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Effects of B_2O_3 Addition on the Sintering Behavior of 0-5-10% ZrO_2 Doped $BaTiO_3$ Based Ceramics

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In this study, the effect of B_2O_3 addition on the sintering behavior of 0-5-10% ZrO_2 doped barium titanate based microwave dielectric ceramics were investigated. For this purpose, the powder mixtures consisting of $BaCO_3$, TiO_2 and ZrO_2 were prepared by ball milling technique in alcohol using ZrO_2 balls at 200 cycle/min for 20 h. The prepared powders were calcined at 900 °C for 2 h. Produced powders were mixed 0.5% B_2O_3 and 5% PVA and pressed as green body under the pressure of 100 MPa. The disc-shaped die-pressed samples were sintered at 1250 °C, 1350 °C and 1450 °C for 4 h. X-ray diffraction analysis showed that the main phases formed in the sintered samples are $BaTiO_3$ and $Ba(Ti_{1-x}Zr_x)O_3$. The scanning electron microscope (SEM) and energy-dispersive X-ray spectroscopy (EDS) were used to investigate microstructure of the sintered samples. The bulk densities of the sintered samples increased with the addition of B_2O_3 content due to the low number of pores trapped between the grains.

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1. Introduction

Barium zirconium titanate ceramics are attractive candidates for dynamic random access memories and tunable microwave devices. Such, lead-free, environmental friendly materials are known to exhibit relaxor behaviour in bulk materials with the increase of the ZrO_2 content. The interest in high-strain piezoelectric materials for electromechanical transducers and various related applications is increasing [1]. Though the large family of lead-based perovskites and relaxors has shown a great potential, lead-free compositions in these families will be of interest due to obvious environmental concern in the future [2–6]. $BaTiO_3$ (BT) is the most promising lead-free material exhibiting superior properties like high dielectric permittivity, low dielectric loss tangent, dielectric reliability, high electromechanical coupling coefficients, good thermal shock resistance and large tunability [7]. Hence, this material finds its applications in tunable microwave devices and thermistor applications [8, 9]. A lot of work was carried out in evaluating the properties of the doped Ba-TiO_3 ceramics. The effect of dopants ranging from metals, semiconductors to insulators including rare-earth dopants like La, Nd, Pr, Gd on the dielectric and ferroelectric properties were investigated [10–12]. Zr is chosen as a B site dopant for such ABO_3 type perovskites due to its effective role in minimising the dielectric loss at low frequencies. When the Zr content is less than 10 mole%, the BZT ceramics show normal ferroelectric behaviour and dielectric anomalies corresponding to cubic to tetragonal (T_c), tetragonal to orthorhombic (T_2), and orthorhombic to rhombohedral (T_3) phase transitions. At around 27 mole%, Zr-doped BZT ceramics exhibit typical diffuse paraelectric to ferroelectric phase transition behavior, whereas Zr-richer compositions exhibit typical relaxor-like behaviour in which T_c shifts to higher temperature with increase of frequency [13]. Three kinds of approaches have been introduced to reduce the sintering temperature of microwave dielectric ceramics, including the low-melting addition, chemical processing, and ultrafine raw materials [14]. Among these methods, low-melting addition is the mostly often used method due to the lower cost and easier experimental procedure [15]. Recently, much attention has been paid to the addition of B_2O_3 [16–21] since it could effectively lower the sintering temperature of ceramics and promote densification without significant deterioration in the microwave dielectric properties, because B_2O_3 volatilizes easily at high temperatures above 900 °C and it does not remain at the boundary of grains. Recently, many research groups have studied the influence of boric acid (H_3BO_3) on the properties of some ceramics [22–24]. Kushnirenko *et al.* [22] investigated the effect of an addition of H_3BO_3 on the sintering of ZnO, and found that the addition of boric acid resulted in a rise of the grain size, an increase of the grain conductivity, a quenching of defect-related luminescence, and the enhancement of exciton emission. Misirli *et al.* [24] investigated the effect of an addition of boric oxide (B_2O_3) to the sintering of Al_2O_3, and found that the porosity of the materials, which were made using a spray-drying technique,

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could be controlled by the level of addition of B_2O_3. This porous structure gave the material a good strength, making it a potential candidate for use in ceramic filters and for ceramic-metal composite preforms [22]. The objective of this experimental study was to examine the effects of small additions of B_2O_3 on the microstructure, density properties, and, in particular the densification, porosity and grain size of $BaTiO_3$.

2. Experimental study

The raw materials of analytical grade: (all from Alfa Aesar Company) $BaCO_3$ (99.5% purity), ZrO_2 (99.5% purity), TiO_2 (99.5% purity), (H_3BO_4, 99.9% purity) were weighed in appropriate proportion to obtain the stoichiometric ratio. The investigated systems were $Ba(Ti_1)O_3$, $Ba(Ti_{0.9}Zr_{0.10})O_3$ and $Ba(Ti_{0.8}Zr_{0.2})O_3$. The different powder mixtures were homogenized by ball milling technique in isopropyl alcohol using ZrO_2 balls at 200 cycle/min for 20 h. The slurry was dried in an oven after removing the zirconia balls. The dried powders were calcined at 900 °C for 2 h. The calcined powders were crushed using planetary ball mill for a short duration. Produced powders were mixed with 0.5% B_2O_3 and pressed into pellets of 15 mm diameter and 3 mm thickness at a pressure of 100 MPa, using polyvinyl alcohol (5% PVA) as a binder. After binder burn out, the pellets were sintered at 1250–1350 and 1450 °C for 4 h in static air in a closed alumina crucible and cooled to room temperature (5 °C/min). The bulk density and porosity of the sintered specimens was measured using the Archimedes' principle. X-ray Diffractometer (Rigaku D/MAX/2200/PC) with a monochromatic Cu-K_α radiation (k = 1.5408 Å) was used to measure (during 2 h) diffraction angles between 20° and 80°, to characterize the crystal structure of the sintered compacts. The surface microstructures of the samples were examined using a scanning electron microscope (SEM, Model JEOL-JSM 6060-LV, Japan). Composition analysis was performed using energy-dispersive spectroscopy (EDS, INCA IE 350, and U.K.).

3. Results and discussion

3.1 XRD analysis

The room-temperature x-ray diffraction patterns recorded for $BaTiO_3$ ceramics mixed with 0.5 wt% B_2O_3 and sintered at 1450 °C are shown in Fig. 1. Figure 1a presents the x-ray diffraction patterns of sintered $Ba(Ti_1)O_3$ ceramics. Figures 1b and 1c present the x-ray diffraction patterns of $BaTiO_3$-based ceramics with the addition of 0.1 and 0.2 mole of ZrO_2, respectively. All the peaks are indexed according to the PDF files No. 01-075-0462, and X-ray diffraction analysis results show single-phase perovskite structure for the $Ba(Ti_{1-x}Zr_x)O_3$ based ceramics (x = 0, 0.2, 0.3) at room temperature. The XRD studies do not show any impurity phases. These results indicate that even though a small amount of B_2O_3 is added to $BaTiO_3$-based ceramics, the phase does not evidently change, because B_2O_3 volatilizes easily at high temperatures and the remnants of B_2O_3 liquid phase cannot crystallize during cooling. Rhim *et al.* [25] has also reported similar results for the 0.5 wt.% B_2O_3-added samples. Lin *et al.* [26], using Na_2O as liquid phase sintering also reported that the platelet-type structure had disappeared.

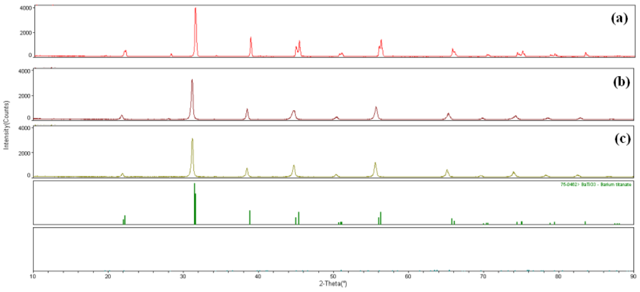


Fig. 1. XRD patterns of $BaTiO_3$ based ceramics with 0.5 wt.% B_2O_3 sintered at 1450 °C for 4 h. (a) $Ba(Ti_1)O_3$, (b) $Ba(Ti_{0.9}Zr_{0.10})O_3$, (c) $Ba(Ti_{0.8}Zr_{0.2})O_3$.

3.3 SEM and EDX analysis

The SEM pictures of 10% ZrO_2 doped barium titanate based microwave dielectric ceramics with and without 0.5 wt.% B_2O_3 addition are shown in Fig. 2a–2f, respectively. SEM images reveal the powder structure and fine size of the milled BZT powder. Figure 2b presents the formation of neck region between two particles, corresponding to the ceramic sintered at 1350 °C. The microstructure of sintered $Ba(Ti_{0.8}Zr_{0.2})O_3$ ceramics changes with sintering temperature. The grain size increases mainly due to increase in grain boundary mobility. Such enhanced grain boundary mobility can be attributed to a variety of aspects, like rise in sintering temperature, fine particles resulting from high energy ball milling, and on improved diffusion coefficient. The addition of B_2O_3 has also enhanced the densification and brought the maximum densification over the 1250 °C, due to the pores structures.

EDX analysis was carried out to identify the composition of large and small grains (Fig. 2f). Figure 3a shows the EDX spectra and the results of compositional analysis taken from the extremely large grains. Figure 3b shows the EDX spectra taken from the relatively small grains. These grains proved that the structure contains approximately 10% of ZrO_2.

3.3 Density and open porosity

The relative density and porosity of the sintered materials were determined using Archimedes' water displacement method, as specified by European Standard EN 99 (ISO 10545-3, 1991) [27]. Theoretical density, relative density and open porosity results of the 0-5-10% ZrO_2-doped barium-titanate-based microwave dielectric

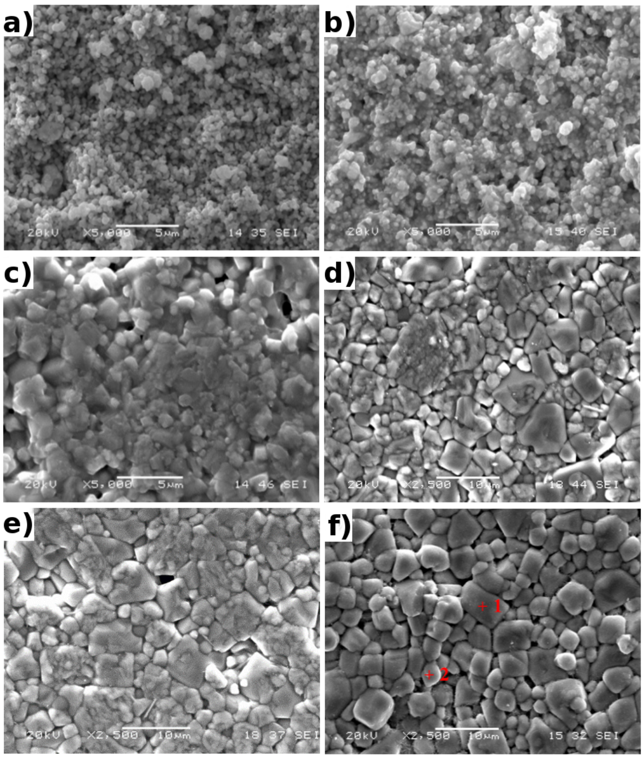
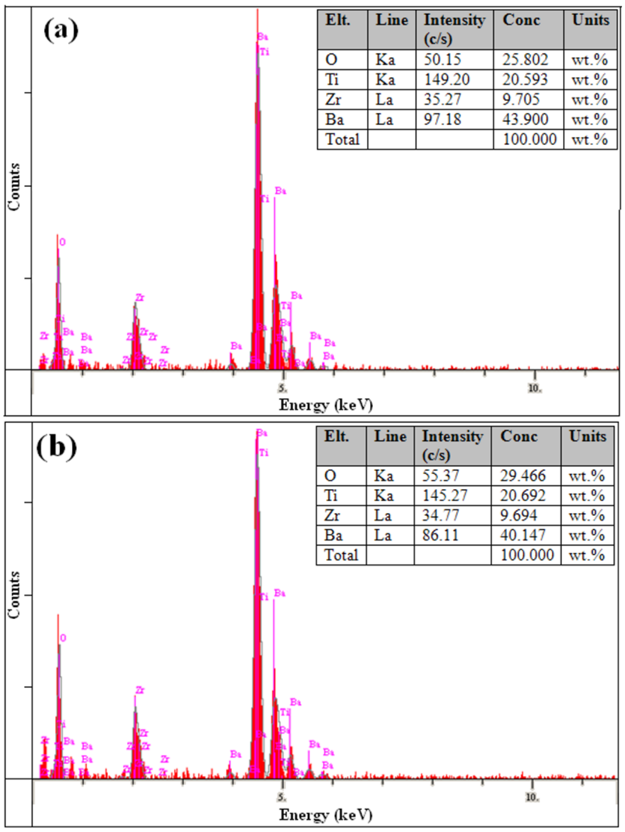


Fig. 2. SEM micrographs of $Ba(Ti_{0.8}Zr_{0.2})O_3$ sintered for 4 h, with and without addition of 0.5 wt.% B_2O_3, (a) 1250 °C, (b) 1350 °C, (c) 1450 °C, (d) 0.5 wt.%, 1250 °C (e) 0.5 wt.%, 1350 °C (f) 0.5 wt.%, 1450 °C.

ceramics are shown in Table I. The vacuum method (ISO 10545-3) was used in the laboratory to determine water absorption with greater precision. Vacuum method allows all open pores to be filled. The vacuum process was conducted in a chamber in which the air pressure was lowered to a value of 10^{-3} mbar. Samples were held at that pressure for 30 minutes. Table I presents the relative density and open porosity in samples sintered at 1450 °C for 4 h, with and without the addition of 0.5 wt.% B_2O_3.

Relative density and open porosity in barium titanate based ceramics sintered at 1450 °C for 4 h, with and without addition of 0.5 wt.% B_2O_3. TABLE I

Composition	Relative density [%]	Open porosity [%]
$Ba(Ti_1)O_3$	93.8	12.28
$Ba(Ti_{0.9}Zr_{0.10})O_3$	89.86	15.82
$Ba(Ti_{0.8}Zr_{0.2})O_3$	75.96	29.2
$Ba(Ti_1)O_3$ +0.5 wt.% B_2O_3	98.93	0.412
$Ba(Ti_{0.9}Zr_{0.10})O_3$ +0.5 wt.% B_2O_3	99.45	0.85
$Ba(Ti_{0.8}Zr_{0.2})O_3$ +0.5 wt.% B_2O_3	98.99	1.46



(a)

Elt.	Line	Intensity (c/s)	Conc	Units
O	Ka	50.15	25.802	wt.%
Ti	Ka	149.20	20.593	wt.%
Zr	La	35.27	9.705	wt.%
Ba	La	97.18	43.900	wt.%
Total			100.000	wt.%

(b)

Elt.	Line	Intensity (c/s)	Conc	Units
O	Ka	55.37	29.466	wt.%
Ti	Ka	145.27	20.692	wt.%
Zr	La	34.77	9.694	wt.%
Ba	La	86.11	40.147	wt.%
Total			100.000	wt.%

Fig. 3. Energy-dispersive spectra captured from the large grains (a) and the small grains (b) of the $Ba(Ti_{0.8}Zr_{0.2})O_3$ ceramic with 0.5 wt% of B_2O_3, sintered at 1450 °C.

4. Conclusions

The effects of the addition of 0.5 wt.% of B_2O_3 on the sintering behaviour, microstructure, of 0-5-10% ZrO_2-doped barium-titanate-based microwave dielectric ceramics were investigated. Addition of B_2O_3 to ZrO_2-doped barium titanate promotes sintering at low temperatures by the formation of a liquid phase. At a higher sintering temperature (over 1250 °C), grain growth occurs due to suppression of the solution and precipitation mechanisms, by increasing the sintering temperature and B_2O_3 addition. The XRD pattern shows that the compositions have a single phase perovskite structure without evidence of any additional phases. The small additions of B_2O_3 to ZrO_2-doped barium-titanate-based microwave dielectric ceramics reduces sintering temperature from 1450 to 1350 °C. Density and grain size of $BaTiO_3$-based microwave dielectric ceramics, doped with 10% of ZrO_2, with addition of 0.5 wt.% of B_2O_3, was found to increase with increasing temperature. Density was increasing at higher sintering temperatures. Density of the 5% zirconia-doped barium titanate was found always to be higher than that of 10%-doped barium titanate for the same sintering cycle. It was so, because a higher sintering temperature was required for higher content of zirconia.

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