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Effects of Mn addition on sintering behavior of $Ba_{0.85}Ca_{0.15}Zr_{0.10}Ti_{0.90}O_3$ ceramics

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ABSTRACT

In this work, (1-x)BCZT-(x)MnO_2 ceramics where x = 0, 0.005, 0.010, and 0.015 were fabricated by a solid state sintering technique. The effects of Mn addition on the sintering behavior of BCZT-based ceramics sintered at 1,300 oC and 1,400 oC were investigated. In the results, we found that the adding of Mn dopants induced oxygen vacancy, which led to facility of grain growth and ion diffusion of the doped ceramics during the sintering process. This enhancement caused significantly increase of bulk and relative densities of the Mn-doped ceramics sintered at 1,300 oC. Also, the dense ceramics could be obtained at such temperature. In case of the sintering at 1,400 oC, the compositional losing induced the porous-like microstructure of the Mn-doped ceramics. The results here indicated that the addition of Mn ions produced the dense ceramic of BCZT-based materials at low temperature, which could be sintering aids for other ceramics requiring high sintering temperature.

INTRODUCTION

In recent years, barium calcium zirconate titanate lead-free ceramic ((0.5)$BaZr_{0.2}Ti_{0.8}O_3$-(0.5)$Ba_{0.7}Ca_{0.3}TiO_3$); BCZT) has promoted attractive piezoelectric properties, which equivalent to better than a commercial lead zirconate titanate (PZT) material [1]. This, therefore, makes that BCZT ceramic becomes a promising candidate to replace PZT in several electronic devices, such as sensors, actuators, and capacitors [2]. However, the dense ceramic fabrication of BCZT material required a high sintering temperature of about 1,400 ^{o}C or higher [2, 3]. There are many efforts to sinter BCZT at low temperatures. Still, the mainly observed problem is a porous microstructure of BCZT ceramic due to the grain growth and ion diffusions during the sintering process, leading to reduced bulk and relative densities at low sintering temperature. This reason is the limitation of BCZT material for other ceramic techniques. Thus, the reduction in the sintering temperature of BCZT to low temperature is, therefore, focused on subsequent research.

In previous work [4], Sun et al., have studied the effects of MnO_2 doping content on electrical properties and sintering behavior in several temperatures of $Ba_{0.98}Ca_{0.02}Zr_{0.02}Ti_{0.98}O_3$ ceramics. They found that the addition of MnO_2 could promote grain growth of the ceramics, led to enhancement in density and microstructure of these ceramics at the sintering condition of 1400 °C for 4 h. However, when MnO_2 concentration was excess, the grain growth was inhibited and induced smaller grains. From this work, the results indicated that the sintering behavior and dense microstructure of Ba-based ceramics could be modified using MnO_2 addition in suitable content. Thus, we are interested in studying the fabrication of BCZT at lower sintering temperatures (1300 °C) via MnO_2 addition. Since the composition of BCZT is adjacent $Ba_{0.98}Ca_{0.02}Zr_{0.02}Ti_{0.98}O_3$ ceramic, we expect that the Mn ions would improve the sintering behavior of BCZT at such temperature. Thus, in this work, BCZT ceramics with the doping of Mn^{2+} ions in several concentrations were fabricated. The scanning electron microscopy (SEM) was used to investigate the microstructure of all ceramics at several sintering temperatures. Bulk and relative densities of all ceramic were measured and calculated, respectively, to optimize the suitable sintering condition and Mn content for these ceramics. With these results, the addition of Mn ions affected the sintering behavior of BCZT ceramics significantly at low temperatures.

METHODOLOGY

The starting materials were $BaCO_3$ (99.95%), $CaCO_3$ (99.95%), ZrO_2 (99.9%), TiO_2 (99.9%), and MnO_2 (99.99%). Initially, the starting oxides were weighed following the chemical formulae of $BaZr_{0.2}Ti_{0.8}O_3$ (BZT) and $(Ba_{0.7}Ca_{0.3})TiO_3$ (BCT). The oxide mixtures were ball-milled in ethanol for 24 h using a conventional mixed-oxide method. The mixed powders were dried at 120 °C for 24 h and calcined in a closed alumina crucible at 1100 °C for 3 h. After sieving, 0.5BZT-0.5BCT (BCZT) powders were mixed again in ethanol for 6 h and dried at 120

°C for 24 h. After that, (1-x)BCZT-(x)MnO_2 (99.99%) powders where x = 0, 0.005, 0.010, and 0.015 wt% were mixed again in mortar.

A conventional solid-state sintering technique was used to fabricate all samples. Initially, one drop of 3 wt% PVA (polyvinyl alcohol) binder was added to the powders, which were subsequently pressed into pellets with a diameter of 10 mm and thickness of 2 mm using a uniaxial press with a pressure of 187.3 MPa. Binder removal was carried out by heating the pellets at 500 °C for 1 h in an air atmosphere with a heating/cooling rate of 5 °C/min. These pellets were then sintered in a temperature range of 1300-1500 °C for 4 h in an air atmosphere with a heating/cooling rate of 5 °C /min on an alumina plate.

The bulk densities of all ceramics were determined using Archimedes' method. Then, the relative densities of the ceramics were calculated from the relationship between the theoretical and bulk densities. In the case of the theoretical density, the value of BCZT (5.76 g/cm^3) from our previous work [3] was used to compare with these ceramics. A scanning electron microscopy (SEM) was used to observe the microstructure of the as-sintered surface of all ceramics.

RESULTS AND DISCUSSION

Firstly, it should be noted that the sintering condition at 1,500 °C for 4 h of all samples had been carried out. However, all samples were melted and deformed. Thus, the results of the ceramics sintered at lower temperatures (1300 and 1400 °C), therefore, were discussed in this work. Figure 1 shows the densities of all ceramics sintered at 1,300 °C and 1,400 °C for 4 h. Regarding bulk densities of all ceramics, as shown in Figure 1 (a), the BCZT ceramic sintered at 1,300 °C showed a minimum value of bulk density. Interestingly, the density value increased abruptly after Mn ions were doped. There was no significant difference between Mn concentration and the densities for the Mn-doped BCZT ceramics sintered at 1,300 °C. The result suggested the enhancement in the physical properties of BCZT ceramics doped using Mn ions. However, the change in bulk densities of the ceramics sintered at 1,300 °C was contrary to the ceramics sintered at 1,400 °C (see in Figure 1 (a)). The bulk density of BCZT became highest, while the density value decreased with the increasing addition of Mn ions. It was normal for BCZT ceramic, in which the material required the sintering temperature of about 1,400 °C or higher [2, 3]. To extend the results, the relative densities of all ceramics sintered at 1,300 °C and 1,400 °C for 4 hrs are therefore plotted in Figure 1 (b). In the figure, the relative density of BCZT ceramic sintered at 1,300 °C was lower than 80%, which accompanied its bulk density. The relative value could indicate the porosity of ceramics. In general, the dense ceramic should have a relative density value of about 95% or higher. Thus, from the result of BCZT ceramic sintered at 1,300 °C, it suggested that the ceramic had high porosity, which caused its poor relative value. For the porosity of BCZT, the ceramic sintered at 1,300 °C would be discussed together with its microstructural image (in Figure 2). After Mn ions were doped in BCZT ceramic, the relative densities increased obviously. The relative values were higher than 95%, suggesting the dense ceramic of Mn-doped BCZT materials. There was no significant difference in relative values for the doped samples, similar to the trend of bulk density. From the results of BCZT ceramic and the ceramics doped by Mn ions, it indicated that the addition of Mn ions could enhance the microstructural evolution of BCZT ceramics at a low sintering temperature (1,300 °C). In the case of the relative values of the ceramic sintered at 1,400 °C, BCZT ceramic showed the maximum relative value of almost 99%. This indicated that the sintering temperature at 1,400 °C was enough to obtain the dense ceramic of the BCZT compound. Interestingly, the relative densities of the Mn-doped ceramics sintered at 1,400 °C decreased to ~85% for the composition x = 0.005 and 0.01 and ~75% for the composition x = 0.015. The compositional degradation or the mass loss might be an important factor, decreased the relative density values of Mn-doped ceramics. The degradation and mass loss during the sintering process at high temperature could induce the pore microstructure of the ceramics. The relationship between porosity and microstructure of all ceramics would be discussed later.

Microstructural observation of the as-sintered surface for all ceramics sintered at 1,300 °C is shown in Figure 2. In the figure, it could be seen that BCZT ceramic showed the microstructure, which was composed of the open pore. This microstructural feature caused the minimum bulk and relative densities of the ceramic (~4.4 g/cm^3 and 78%, respectively). The quantitative data of the average grain size of all ceramics sintered at 1,300 °C and 1,400 °C is listed in Table 1. The average grain size of BCZT ceramic was about 0.76 μm, which was different from the grain size of BCZT ceramics observed in several previous works [2, 3]. It was possible that the sintering temperature at 1,300 °C was quite low and not enough for BCZT grain growth. This reason, therefore, resulted in fewer ions diffusion during the sintering process, leading to the porous-like microstructure of BCZT ceramic. The relative density of this ceramic was associated with its microstructure. Interestingly, the BCZT ceramics doped via Mn ions showed the dense microstructure, which accompanied well with their relative densities in Figure 1 (b) (>95%). This result suggested that the addition of Mn ions could induce the microstructural enhancement of BCZT ceramic at 1,300 °C. As seen in Table 1, the average grain size of the ceramics increased with the increase of Mn concentration. The

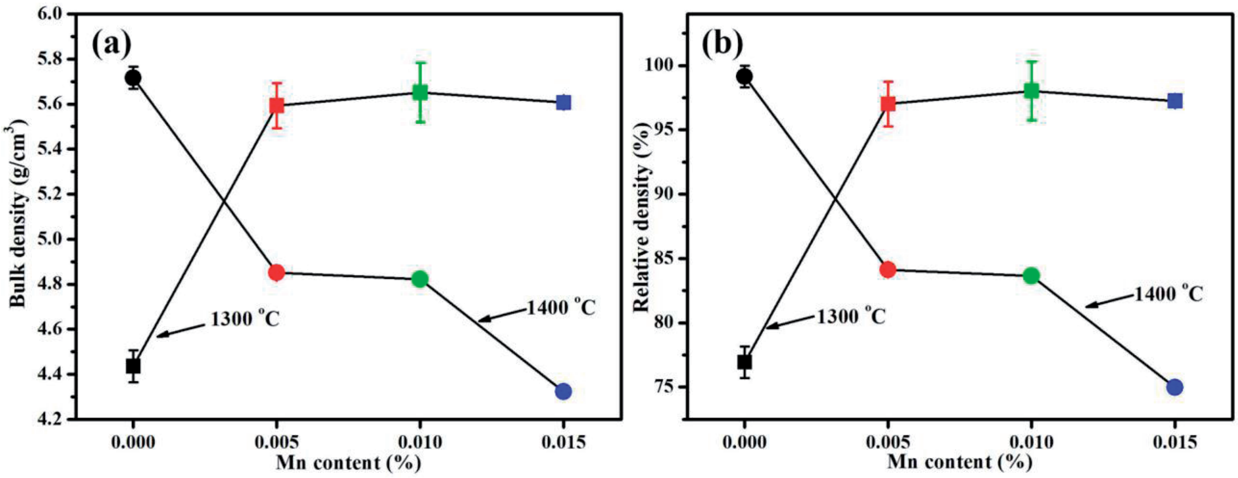

Figure 1. The density of all ceramics sintered at 1,300 °C and 1,400 °C when (a) and (b) are bulk densities and relative densities, respectively.

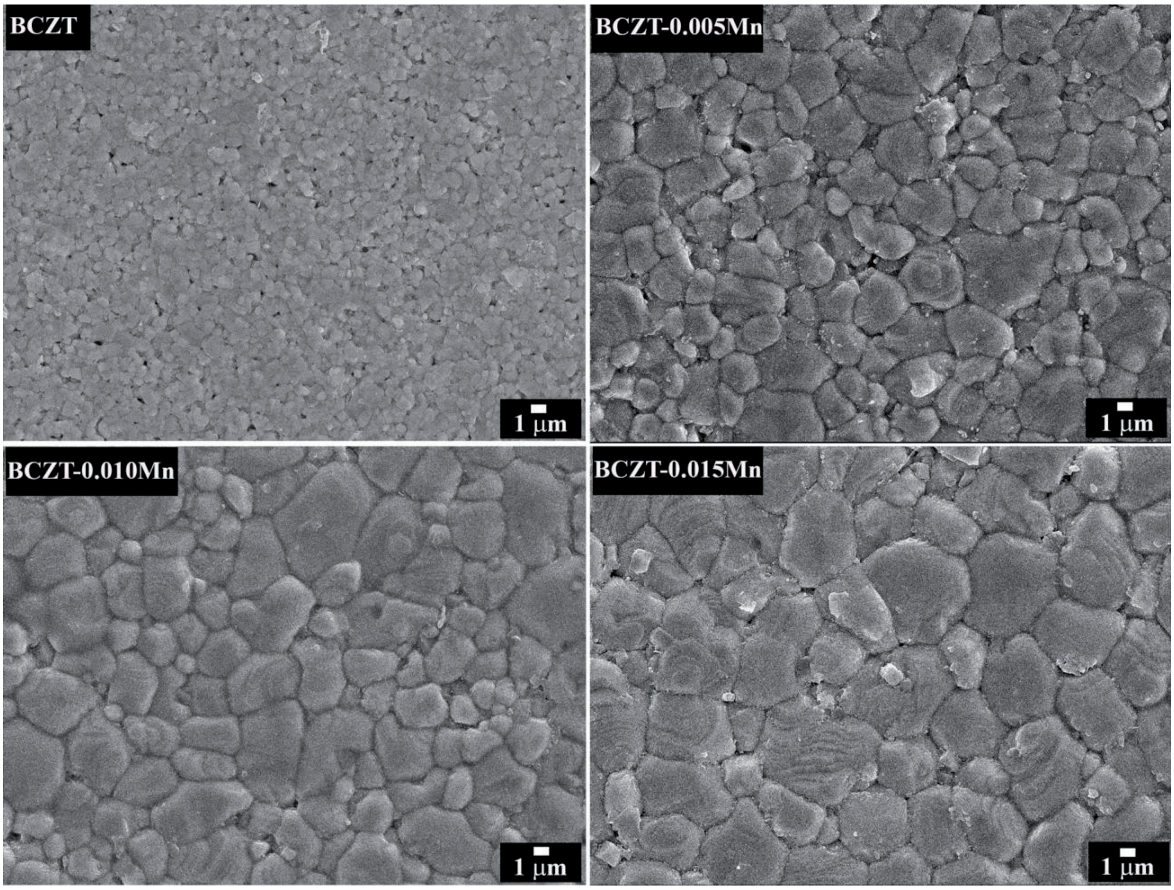

Figure 2. SEM images of all ceramics sintered at 1,300 °C.

Table 1. Average grain sizes of all ceramics sintered at 1,300 °C and 1,400 °C.

Ceramicas (Mn content (%))	1,300 °C		1,400 °C	
	Average grain size (μm)	Standard deviation	Average grain size (μm)	Standard deviation
x = 0	0.76	± 0.13	10.41	± 1.48
x = 0.005	1.96	± 0.35	10.38	± 2.45
x = 0.010	2.86	± 0.42	9.89	± 1.13
x = 0.015	3.84	± 0.75	10.02	± 1.40

composition $x = 0.015$ showed the maximum grain size of about 3.84 μm, which was larger than the BCZT ceramic ~3 μm under the low sintering temperature. This result reflected in the enhancement of grain growth of BCZT ceramic at low temperatures due to the Mn addition. The creation of oxygen vacancy ($V_O^{\bullet\bullet}$) in these ceramics was the main factor for this enhancement. It was worth mentioning that how did such defect introduce in BCZT ceramic? When acceptor dopants, i.e., Mn^{2+} ions, substituted Ti^{4+} and Zr^{4+} ions at B-site of perovskite lattices, the $V_O^{\bullet\bullet}$ could be introduced by chemical equation described as follows:

$$Mn^{2+} \rightarrow Mn''_{Zr,Ti} + V_O^{\bullet\bullet} \tag{1}$$

The formation of oxygen vacancies would facilitate grain growth [5, 6]. This was accompanied well with the contribution of Mn dopants, adding to $Ba_{0.98}Ca_{0.02}Zr_{0.02}Ti_{0.98}O_3$ ceramics in Sun et al., [4].

Figure 3 shows SEM images of the as-sintered surface for all ceramics sintered at 1,400 °C. As seen in the figure, BCZT ceramic showed the dense microstructure, which was the agreement with its relative density value (~99% in Figure 1 (b)). The average grain size of BCZT ceramic increased significantly (~10.41 μm) when compared with the average grains of ceramic sintered 1,300 °C (~0.76 μm). This result confirmed that the sintering temperature at 1,400 °C was high enough for BCZT material, and could promote the proper grain growth, leading to the creation of its dense ceramic at such temperature. However, it was found that the sintering temperature at 1,400 °C might not be suitable for Mn-doped BCZT ceramics, although the average grain size of BCZT and the doped ceramics did not differ significantly for each other. The microstructure of Mn-doped ceramics was composed of many pores or void on the as-sintered surface, which resulted in low relative density values of all ceramics (<85% in Figure 1 (b)). The melting of

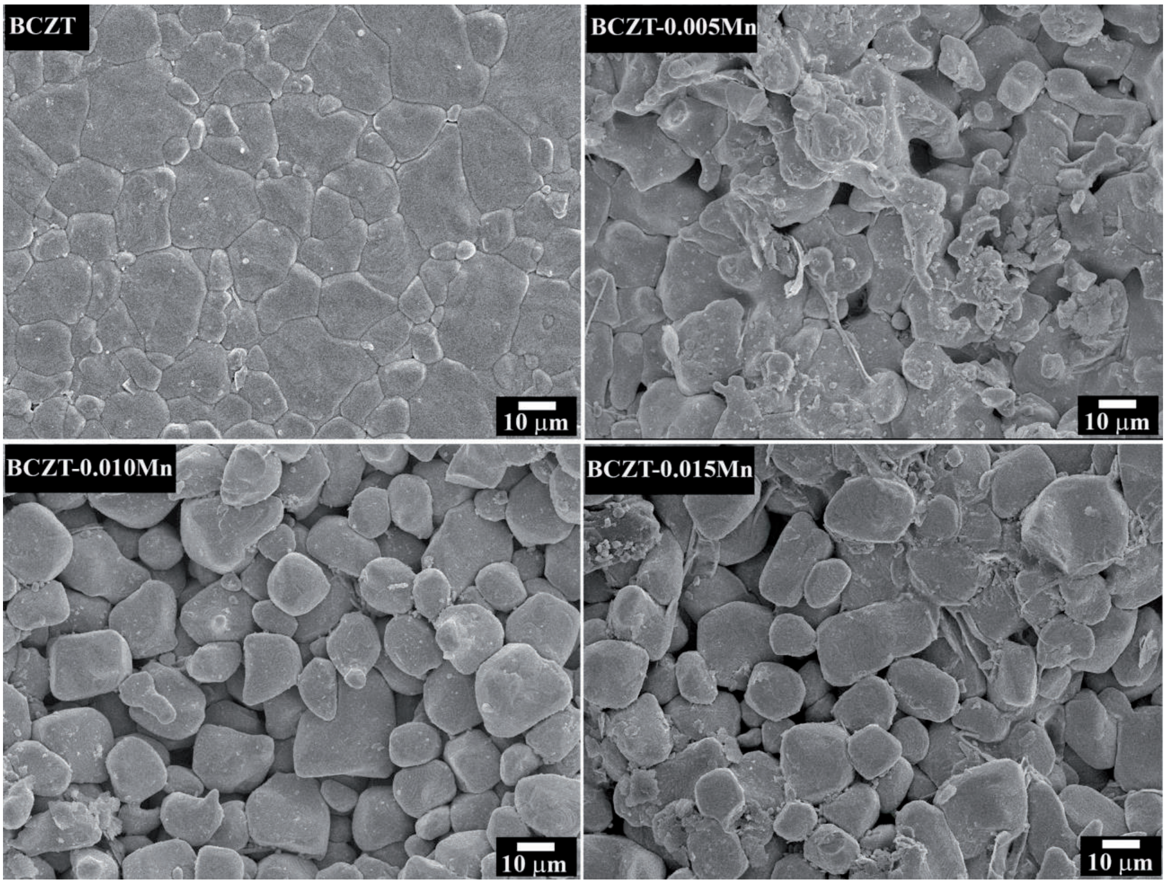

Figure 3. SEM images of all ceramics sintered at 1,400 °C.

the composition in Mn-doped ceramics was expected to be a primary factor, which produced such a porous-like microstructure. We observed the track of partial melting in these ceramics on the alumina plate after the finish of the sintering process (the result was not shown here).

CONCLUSION

In this work, BCZT dense ceramic could be fabricated at low sintering temperature using Mn dopants through the solid-state sintering technique. The information on oxygen vacancy due to acceptor doping was the main factor for the enhancement in sintering behavior at a low temperature of Mn-doped BCZT ceramics. The result, here, suggested that the addition of Mn ions could decrease the required sintering temperature of BCZT-based ceramics, which may use Mn ions for sintering aids in other ceramics that have high sintering temperature.

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