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Production and properties of In and Ir doped $Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$ pyrochlores

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Abstract

In and Ir were doped into $Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$ (BZN) pyrochlore using the chemical formulas of $Bi_{1.5}Zn_{0.92-3x/2}In_xNb_{1.5}O_{6.92}$ and $Bi_{1.5}Zn_{0.92}Nb_{1.5-4x/5}Ir_xO_{6.92}$. While In was doped into Zn site of BZN, Ir was added into the Nb site. The solubility limits of In and Ir cations in BZN were $x = 0.1$ and $x = 0.12$–0.15, respectively. Above the solubility limits second phases of $BiNbO_4$ and $InNbO_4$ formed for In doping but $Bi_2Ir_2O_7$ and ZnO phases appeared in Ir doping. SEM investigation confirmed the XRD results. Lattice parameters of BZN pyrochlores slightly increased with In doping but decreased with Ir due to their ionic radii. The dielectric constant of Ir doped BZN slightly decreased with Ir content. However, In doping into the BZN generally decreased the dielectric constant at low doping ratios but increased it at high dopings. Temperature coefficients of Ir and In doped BZN ceramics were significantly affected by doping amount.

Keywords: BZN pyrochlore; Doping; Dielectric properties; XRD

1. Introduction

Pyrochlore oxides have a wide range of application areas due to their different electrical, magnetic, dielectric, optical and catalytic properties and also due to their convenient structure for doping with various elements without changing its structure.[1] Pyrochlore structures have a general formula of $A_2B_2O_7$ where A is trivalent or bivalent cations and B is quadrivalent and quinquevalent cations.

In recent years, many researchers have focused on the application of high-frequency dielectrics, such as Ba–Nd–Ti–O system and Bi–Zn–Nb–O system.[2,3] Pyrochlore oxide in the Bi_2O_3–ZnO–Nb_2O_5 system exhibit high dielectric constants, relatively low dielectric losses, and compositionally tunable temperature coefficients of capacitance.[4] Although two different formulas ($Bi_{1.5}Zn_{1.0}Nb_{1.5}O_7$ and $Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$) were suggested in literature for pyrochlore in the Bi_2O_3–ZnO–Nb_2O_5 system, researchers showed that appropriate formula was $Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$.[5–7] Tan et al.[8] reported that cubic pyrochlore phase in the Bi_2O_3–ZnO–Nb_2O_5 system forms a solid solution area that does not include the so called ideal composition, $Bi_{1.5}ZnNb_{1.5}O_7$. It was reported that pyrochlore is ZnO-deficient and extensive range of solid solutions can be formed in this system by variation in the Bi/Nb ratio to either side of unity.[8]

$Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$ (BZN) has a high dielectric constant (∼121) and low quality factor ($Q \times f \sim 487$ GHz) at 2.27 GHz.[9] BZN pyrochlore also indicates dielectric relaxation between 100 K and 400 K at 1.8 GHz peaking around 230 K. Dielectric relaxation may occur near room temperature at THz level frequencies.[6] Dielectric relaxation at microwave frequencies could occur due to substitutional point defects in BZN or due to polarization of the pyrochlore crystal lattice associated with off-center displacement of Bi and Zn cations on the A site, linked to off-center displacement of oxygens.[5,6] The other significant advantage of BZN pyrochlore is the low sintering temperatures of <950 °C. Desired dielectric properties and low sintering temperature render BZN pyrochlore as attractive candidates for capacitor and high frequency filter applications in multilayer structures cofired with silver electrodes.[10,11]

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Additives affect ceramics in many ways by changing the density, microstructure, defect structure and possibly crystal structure. These changes influence the dielectric properties such as a higher relative density results in a higher dielectric constant. Addition of 3 wt% CuO into BZN decreased the sintering temperature below 900 °C and increased the dielectric constant to 120 at 2.3 GHz.[12] Solid solution of Ti and Zr with $Bi_{1.5}Zn_{1.0}Nb_{1.5}O_7$ had dielectric constants in the range of 100–200, temperature coefficients varying from −1300 ppm/K to −88 ppm/K and low dielectric loss values.[10] Ti, Cu, Ta, Sn and Sr dopings into the BZN system resulted in a dielectric constant in the range of 60–200, higher dielectric loss and larger negative temperature coefficient.[4,10,13,14] Sb addition into the BZN by replacing Nb decreased the dielectric constant (from 100 to 35), dielectric loss and gave more negative temperature coefficients.[15] Recently, Mergen et al. [16,17] introduced Cr, Co, Sm, Nd and Fe into the $Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$ pyrochlore and investigated into their dielectric properties.

In this study, some precious elements (Ir and In) were added into the $(Bi_{1.5}Zn_{0.46})(Zn_{0.46}Nb_{1.5})O_{6.92}$ pyrochlore structure to substitute Nb and Zn. Solubility limit of each additive in BZN structure was determined, and new single phase pyrochlore ceramics were produced. The sintering behaviour and dielectric properties of Ir and In doped BZN ceramics were examined.

2. Experimental

Powder samples having the formulas of $Bi_{1.5}Zn_{0.92-3x/2}In_xNb_{1.5}O_{6.92}$ and $Bi_{1.5}Zn_{0.92}Nb_{1.5-4x/5}Ir_xO_{6.92}$ were prepared by the conventional solid state reaction. The starting materials were reagent grade powders of Bi_2O_3 (99,9%; Acros), ZnO (99%; Sigma–Aldrich), Nb_2O_5 (99.9%; Alfa Aesar), In_2O_3 (99.9%; Alfa Aesar), IrO_2 (99%; Alfa Aesar). After mixing the powders by ball milling for 15 h in ethanol using zirconia balls, they were dried and calcined at 800 °C for 4 h. The calcined powders were milled in an agate mortar and then pressed into disks (1–2 mm × 10 mm). In and Ir doped pellets were sintered between 1000 °C and 1075 °C for 4 h in a tightly closed alumina crucible to prevent evaporation losses. Crystalline phases of sintered pellets were identified by X-ray powder diffraction technique using Cu Kα radiation by Rigaku diffractometer at 1°/min. Lattice parameters were determined using an internal standart and calculated using a least square method. Microstructure of the sintered samples was investigated using scanning electron microscope equipped with energy dispersive spectrometer (JEOL 5910LV). Backscattered and secondary electron imaging modes were used in SEM. The circular faces of the pellets were painted with Ag paste using vacuum coating system, Boc Edwards Auto 500, then Cu leads were attached on the surfaces using Ag and disks were dried in an air oven for dielectric measurements. Dielectric constant and dielectric loss were measured using HP 4284A LCR meter in the frequency range from 1 kHz to 2 MHz between 20 °C and 200 °C. The temperature coefficient of dielectric constant (α_ε) was calculated by the following formula:

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

where ε_{T_2} = dielectric constant at 120 °C (T_2), ε_{T_1} = dielectric constant at 25 °C (T_1).

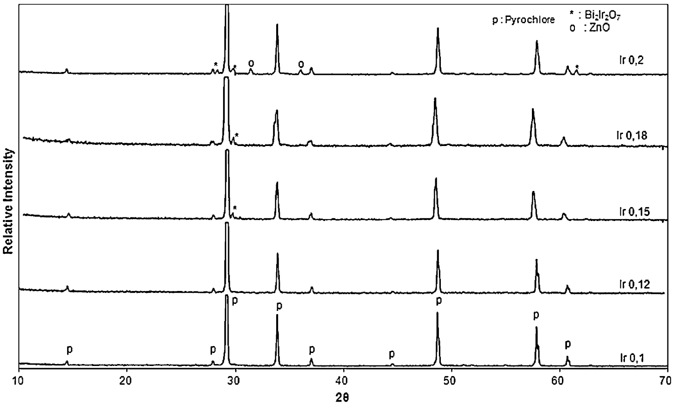

Fig. 1. XRD patterns of $Bi_{1.5}Zn_{0.92}Nb_{1.5-4x/5}Ir_xO_{6.92}$ compositions for x values of 0.1, 0.12, 0.15, 0.18 and 0.2.

3. Results and discussion

3.1. Solubility limit of cations

The solubility limit of Ir and In cations in BZN pyroclore was determined using the compositions $Bi_{1.5}Zn_{0.92}Nb_{1.5-4x/5}Ir_xO_{6.92}$ and $Bi_{1.5}Zn_{0.92-3x/2}In_xNb_{1.5}O_{6.92}$. Ir addition into the BZN replacing Nb gave only single phase until doping levels of $x = 0.12$ (Fig. 1). $Bi_2Ir_2O_7$ (JCPDS No: 41-953) started to form when x reached to 0.15 and ZnO (JCPDS No: 36-1451) began to form at $x = 0.20$. The amount of these phases increased with increasing Ir content. These results indicate that a limited substantial solid solution occurs although Ir^{4+} (0.63 Å) have identical radius with Nb^{5+} (0.64 Å). XRD patterns of In doped BZN suggest that a solid solution occurs until $x = 0.1$ (Fig. 2). However, when $x > 0.12$, $BiNbO_4$ (JCPDS No: 16-295) started to form increasing in amount with x. At higher In concentrations

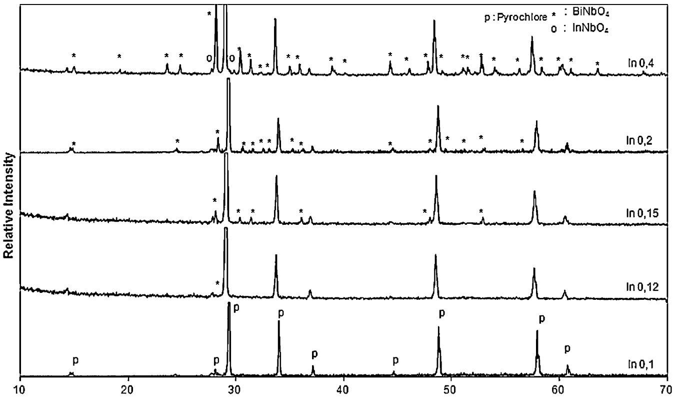

Fig. 2. XRD patterns of $Bi_{1.5}Zn_{0.92-3x/2}In_xNb_{1.5}O_{6.92}$ compositions for x values of $x = 0.1$, 0.12, 0.15, 0.2 and 0.4.

Table 1
Lattice parameters of Ir and In doped BZN ceramics.

Substitute for	Cation	Additive proportion	Lattice parameter (Å)	Sintering temperature (°C)
Nb	Ir	$x = 0.1$	10.5446	1025
		$x = 0.12$	10.5414	1025
Zn	In	$x = 0.05$	10.5643	1025
		$x = 0.1$	10.5656	1050

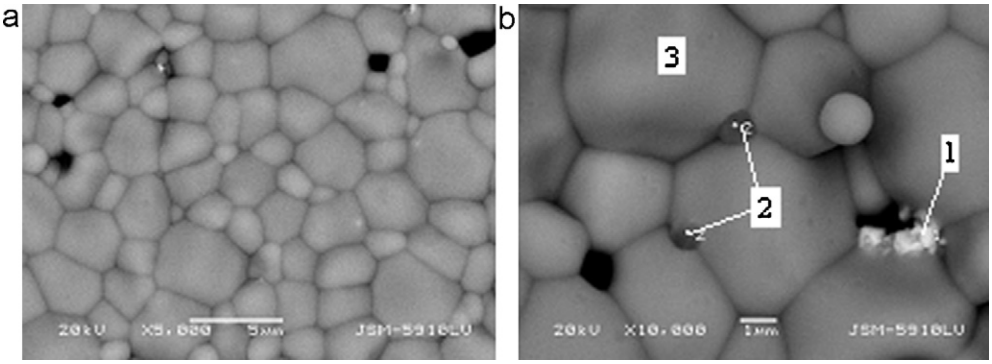

Fig. 3. Backscattered electron images of $Bi_{1.5}Zn_{0.92}Nb_{1.5-4x/5}Ir_xO_{6.92}$ (a) $x = 0.12$ and (b) $x = 0.15$ ceramics sintered at 1000 °C for 4 h. At $x = 0.15$, microstructure contains three phases: Ir-rich phase (point 1), ZnO grains (point 2) and pyrochlore grains (point 3).

($x = 0.40$) $InNbO_4$ phase (JCPDS No: 25-384) appeared as second phase. As the Ir^{4+} incorporation into the BZN pyrochlore increased, the lattice parameter of the single phase pyrochlore decreased because of smaller ionic radius of Ir^{4+} (0.63 Å) than Nb^{5+} (0.64 Å) (Table 1). However, In^{3+} doping into the BZN leads to an increase in the lattice parameter due to larger ionic radius of In^{3+} (0.92 Å) than that of Zn^{2+} (0.90 Å at coordination number = 8; 0.74 Å at coordination number = 6). These results indicate that Ir and In occupy the Nb- and Zn-sites, respectively, to form homogeneous solid solution phases.

3.2. *Microstructure of Ir and In Samples*

The microstructure of Ir doped BZN samples was examined using the specimens $x = 0.12$ (solubility limit) and $x = 0.15$ (above the solubility limit). SEM investigation revealed only single phase pyrochlore at $x = 0.12$ as observed in XRD (Fig. 3). But when $x = 0.15$, SEM disclosed three phases (Fig. 3); pyrochlore, ZnO and Ir-rich phase consistent with XRD results where $Bi_2Ir_2O_7$ and ZnO phases were detected in addition to pyrochlore (Fig. 1). EDS analysis taken from each specific phases clearly indicated the existence of these phases. The composition of Ir-rich phase was near to the theoretical composition of $Bi_2Ir_2O_7$. On the other hand, the other second phase which was not observed in XRD possibly due to its low content was ZnO phase (point 2). BZN sample containing high amount of Ir ($x = 0.15$) sintered at the same temperature with $x = 0.12$ (1000 °C for 4 h) had high amount of porosity. Although SEM investigation of In doped BZN sample at solubility limit ($x = 0.10$) revealed only single phase, SEM of In doped BZN above solubility limit ($x = 0.12$) disclosed two phases (Fig. 4). In addition to pyrochlore, an In-rich phase was also detected as observed in XRD where $BiNbO_4$ phase appeared as second phase (Fig. 2). Doping elements also significantly affected the BZN grain size. Although In doping at $x = 0.10$ gave a grain size of 5–12 μm, higher In doping at $x = 0.12$ resulted in lower grain sizes of 2–9 μm (Fig. 5). Ir and In-doped BZN ceramics were sintered between 1000 °C and 1075 °C for 4 h and high

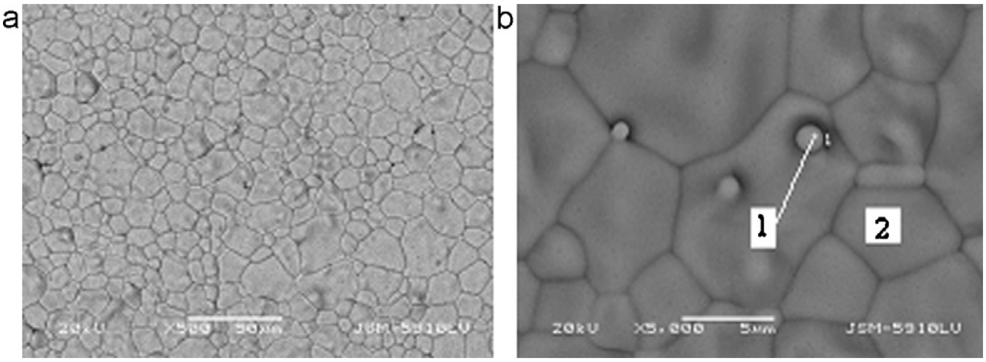

Fig. 4. Secondary electron SEM images of $Bi_{1.5}Zn_{0.92-3x/2}In_xNb_{1.5}O_{6.92}$ (a) $x = 0.1$ and (b) $x = 0.12$ ceramics sintered at 1000 °C for 4 h (point 1, $BiNbO_4$ phase; point 2, pyrochlore grains).

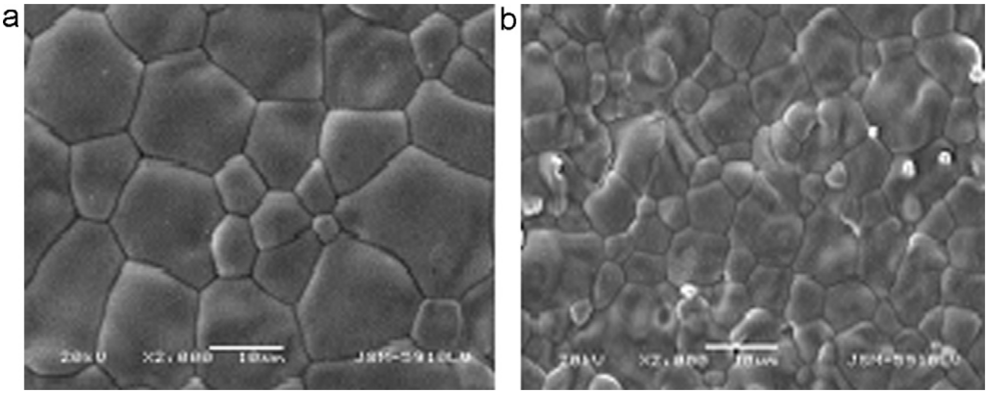

Fig. 5. Effect of In addition on the BZN grain size (a) $Bi_{1.5}Zn_{0.77}In_{0.1}Nb_{1.5}O_{6.92}$ ($x = 0.10$) and (b) $Bi_{1.5}Zn_{0.74}In_{0.74}Nb_{1.5}O_{6.92}$ ($x = 0.12$).

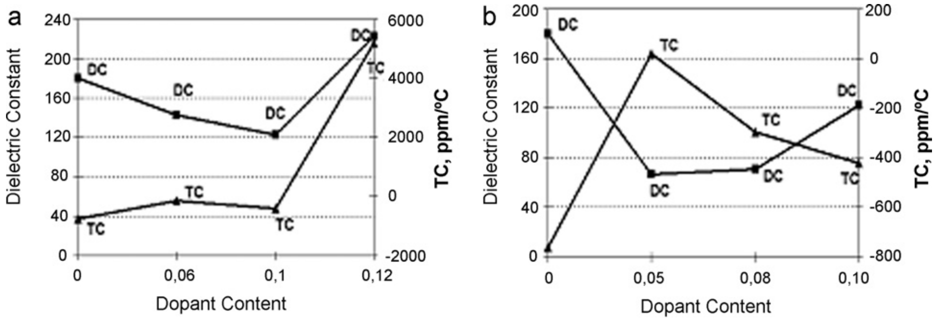

Fig. 6. Dielectric constant (DC) and temperature coefficient of dielectric constant (TC) of (a) Ir doped BZN and (b) In doped BZN as a function of dopant content (25 °C–1 MHz).

density ceramics with relative density over 97% were obtained for dielectric measurements. While Ir cation led to a decrease in densities with dopant concentration, In cation resulted in an increase in densities with doping concentration.

3.3. Dielectric properties of doped BZN pyrochlores

Dielectric constant of Ir doped BZN structure slightly and continuously decreased to 123 with inreasing the doping amount up to $x = 0.1$ (Fig. 6a). The decrease in dielectric constant until $x = 0.1$ could be due to lower polarizability of Ir (7.6 of Ir, 10^{-24} cm^3) than Nb (15.7 of Nb, 10^{-24} cm^3). However, dielectric constant sharply increased to 222 at $x = 0.12$ and this could be due to existence of second phases that was detected in XRD due to its lower detection limit. Although the doping level up to $x = 0.10$, did not cause any substantial change in temperature coefficient of dielectric constant, it increased sharply to 5176 ppm/°C at $x = 0.12$. The increase in temperature coefficient at $x = 0.12$ could be due to existence of second phases. In doping into BZN generally decreased the dielectric constant at low doping ratios but increased it at high doping ratios (Fig. 6b). Temperature coefficient decreased with increasing In doping until $x = 0.05$ giving about 18 ppm/°C but then it increased continuously reaching to around −420 ppm/°C at $x = 0.1$ (Fig. 6b).

The dielectric properties of Ir and In doped BZN ceramics at different doping concentrations indicated identical behaviour with frequency and temperature. The change of dielectric constant and dielectric loss of In doped $Bi_{1.5}Zn_{0.92-3x/2}In_xNb_{1.5}O_{6.92}$ composition for $x = 0.08$ ($Bi_{1.5}Zn_{0.80}In_{0.08}Nb_{1.5}O_{6.92}$) is given in Fig. 7. The dielectric constant slightly increased with frequency. But temperature had a higher prominent effect on dielectric constant that it increased from 67 to 72 at 1 MHz. No peaks were observed in the dielectric constant-frequency curve which could be due to lattice polarization with no dipole

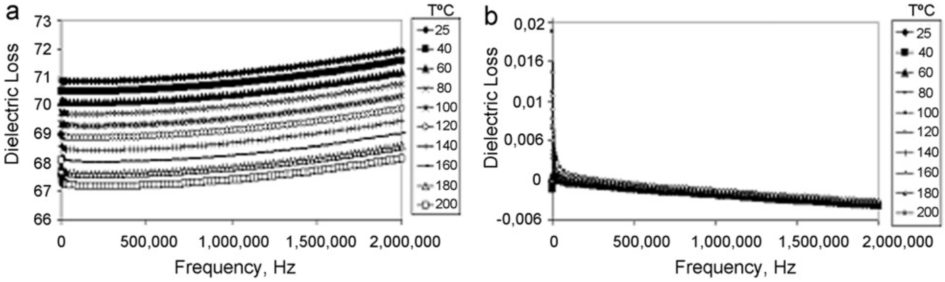

Fig. 7. Variation of (a) dielectric constant and (b) dielectric loss with frequency and temperature for In doped BZN structure ($x = 0.08$).

formation. The dielectric loss of In doped BZN for $x = 0.08$ had a sharp decrease at low frequency (<100 kHz) but then the decrease was gradual above 50 kHz until 2 MHz (Fig. 7b). The decrease in dielectric loss with frequency is one of the features of normal dielectrics.[18] The dielectric loss was below 0.006 at all frequency and temperature ranges above 100 kHz. The decrease in dielectric loss with frequency is due to leakage conduction.[19,20] Although temperature did not have any significant effect on dielectric loss, it increased slightly with temperature which could be due to increase in the number of charge carriers.

4. Conclusions

Ir and In were doped into $(Bi_{1.5}Zn_{0.46})(Zn_{0.46}Nb_{1.5})O_{6.92}$ structure (BZN) in specific amounts and new microwave dielectric materials were produced. While Ir was doped instead Nb in the B-site, In dopants were added to replace Zn cation. The solubility limit of each cation was determined as 0.12 and 0.1 for the Ir and In cations, respectively. The relative densities of doped BZN structures had a value more than 97%. The dielectric constant of BZN generally decreased with Ir doping, however, In incorporation into BZN initialy decreased dielectric constant but then led to an increase above $x = 0.05$. The variation of dielectric properties of doped BZN ceramics with frequency and temperature was identical. The dielectric constant was nearly stable with frequency and temperature. Dielectric loss and temperature coefficients were also affected by Ir and In doping content.

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