0.96})O_3$ and 1 mol% CuO-added $Ba(Zr_{0.04}Ti_{0.96})O_3$ ceramics were also investigated and analyzed in correlation with the various sintering temperatures.

2. Experimental

$Ba(Zr_{0.04}Ti_{0.96})O_3$ and 1 mol% CuO-added $Ba(Zr_{0.04}Ti_{0.96})O_3$ ceramics (hereafter referred to as BZT and CuO-added BZT, respectively) were fabricated using the conventional mixed oxide method. $BaCO_3$ (purity 99.9%, Sigma-Aldrich Co., Ltd.), TiO_2 (purity 99.9%), and ZrO_2 (purity 99.0%) were employed as the starting materials. The starting powders were weighed according to the stoichiometric ratio and were then ball milled for 24 h using ethyl alcohol and zirconia balls. After drying, the mixture was calcined at 1130 °C for 4 h. Then, 1 mol% CuO (purity 99.0%) powder was added

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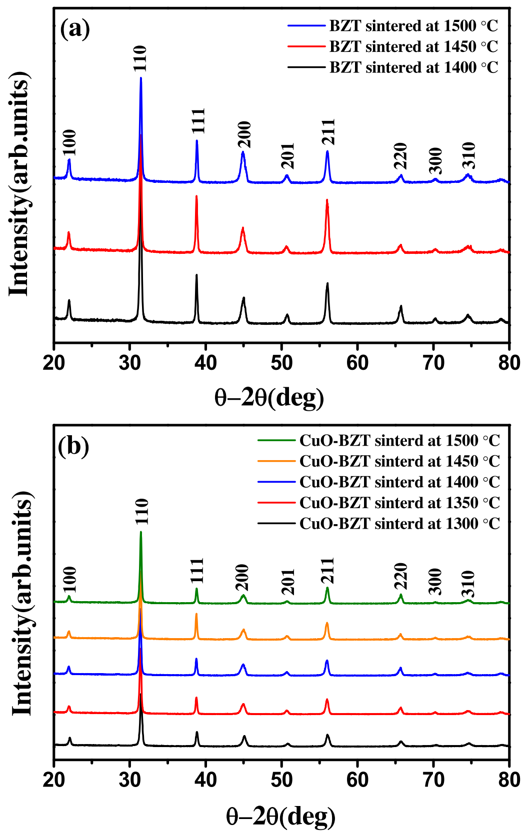

Fig. 1. (a) X-ray diffraction pattern of BZT ceramics sintered at 1400–1500 °C and (b) X-ray diffraction pattern of 1 mol% CuO-added BZT ceramics sintered at 1300–1500 °C.

to the calcined $Ba(Zr_{0.04}Ti_{0.96})O_3$ for the preparation of the CuO-added BZT ceramics. The mixtures were ball milled again for 12 h by high energy ball milling and then dried in an electric oven. The powders were mixed with a binder of poly vinyl alcohol (PVA) and pressed into disks 12 mm in diameter and 1 mm in thickness. The BZT ceramics were then sintered at 1400, 1450, and 1500 °C for 2 h. For comparison, CuO-added BZT ceramics were prepared under a similar procedure but sintered at 1300, 1350, 1400, 1450, and 1500 °C for 2 h. To characterize the dielectric and piezoelectric properties, the specimens were coated with silver paste on the upper and bottom surfaces and cured at 120 °C for 20 min. The samples were poled at 25 °C in silicon oil under 3.5 kV/mm for 30 min. The crystalline structure was investigated through X-ray diffraction (XRD) analysis (θ-2θ scans with Cu-Kα source). The piezoelectric coefficient, d_{33}, was measured employing a Berlincourt type quasi-static meter. The polarization versus electric (P-E) hysteresis loops of the ceramics were then measured.

3. Results and discussion

The X-ray diffraction patterns of the BZT and CuO-added BZT ceramics with various sintering temperatures are shown in Fig. 1. As can be seen in Fig. 1, a pure perovskite phase was formed for all the ceramics and no other second phase was observed in the XRD peaks. In Fig. 1(a), the BZT ceramics sintered between 1400 and 1500 °C show an orthorhombic phase at room temperature, which is consistent with the result obtained from the analysis of the temperature dependence of the dielectric properties shown in Fig. 6, as will be discussed later. Similar to the results shown in Fig. 1(a), the CuO-added BZT ceramics sintered at 1300–1500 °C show an orthorhombic structure at room temperature.

Fig. 2(a)-(c) show the surface morphologies of the BZT ceramics sintered between 1400 and 1500 °C and Fig. 2(d)-(h) show the surface morphologies of the CuO-added BZT ceramics sintered between 1300 and 1500 °C. In Fig. 2(a), the distinction of grain size

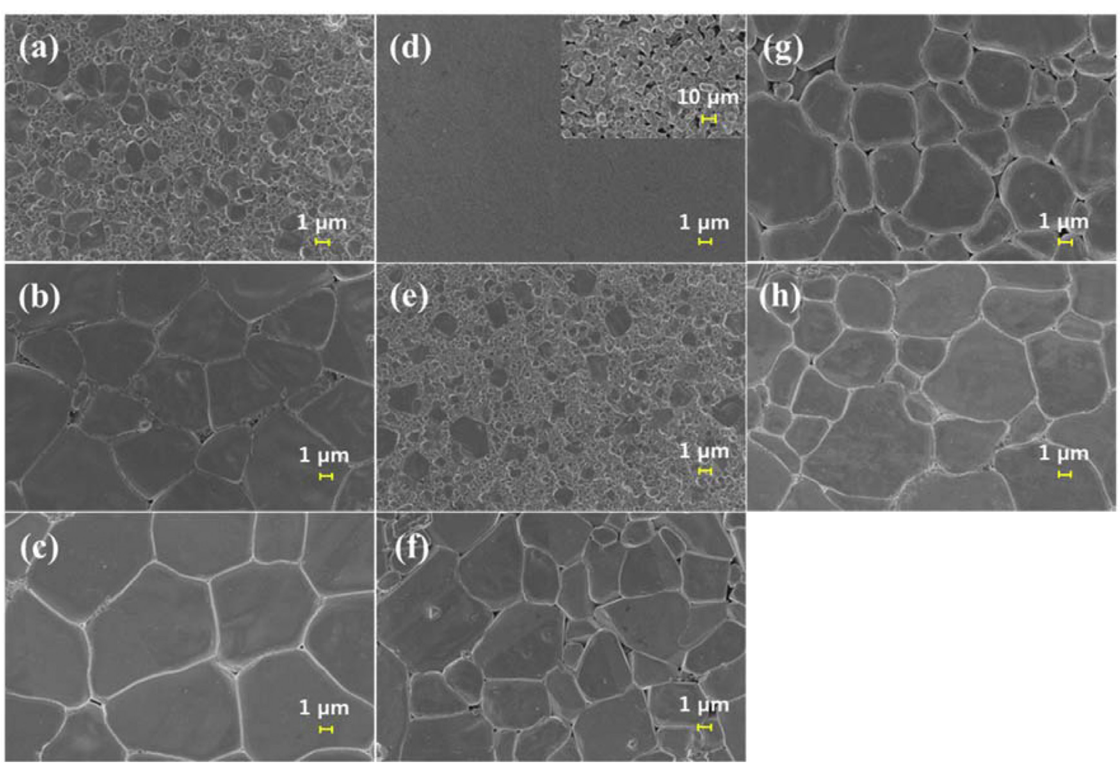

Fig. 2. (a)-(c) Surface morphologies of BZT ceramics sintered at 1400–1500 °C and (d)-(h) 1 mol% CuO-added BZT ceramics sintered at 1300–1500 °C.