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Effect of In, Ce and Bi dopings on sintering and dielectric properties of $Ba(Zn_{1/3}Nb_{2/3})O_3$ ceramics

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Abstract

In, Ce and Bi doped $Ba(Zn_{1/3}Nb_{2/3})O_3$ (BZN) ceramics were prepared by conventional mixed oxide technique. In doping between 0.2 and 4.0 mol% increased the density of BZN at 1300 °C, Ce doping caused a decrease in density at 1250 °C. Levels of Bi_2O_3 up to 1.0 mol% had negative effect on densification, while high level doping could significantly improve the densification of the specimens. XRD of the samples indicated that In, Ce and Bi doping resulted in single phase formation at all concentrations, except 0.5 mol% Bi. SEM of Bi doped BZN indicated only single phase structure and Ce doping even at 0.2 mol% gave some secondary phases. In and Ce doping increased the dielectric constant from 41 to around 66 at 1 MHz. Bi doping decreased the dielectric constant to about 37 at 0.2 mol%, and then higher doping led to dielectric constant to increase to about 63.

Keywords: Powders-solid state reaction; Sintering; Perovskites; $Ba(Zn_{1/3}Nb_{2/3})O_3$; Dielectric properties

1. Introduction

Due to their wide range of applications ranging from cellular phones to global positioning systems, dielectric ceramics occupy an important place in electronic ceramics. With the recent revolution in communication industry, dielectric ceramics used in microwave communication systems and mobile phones have been a remedy for minimization of size and cost of devices. Requirements for these microwave dielectric materials include a high relative permittivity (ε_r), low dielectric loss (high Q value) and a near-zero temperature coefficient of resonant frequency (τ_f). These three parameters are related to the size, frequency selectivity and temperature stability of the system and each dielectric property must be precisely controlled to satisfy the demands of microwave circuit designs.[1]

Complex perovskite $Ba(B'_{1/3}B''_{2/3})O_3$ ceramics have been found to exhibit excellent microwave dielectric properties.[2–5] Modified perovskite, barium zinc tantalate ($Ba(Zn_{1/3}Ta_{2/3})O_3$) (BZT), was reported in the 1980s to offer a combination of high permittivity coupled with exceptionally high Q (ε_r: ~30, $Q \times f$: ~110,000 GHz).[6] However, niobium based complex perovskites have attracted considerable attention due to the high cost of Ta_2O_5. Much research has been conducted on $Ba(Zn_{1/3}Nb_{2/3})O_3$ ceramic as a replacement of the Ta-based complex perovskite ceramics such as $Ba(Zn_{1/3}Ta_{2/3})O_3$ and $Ba(Mg_{1/3}Ta_{2/3})O_3$.[7] In recent years, $Ba(Zn_{1/3}Nb_{2/3})O_3$ (BZN) type microwave dielectric materials have been studied extensively in this field. BZN ceramics have potential applications in communication technology as resonators, filters and tuners. They have high dielectric constant ($\varepsilon_r = 41$), low dielectric loss or high quality factor of around 54,000 ($Q \times f = 54{,}000$ at 10 GHz), high resistivity and resonance frequency temperature coefficient of around 27 ppm/°C ($\tau_f = 27$ ppm/°C).[5]

BZN is generally prepared following the conventional mixed oxide route by ball milling the stoichiometric amounts of raw materials ($BaCO_3$, ZnO, and Nb_2O_5) and calcining in the temperature range 1100–1200 °C followed by sintering in the temperature range 1400–1500 °C.[8] BZN ceramics have high sintering temperatures which prevent the usage of Cu and Ag electrods that have low melting temperatures ($T_{m(Ag)} = 961$ °C).[7] Furthermore, the resonance frequency temperature coefficient of the BZN ceramic is relatively high ($\tau_f = 27$ ppm/°C), and this limits BZN ceramics to be used in microwave applications.[1] Thus, synthesis of BZN ceramics with different dielectric con-

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stants, low dielectric loss, nearly zero resonance frequency temperature coefficient and low sintering temperature, will enhance the application areas of these ceramics. Different methods can be used in order to enhance the properties of BZN dielectric ceramics. Some of these methods are, employment of chemical methods, addition of low melting temperature-glassy phases, and doping.

In this paper, In, Ce and Bi doped $Ba(Zn_{1/3}Nb_{2/3})O_3$ (BZN) ceramics were prepared by conventional mixed oxide technique. The effect of each dopant on the sintering temperature and dielectric properties were investigated. In, Ce and Bi doped BZN ceramics were characterized by XRD and SEM.

2. Experimental details

Powders of $BaCO_3$ (Fluka; >98.5%), ZnO (Sigma–Aldrich; 99%) and Nb_2O_5 (Alfa Aesar; 99.9%) were mixed in stoichiometric proportion in ethanol medium in a plastic container for 20 h. After drying the slurries at 100 °C for 24 h, they were milled in an agate mortar and calcined at 1100 °C for 4 h in a closed crucible. Oxides of dopant (In_2O_3, 99.9% Alfa Aesar; Bi_2O_3, 99.9%, Acros; CeO_2, 99.9%, Acros) additives were added in the molar ratios of 0.2%, 0.5%, 1.0%, 2.0%, 4.0% into the fabricated BZN powders and the mixtures were ball milled again in ethanol for 20 h. The slurry was dried and milled in the agate mortar and pressed into pellets with 10 mm diameter and 1–2 mm thickness by a uniaxial press with 2 MPa pressure. The pellets were buried in the BZN powder and sintered at different temperatures in a high temperature furnace for 4 h in a tightly closed alumina crucible to minimise the loss of volatile species. High temperature furnace was heated to 1250–1500 °C at of 250 °C/h, and samples were cooled from sintering temperature to 900 °C at 120 °C/h and to room temperature at 250 °C/h.

Surfaces of the pellets were grinded to ensure proper density measurements. Bulk densities of the samples were measured by Archimedes method. The theoretical densities of the doped BZN samples were calculated using the respective lattice parameters of each sample calculated by X-ray diffraction. The phases were characterized by X-ray diffractometry with Cu Kα radiation (λ = 1.5418 Å) in the range 2θ: 20–70°. The fracture surfaces of the specimens were examined in the SEM at 20 kV after coating with Au/Pd alloy by sputter coater. Chemical analysis was conducted by means of dispersive spectrometry (EDS) in the SEM.

Pellets with a relative density over 97% have been used for dielectric measurements. The circular faces of the dense and single phase pellets were painted with silver paste using vacuum coating system, then copper leads were attached on the surfaces using silver and disks were dried in an air oven. These disks were used for dielectric measurements. The dielectric constant and dielectric loss were measured using LCR meter in the low frequency range from 1 kHz to 2 MHz between 20 and 200 °C. The temperature coefficient of dielectric constant was calculated by the following formula:

$$\alpha_\varepsilon = \frac{\varepsilon_{T_2} - \varepsilon_{T_1}}{\varepsilon_{T_1}(T_2 - T_1)}$$

where α_ε, temperature coefficient of dielectric constant; ε_{T_2}, dielectric constant at 120 °C; ε_{T_1}, dielectric constant at 20 °C; $T_2 = 120$ °C; $T_1 = 20$ °C.

Table 1
Relative densities of doped BZN samples sintered at different temperatures.

	Relative density (%)					
	0.2 mol%	0.5 mol%	1.0 mol%	2.0 mol%	4.0 mol%	Sintering temperature
In	91.86	97.59	97.99	99.67	99.79	1300 °C
Ce	97.85	95.25	96.71	96.95	92.84	1400 °C
Bi	94.68	91.44	90.70	95.92	95.87	1250 °C

Theoretical density of undoped BZN ceramic is 6.516 g/cm^3.

3. Results and discussion

3.1. Densities of doped BZN ceramics

In doping into the BZN improved the sintering of BZN ceramics. Densities of In-doped BZN samples sintered at 1300 °C for 4 h increased with In content in the range of 0.2–4.0 mol% (Table 1). Although 0.2 mol% In doped BZN had a 92% of relative density, 4.0 mol% of In doping resulted in ~99% of relative density. Increasing sintering temperatures raised the densities of In doped BZN samples even at low doping concentrations. 0.2 mol% In-doped BZN had a relative density of 97% at sintering temperature of 1500 °C. Dense Ce-doped BZN ceramics were produced by 0.2 mol% of Ce doping at lower temperatures like 1250 °C. Nevertheless, as the Ce-doping concentration increased, the densities of Ce-doped BZN pellets decreased. Therefore, the density of Ce-doped BZN ceramics with amount of dopants was evaluated at 1400 °C. High relative density of around 98% was obtained at 0.2 mol% Ce but the density decreased to 92% at 4 mol% of Ce. This could be due to formation of secondary phases as inclusions in the microstructure of BZN as supported by SEM. The density of Bi-doped BZN samples sintered at 1250 °C for 4 h did not change consistently with the amount of Bi. Although 94.5% of relative density was achieved at 0.2 mol% of Bi, the density decreased ~4% at 0.5 and 1 mol% and again increased to 95.9% at 2.0 and 4.0 mol% of doping. The sharp decrease in density at 0.5 mol% doping could be due to formation of secondary phases as suggested by XRD. Although XRD of 1.0 mol% Bi-doped BZN did not give any secondary phases, the density decrease at 1.0 mol% could be possibly due to secondary phases which could not be detected by XRD due to its high detection limit. Around 96% of relative density was obtained in samples doped with 2.0 and 4.0 mol% Bi. Higher sintering temperatures above 1250 °C to obtain higher densities led to melting of samples.

3.2. XRD

XRD of In-doped BZN ceramics showed single phase perovskite structure for all In doping contents ranging between 0.2 and 4.0 mol% at sintering temperature of 1300 °C. No additional peaks on the XRD pattern were observed after doping indicating the absence of secondary phases (Fig. 1). Ce-doped BZN ceramics sintered at 1400 °C for 4 h also produced single phase BZN and no secondary phases were detected. In order to investigate the effect of sintering temperature on the phase development, 0.5 mol% Ce doped BZN was sintered between 1150 °C and 1450 °C for 4 h (Fig. 2). At 1150 °C, there were secondary phases in addition to BZN and their amounts decreased with sintering temperature finally giving single phase at 1300 °C. Sintering at higher temperatures above 1400 °C gave no dissociation of BZN or any other secondary phases. These results indicated that BZN formation depends strongly on temperature and high temperatures were required to obtain single phase BZN. XRD of Bi-doped BZN samples sintered at 1250 °C showed single phase perovskite structure for all doping contents except for 0.5 mol% doping (Fig. 3). Since XRD of 0.5 mol% Bi doped BZN sintered at 1250 °C gave secondary phases, it was sintered at various temperatures for 4 h to obtain single phase at higher temperatures. Although at 1200 °C there were high amounts of unidentified second phases, they disappeared completely at 1300 °C giving single phase (Fig. 4). This revealed that sintering temperature of 1250 °C was not enough for the formation of single phase BZN when Bi doping amount was 0.5 mol%. However, it was not understood that same kind of behaviour was not observed for the other doping contents which gave single phase at 1250 °C.

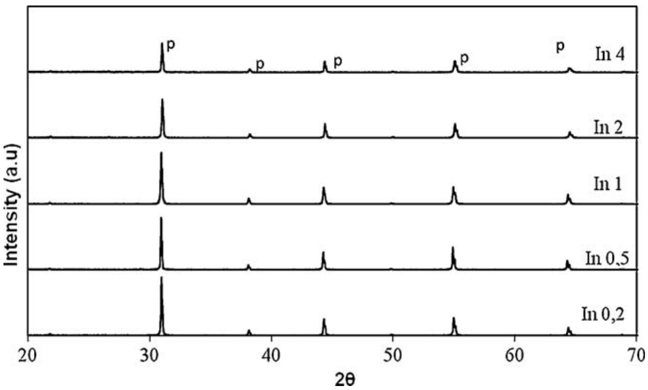

Fig. 1. XRD patterns of 0.2, 0.5, 1.0, 2.0 and 4.0 mol% In-doped BZN ceramics sintered at 1300 °C for 4 h (p = BZN phase).

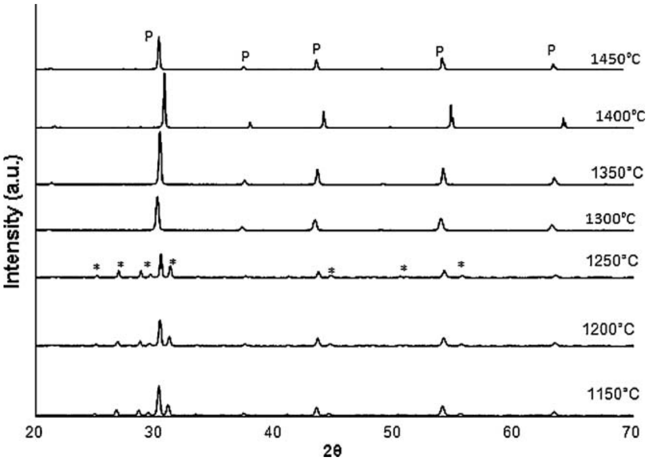

Fig. 2. XRD patterns of 0.5 mol% Ce-doped BZN ceramics sintered at various temperatures for 4 h (p = BZN phase; * = unidentified phase).

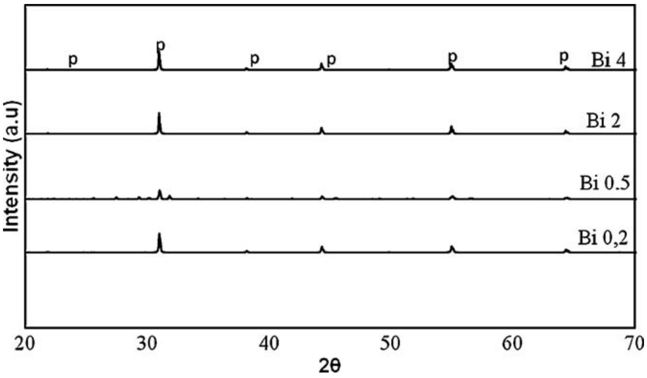

Fig. 3. XRD patterns of 0.2, 0.5, 2.0 and 4.0 mol% Bi-doped BZN ceramics sintered at 1250 °C for 4 h (p = BZN phase).

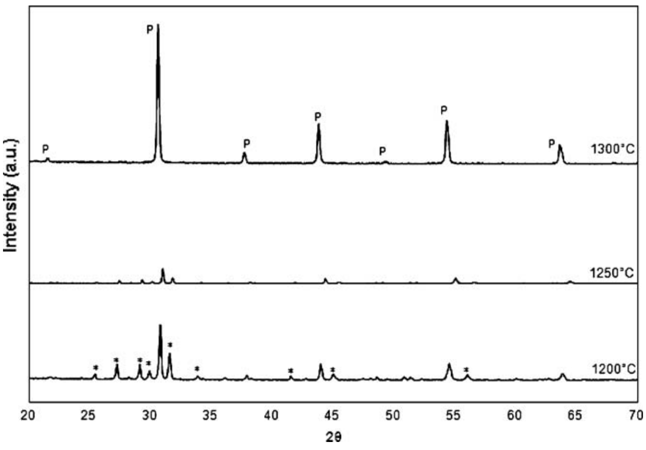

Fig. 4. XRD patterns of 0.5 mol% Bi doped BZN ceramics sintered at various temperatures for 4 h (p = BZN phase, * = unidentified phase).

3.3. Lattice parameters

Avarage lattice parameters of doped BZN samples are given in Table 2. In and Ce dopings generally increased the lattice parameter of BZN. The increase in lattice parameter was due to the greater ionic radius of In^{3+} and Ce^{4+} than that of Zn^{2+} (Table 3). It was thought that In and Ce dopants replaced the Zn cation in the BZN structure and formed substutional solid solution and therefore they resulted in an increase in the lattice parameter. On the other hand, Bi doping did not cause a

Table 2
Lattice parameters of doped BZN samples.

	Lattice parameter (Å)					
	0.2 mol%	0.5 mol%	1.0 mol%	2.0 mol%	4.0 mol%	Sintering temperature
In	4.0941	4.0962	4.1008	4.1155	4.1202	1300 °C
Ce	4.1369	4.1379	4.1434	4.1437	4.1543	1400 °C
Bi	4.0913	4.0893	4.0862	4.0922	4.0935	1250 °C

Lattice parameter of undoped BZN ceramic is 4.09408 Å.

Table 3
Ionic radii values of dopants and Ba, Zn, Nb cations depending on coordination numbers.

Element	Coordination number	Ionic radius (Å)
Ba	8	1.42
	12	1.61
Zn	6	0.74
	8	0.90
Nb	6	0.64
In	6	0.81
Ce	6	0.87
	8	0.97
Bi	6	1.03
	8	1.17

consistent increase or decrease with doping content possibly due to the formation of second phases as detected by XRD in 0.5 mol% Bi doped BZN sintered at 1250 °C or due to the evaporation of bismuth oxide and/or zinc oxide[4,9–11] which may cause nonstoichiometric phases. Slight weight losses were observed in ceramics after sintering which indicates evaporation from material.

3.4. SEM

SEM of 0.5 and 4.0 mol% Bi doped BZN ceramic showed only single phase BZN (Fig. 5). No secondary phase was detected, as observed by XRD. It can be seen from the figures that as the Bi doping content increased the perovskite grain size significantly increased which could be due to formation of liquid phases at high Bi content. EDS analyses taken from grains indicated identical composition with theoretical BZN composition (Fig. 5c).

Although XRD results showed that even 4.0 mol% of CeO_2 dissolved within BZN, SEM investigation indicated some secondary phases even at 0.2 mol% Ce doping (Fig. 6). Some needle like grains which were identified as barium oxide phase by EDS were observed in the microstructure of 0.2 mol% doped BZN (Fig. 6c). When Ce amount increased to 4.0 mol%, barium oxide phase disappeared in the microstructure but a Ce-rich phase occurred (Fig. 7). Ce-rich phase generally occurred as small inclusion particles either at grain boundaries or within the grains. Comparing the microstructure of 0.2 and 4.0 mol% Ce doped BZN ceramics, it is obvious that perovskite grains in the later case were much bigger. A small amount (0.2 mol%) of Ce doping significantly reduced the grain size but a consider-

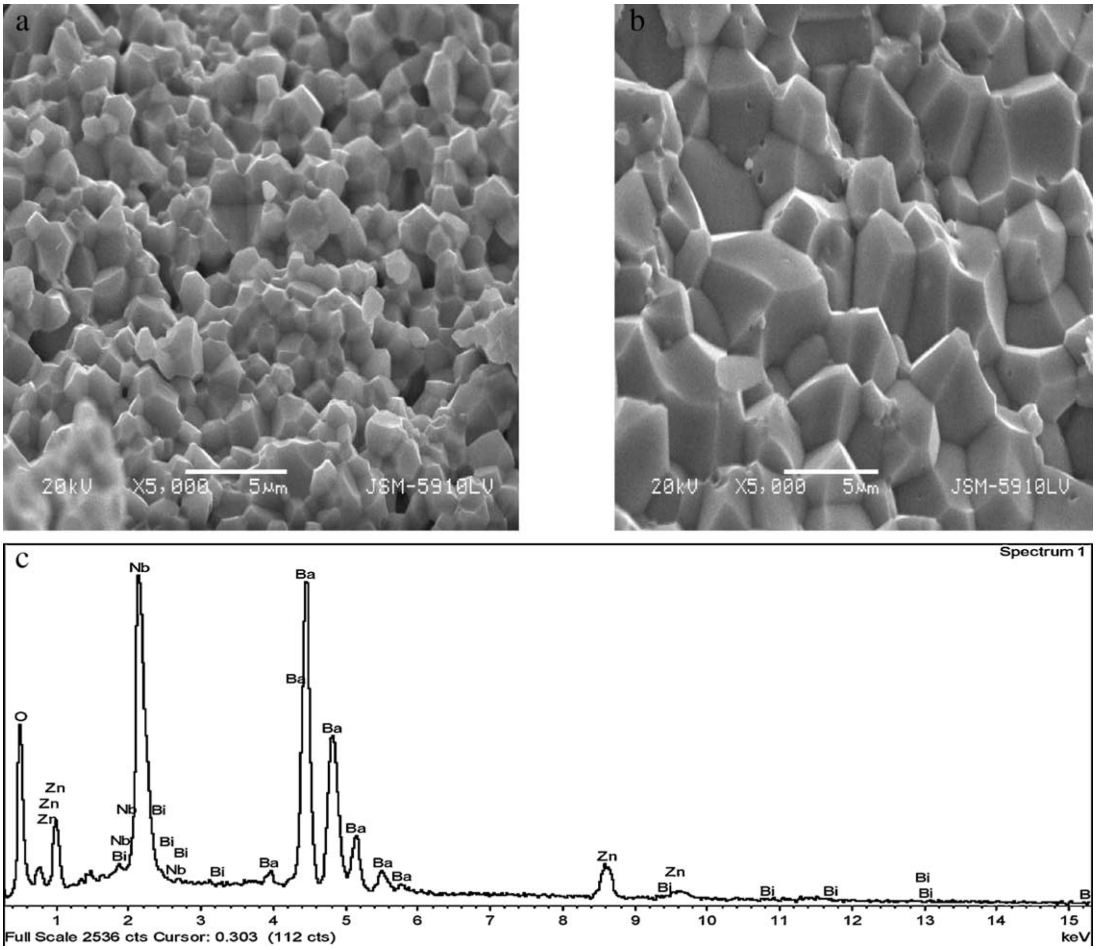

Fig. 5. SEM micrographs and EDS analysis of Bi-doped BZN ceramics sintered at 1250 °C for 4 h. (a) SEM micrograph of 0.5 mol% Bi_2O_3, (b) SEM micrograph of 4.0 mol% Bi_2O_3 and (c) EDS analysis from perovskite grains.

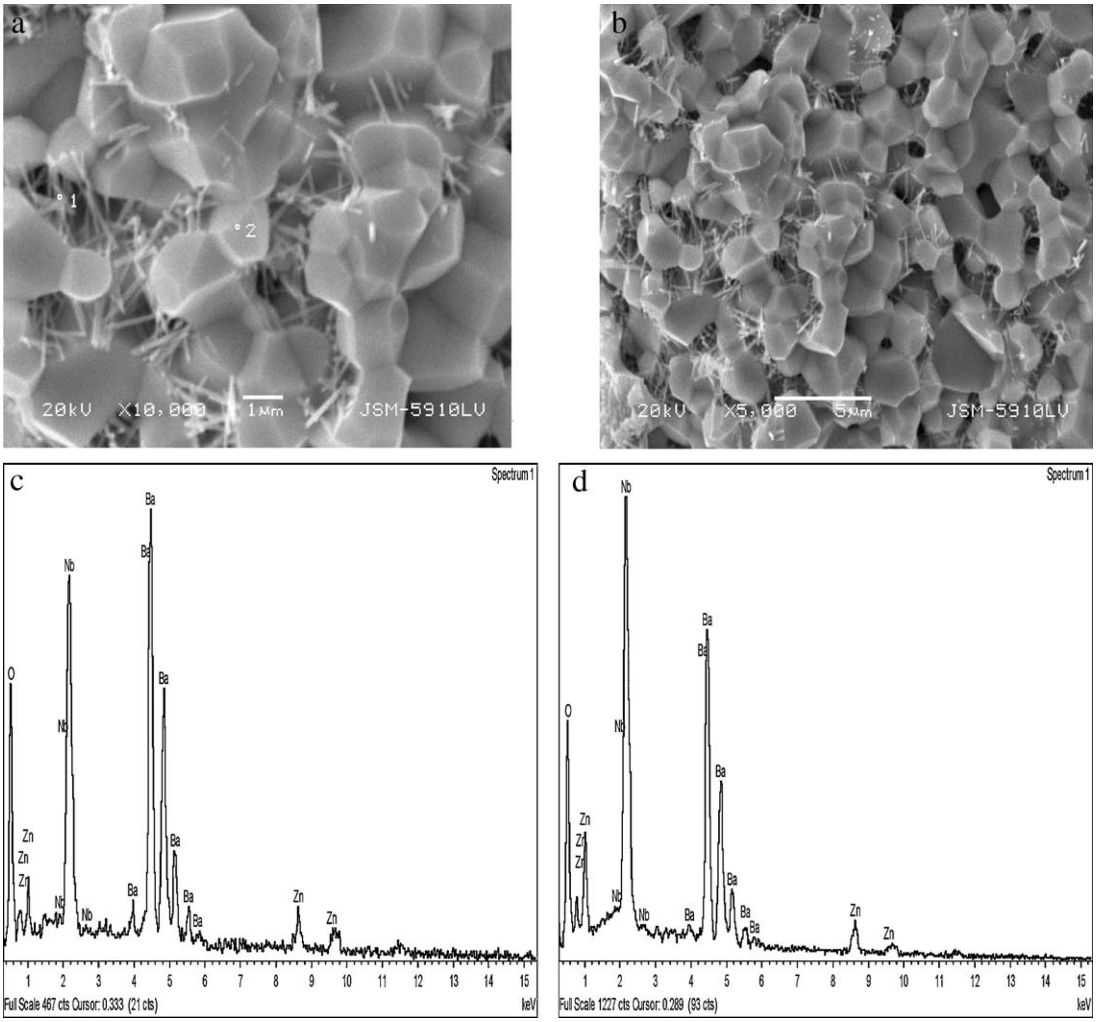

Fig. 6. SEM micrographs and EDS analysis of 0.2 mol% Ce-doped BZN ceramic sintered at 1400 °C for 4 h. (a) SEI at 10,000×, (b) SEI at 5000×, (c) EDS analysis from barium oxide phase (point 1) and (d) EDS analysis from perovskite grains (point 2).

able grain growth was observed at higher Ce-doping (4.0 mol%), probably due to a liquid phase occurring during sintering at high Ce content and/or due to the large distortion of the surrounding lattice that facilitates defect migration.[12,13]

3.5. Dielectric measurements

Compared with undoped BZN ceramic, In and Ce dopings into the BZN generally increased the dielectric constant of BZN

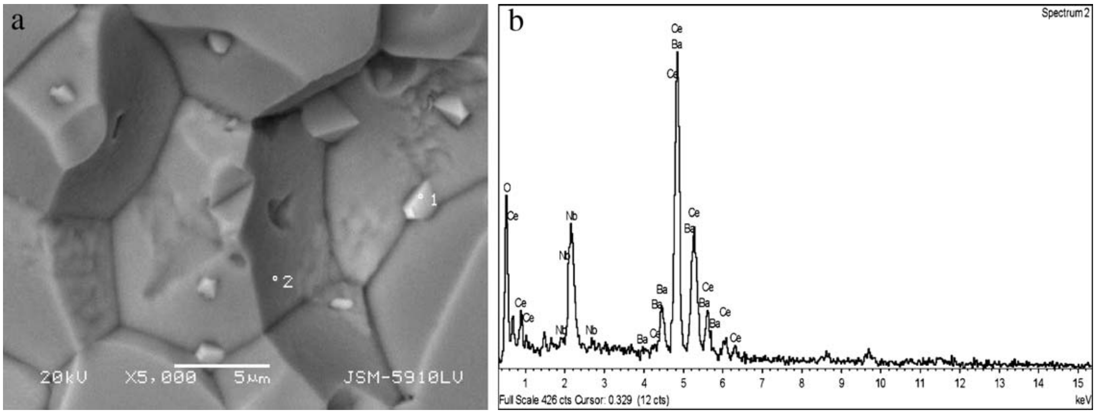

Fig. 7. SEM micrograph and EDS analysis of 4.0 mol% Ce-doped BZN ceramic sintered at 1400 °C for 4 h. (a) SEI at 5000× and (b) EDS analysis from Ce-rich phase (point 1).

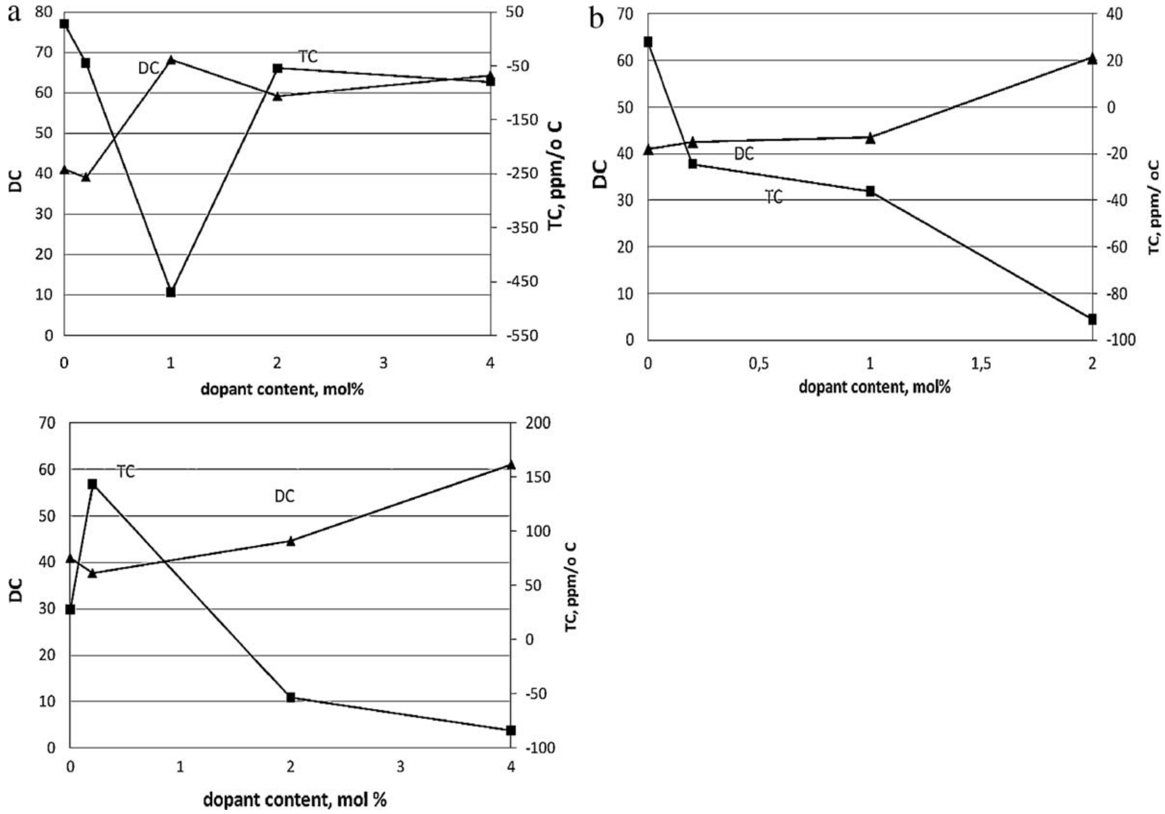

Fig. 8. Variation of dielectric constant (DC) and temperature coefficient of dielectric constant (TC) of (a) In doped, (b) Ce doped and (c) Bi doped BZN as a function of dopant content at 25 °C, at 1 MHz.

(Fig. 8). While Ce doping increased the dielectric constant from 41 to over 66, Ce doping increased it from 41 to around 60. The increase in dielectric constant could be due to higher polarizability of In and Ce than that of Zn (Zn: 7.1×10^{-24} cm^3; In: 10.2×10^{-24} cm^3; Ce: 26.6×10^{-24} cm^3).[14] Temperature coefficient of dielectric constant decreased with increasing In doping until 1.0 mol% In giving temperature coefficient of −469 ppm/°C but then it increased to around −54 ppm/°C above 1.0 mol% doping (Fig. 8). The sharp decrease in temperature coefficient at 1.0 mol% In could be due to formation of remnant impurity phases which could not be detected in SEM. Ce doping into the BZN structure decreased the temperature coefficient of dielectric constant giving a minimum value of −91 ppm/°C at 2.0 mol% Ce (Fig. 8). The decrease in temperature coefficient could be due to increase in the amount of secondary phases as observed by SEM (Figs. 6 and 7). Bi doping into the BZN also caused a general increase in dielectric constant (from 41 to 63) which could be due to higher densities of BZN at higher Bi dopings. Temperature coefficient of dielectric constant increased to around 151 ppm/°C at 0.5 mol% Bi and then decreased with Bi doping reaching to a value of −81 ppm/°C at 4.0 mol% Bi. Although XRD and SEM of Bi doped BZN indicated only single phase, the decrease in temperature coefficient could be due to secondary phases which could occur at grain boundaries or grain junctions in low amounts that cannot be detected by SEM.

The change in dielectric constant and dielectric loss of In, Ce and Bi doped BZN ceramics were investigated as a function of frequency and temperature. Doped ceramic had identical behaviours. Fig. 9 shows the change of dielectric properties of 2.0 mol% Ce doped BZN with frequency and temperature. It

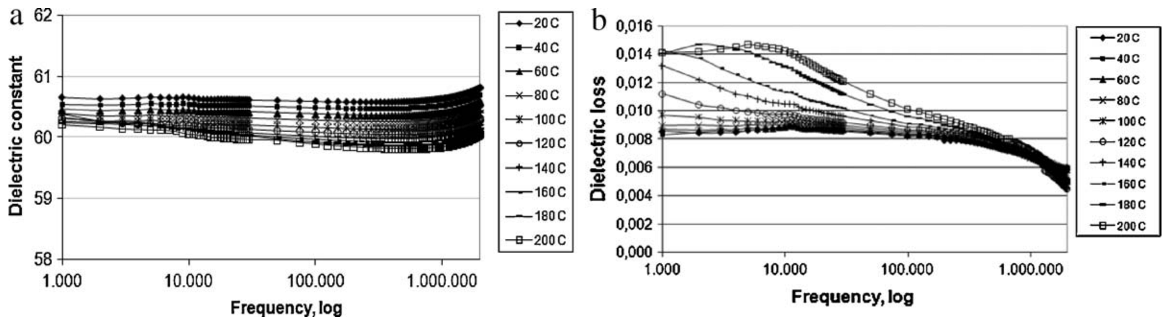

Fig. 9. Change of dielectric properties of 2.0 mol% Ce doped BZN with frequency and temperature (a) dielectric constant and (b) dielectric loss.

was observed that the dielectric constant did not change considerably with increasing frequency and temperature, as it varied just between 59.9 and 60.2. Temperature had a more pronounced effect than frequency. The dielectric loss slightly decreased with increasing frequency probably due to increase in leakage current.[15,16] Although dielectric loss of Ce-doped BZN was not dependent on temperature between 20 and 100 °C at all frequencies, it was significantly changed with temperature above 100 °C at low frequencies (below 100 kHz). Dielectric losses of doped BZN ceramics were generally below 0.015 and it generally raised with temperature possibly due to increase in the number of charge carriers.[17]

4. Conclusion

In the current study, BZN ceramics doped with In, Ce and Bi with the molar ratios of between 0.2 and 4.0 mol% were produced by mixed oxide technique. XRD examinations of doped ceramics indicated that In and Ce doped ceramics sintered at 1300 and 1400 °C, respectively, gave single phase. But, Bi doped BZN sintered at 1250 °C gave secondary phases at 0.5 mol% Bi, although single phase BZN was obtained at the other doping contents. Sintering temperature had a substantial effect on the BZN single phase formation. While the densities of In doped BZN ceramics increased with In doping, increase in Ce doping led to a decrease in density of BZN due to formation of secondary phases. SEM investigation revealed that increase in Bi and Ce doping contents increased the BZN grain size probably due to formation of a liquid phase. Although SEM of Bi doped BZN revealed only single phase, Ce doping resulted in formation of BaO second phase at low Ce doping and Ce-rich phase at high Ce doping. In, Ce and Bi dopings generally increased the dielectric constant possibly due to the greater polarizabilities of the dopant cations than the host cations. For all dopings, it was observed that dielectric constant did not change significantly with increasing frequency but temperature had a more pronounced negative effect on dielectric constant which decreased with temperature increase. The dielectric loss of doped BZN ceramics generally decreased at high frequencies.

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