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Dielectric properties of Sm, Nd and Fe doped $Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$ pyrochlores

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Abstract

New pyrochlore ceramics have been produced by doping Sm and Nd into the Bi site and Fe into the Nb site in the $Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$ (BZN) pyrochlore. Doped pyrochlore ceramics were produced by conventional solid state mixing of oxides at different doping levels using the compositions of $Bi_{1.5-x}Sm_xZn_{0.92}Nb_{1.5}O_{6.92}$, $Bi_{1.5-x}Nd_xZn_{0.92}Nb_{1.5}O_{6.92}$ and $Bi_{1.5}Zn_{0.92}Nb_{1.5-x}Fe_xO_{6.92-x}$. The solubility limit of cations was determined as $x = 0.13$, 0.18 and 0.15 for Sm, Nd and Fe, respectively. While Sm and Nd increased the dielectric constant (ε), Fe doping led a decrease in ε. Dielectric constant of Sm and Nd doped BZN increased to 199 at $x = 0.13$ (Sm) and to 219 at $x = 0.18$ (Nd). At low Fe dopings ($x = 0.05$), the dielectric constant of BZN increased to 242 but decreased to 211 at $x = 0.15$. The dielectric losses were lower for Sm and Nd dopings than Fe but in all cases it was lower than 0.006. The dielectric constant of Sm, Nd and Fe doped BZN ceramics was nearly independent of frequency within the frequency range between 1 kHz and 2 MHz, but decreased considerably with temperature between 20 and 200 °C. Temperature coefficient of Sm doped BZN (−354 ppm/°C) was lower than Nd and Fe doped BZN ceramics at solubility limits (−538 ppm/°C for Nd and −565 ppm/°C for Fe).

Keywords: C. Dielectric properties; Bismuth zinc niobate pyrochlore; Dopants

1. Introduction

Pyrochlore compounds have a face centered cubic structure with a lattice parameter of around 10 Å [1]. Considering that pyrochlore compounds have a general formula of $A_2B_2X_6Z$, where A and B are cations and X and Z are anions, there are 16 A cations, 16 B cations, 48 X anions and 8 Z anions within the unit cell. Pyrochlore structures are interesting due to their ability to form substituted and defective structures. Pyrochlores can accommodate various ions either in place of A and B cations or X and Z anions [1,2]. Various defect pyrochlores can also be produced by removing ions from the structure like A, B cations and/or Z anion resulting in compositions with chemical formulas of $A_2B_2X_6Z_{1-x}$ (e.g. $Pb_2(Cr_{0.5}Sb_{1.5})O_{6.5}$ and $Pb_2(TiSb)O_{6.5}$), $A_{2-x}B_2X_6Z_{1-x}$ (e.g. $Pb_{1.5}M_2O_{6.5}$, where M = Nb, Ta and) and $A_{2-x}B_{2-x}X_{6-x}$ (e.g. as $TaWO_{5.5}$) [3–5].

$Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$ (BZN) pyrochlore form in the Bi_2O_3–ZnO–Nb_2O_5 system [8] has attracted more attentions in recent years as capacitors and high frequency filter applications due to their excellent dielectric properties in RF and microwave range. BZN pyrochlore compound has a high dielectric constant (∼121) and low quality factor ($Q \times f \sim 487$ GHz) at high frequency levels of 2.27 GHz [6]. BZN pyrochlore also indicates dielectric relaxation between 100 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 [6] or due to polarization of the pyrochlore crystal lattice associated with off-center displacement of bismuth and zinc cations on the A sites, linked to off-center displacement of oxygens [7].

In addition to advantageous dielectric properties, BZN pyrochlore has a low firing temperature which depress the dielectric loss due to higher conductivity of Ag and decrease the

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cost because low firing temperature enable the ceramic to be cofired with low cost electrodes like Ag [9,10].

Various ions are doped into the BZN cubic pyrochlore either to lower its sintering temperature or to obtain materials with diverse dielectric properties and near to zero temperature coefficient of capacitance. 3 wt% CuO-based dopants were added into BZN which decreased the sintering temperature below 900 °C and increased the dielectric constant to 120 at 2.3 GHz [11]. Extensive range of solid solution formation was discovered in Ti and Zr substituted $Bi_{1.5}Zn_{1.0}Nb_{1.5}O_7$. The resultant solid solutions had dielectric constants in the range of 100–200, temperature coefficients varying from −1300 to −88 ppm/K and low dielectric loss values [12]. The introduction of Ti, Cu, Ta, Sn and Sr ions into the BZN system resulted in a dielectric constant in the range of 60–200, higher dielectric loss and larger negative temperature coefficient [12–15]. Sb replacing Nb in the series $(Bi_{1.8}Zn_{0.2})(Zn_{0.6}Nb_{1.4-x}Sb_x)O_7$. $(0 \leq x \leq 1.4)$ decreased the dielectric constant linearly from 100 to 35, led to low dielectric losses ($\leq 4 \times 10^{-4}$) and more negative temperature coefficients with the lowest value of −180 ppm/°C at $x = 0.6$ [16].

The present paper reports the solubility limits of Sm, Nd and Fe cations in BZN pyrochlore and explore the dielectric properties of doped BZN at different frequencies and temperatures.

2. Experimental

Powder samples having the formula $Bi_{1.5-x}M_xZn_{0.92}Nb_{1.5}O_{6.92}$ (M = Sm, Nd) and $Bi_{1.5}Zn_{0.92}Nb_{1.5-x}M_xO_{6.92-x}$ (M = Fe) ($x = 0.1$–0.6) were prepared by the conventional high temperature solid state reaction technique. Bi_2O_3 (99.99%, Aldrich), Nb_2O_5 (99.5%, Merck), ZnO (99.5%, Aldrich), Sm_2O_3 (99.9%, Alfa Aesar), Fe_2O_3 (99.5%, Alfa Aesar) and Nd_2O_3 (99%, Alfa Aesar) were used as starting materials. After mixing 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 with 1–2 mm thickness and 10 mm diameter. While Sm and Nd doped pellets were sintered at 1000 °C for 4 h, Fe doped samples were sintered at 900 °C for 4 h in air in a tightly closed alumina crucible to prevent evaporation losses.

Crystalline phases of sintered pellets were identified by X-ray powder diffraction technique using Ni filtered Cu Kα radiation by the Rigaku diffractometer at a scan rate of 1°/min and the unit cell parameters were computed by the least square method. Microstructure of the sintered samples was investigated using scanning electron microscope JEOL JSM 5600 LV. The circular faces of the pellets were painted with silver paste using vacuum coating system, Boc Edwards Auto 500, 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 HP 4284A 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 25 °C, $T_2 = 120$ °C and $T_1 = 25$ °C.

3. Results and discussion

3.1. Solubility limit of cations

The solubility limit of Sm, Nd and Fe cations in BZN pyrochlore was determined using the compositions $Bi_{1.5-x}M_xZn_{0.92}Nb_{1.5}O_{6.92}$ (M = Sm, Nd) and $Bi_{1.5}Zn_{0.92}Nb_{1.5-x}M_xO_{6.92-x}$ (M = Fe). Sm and Nd addition into the BZN replacing Bi gave only single phase until doping levels of $x = 0.13$ and 0.18, respectively (Figs. 1 and 2). ZnO (JCPDS: 36-1451) and $MNbO_4$, where M = Sm and Nd (JCPDS: 22-1303 for Sm and 32-680 for Nd), phases started to form when $x \geq 0.15$ for Sm and $x > 0.18$ for Nd. The amount of these phases increased with increasing Sm and Nd contents. No any other phases formed in the system even at $x = 0.6$. These results indicate that a limited substitutional solid solution occurs although Nd^{3+} (0.112 nm) and Sm^{3+} (0.109 nm) have identical

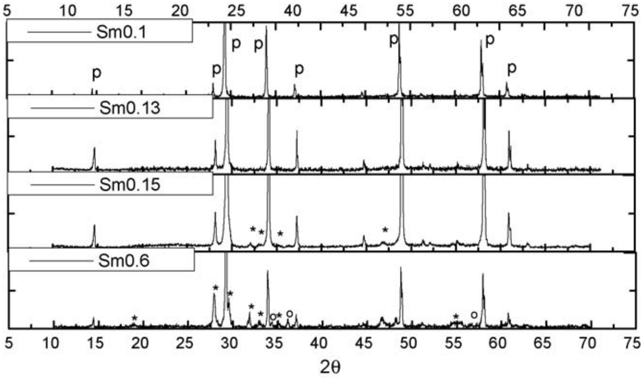

Fig. 1. XRD patterns of $Bi_{1.5-x}Sm_xZn_{0.92}Nb_{1.5}O_{6.92}$ pyrochlore with different Sm dopings ($x = 0.1$, 0.13, 0.15, 0.2, 0.3, 0.4, 0.5 and 0.6) (*$SmNbO_4$, °ZnO).

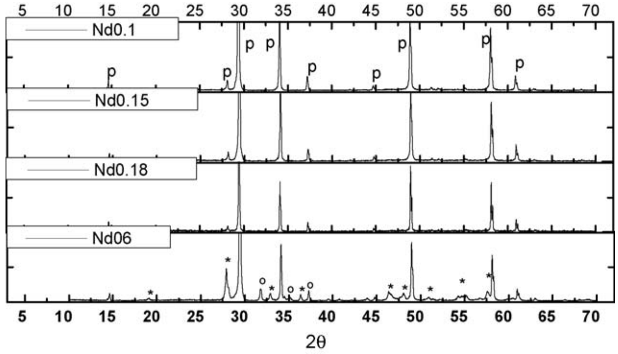

Fig. 2. XRD pattern of $Bi_{1.5-x}Nd_xZn_{0.92}Nb_{1.5}O_{6.92}$ pyrochlore with different Nd dopings ($x = 0.1$, 0.15, 0.18, 0.2, 0.3, 0.4, 0.5 and 0.6) (*$NdNbO_4$, °ZnO).

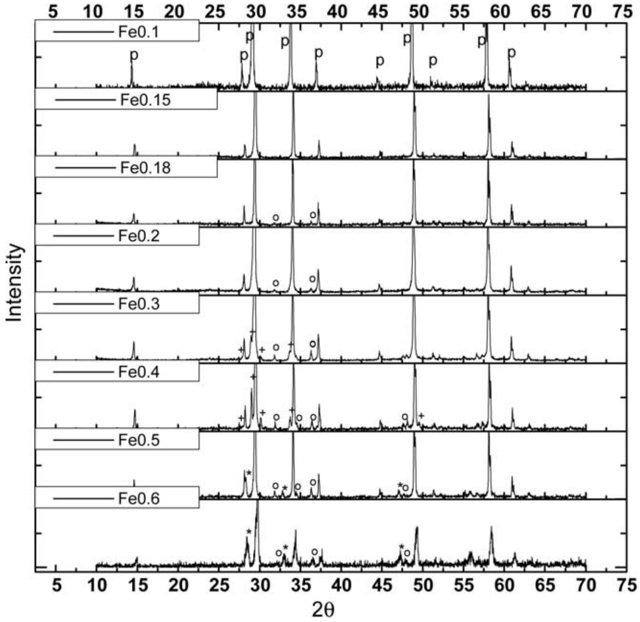

Fig. 3. XRD pattern of $Bi_{1.5}Zn_{0.92}Nb_{1.5-x}Fe_xO_{6.92-x}$ pyrochlore with different Fe dopings ($x = 0.1$, 0.15, 0.18, 0.2, 0.3, 0.4, 0.5 and 0.6) (°ZnO, +unknown phase and *$Bi_{3.43}Fe_{0.57}O_6$).

radius with Bi^{3+} (0.117 nm) and balanced valence [16]. Since iron has a lower valence than Nb, introduction of iron cations into the BZN leads to formation of oxygen vacancies to maintain the charge neutrality. XRD patterns of Fe doped BZN suggest that a solid solution occurs until $x = 0.15$ (Fig. 3). However, when $x > 0.15$, ZnO phase (JCPDS: 36-1451) started to form increasing in amount with x. At $x = 0.3$, an unknown phase started to form and its content rised with x eventually disappearing at $x = 0.5$ converting to a bismuth-iron phase ($Bi_{3.43}Fe_{0.57}O_6$; JCPDS: 43-184). At $x = 0.6$, there were only ZnO and bismuth-iron phases in addition to pyrochlore. The formation of these phases was also observed for the same compositions sintered at lower temperatures.

The solubility limits of Sm, Nd and Fe were similar. The stability of pyrochlore structure is essentially determined by the ionic radius ratio (r_A/r_B) although some other factors are also influential like electronegativity of the cations, charge neutrality criteria and thermodynamic stability of phases [1,12]. Subramanian et al. [1] gave the ionic radius ratio limits (r_A/r_B) as $1.46 < r_A/r_B < 1.80$ and $1.40 < r_A/r_B < 2.20$ for 3+, 4+ and 2+, 5+ pyrochlores ($A_2^{3+}B_2^{4+}O_7$ and $A_2^{2+}B_2^{5+}O_7$ pyrochlores). The radius ratio (r_A/r_B) for BZN pyrochlore is 1.668 and substitution of Sm and Nd into the A site of pyrochlore decreases the r_A/r_B ratio but Fe increases this ratio (Table 1). However, in all cases the radius ratio remain within the radius ratio limits for the formation of pyrochlores [1].

3.2. Lattice parameters of doped BZN pyrochlores

The ionic radius of Bi, Zn and Nb and additives are given in Table 2 with their corresponding coordination numbers. As the Sm^{3+}, Nd^{3+} and Fe^{2+} incorporation into the BZN pyrochlore increases, the lattice parameter of the single phase pyrochlore decreases due to smaller ionic radius of Sm^{3+}, Nd^{3+} than Bi^{3+} and that of Fe^{2+} than Nb^{5+} (Table 2). This indicates that Sm and Nd ions randomly occupy the Bi site and Fe ion occupy the Nb site to form homogeneous solid solution [2].

Table 1
Lattice parameters of doped BZN pyrochlores with radius ratio.

	x value	r_A/r_B	Lattice parameter (Å)
$Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$	–	1.668	10.5616
$Bi_{1.5-x}Sm_xZn_{0.92}Nb_{1.5}O_{6.92}$	$x = 0.05$	1.665	10.5501
	$x = 0.1$	1.662	10.5472
	$x = 0.13$	1.660	10.5468
$Bi_{1.5-x}Nd_xZn_{0.92}Nb_{1.5}O_{6.92}$	$x = 0.1$	1.664	10.5452
	$x = 0.15$	1.662	10.5349
	$x = 0.18$	1.661	10.5330
$Bi_{1.5}Zn_{0.92}Nb_{1.5-x}Fe_xO_{6.92-x}$	$x = 0.05$	1.669	10.5544
	$x = 0.1$	1.672	10.5498
	$x = 0.15$	1.674	10.5336

3.3. Microstructure of Nd samples

The microstructure of Nd doped BZN samples was examined using the specimens $x = 0.18$ (solubility limit) and $x = 0.20$ (above the solubility limit). SEM investigation revealed only single phase pyrochlore at $x = 0.18$ as observed in XRD (Fig. 4). But when $x = 0.20$, SEM disclosed three phases (Fig. 5); pyrochlore, ZnO and Nd-rich phase consistent with XRD results where $NdNbO_4$ and ZnO phases were detected in addition to pyrochlore (Fig. 2). EDS analysis taken from each specific phases clearly indicated the existence of these phases. The composition of Nd-rich phase was near to the theoretical composition of $NdNbO_4$. Higher amount of Nd doping resulted in smaller pyrochlore grains in the microstructure. While the grain sizes varied between 1 and 6 μm for Nd doping of $x = 0.18$, higher amount of Nd doping ($x = 0.20$) led to smaller grain sizes (1–3 μm).

3.4. Dielectric properties of doped BZN pyrochlores

The dielectric constant of BZN generally increased with Sm and Nd dopings but decreased with Fe. This could be due to higher polarizability of Sm and Nd than Bi (7.4 of Bi, 28.8 of Sm and 31.4 Nd, 10^{-24} cm^3) and lower polarizability of Fe than

Table 2
Ionic radius and coordination number of Bi, Zn, Nb in BZN pyrochlore and doped elements.

Cation	Coordination no.	Ionic radius (Å)
Bi^{3+}	8	1.17
Zn^{2+}	8	0.9
Zn^{2+}	6	0.74
Nb^{5+}	6	0.64
Nd^{3+}	8	1.12
Sm^{3+}	8	1.09
Fe^{2+}	6	0.61

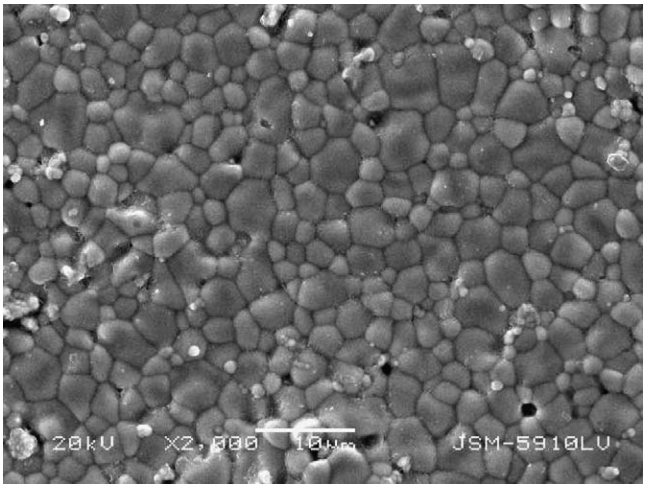

Fig. 4. SEM micrograph of $Bi_{1.32}Nd_{0.18}Zn_{0.92}Nb_{1.5}O_{6.92}$ ($x = 0.18$) ceramic sintered at 1025 °C for 4 h.

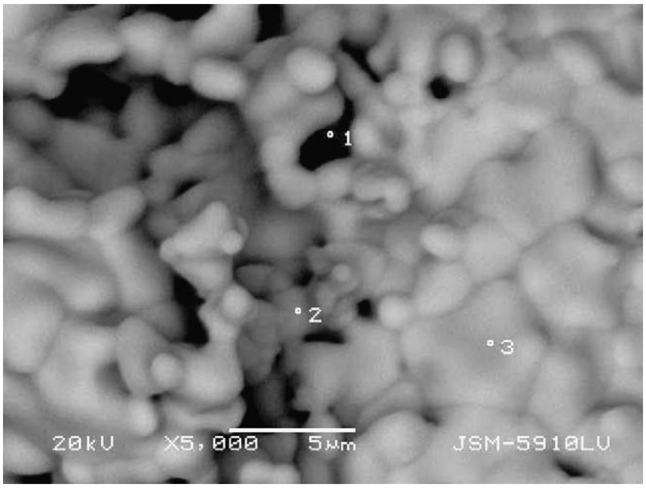

Fig. 5. SEM micrograph of $Bi_{1.30}Nd_{0.20}Zn_{0.92}Nb_{1.5}O_{6.92}$ ($x = 0.20$) ceramic sintered at 1025 °C for 4 h showing ZnO grains (point 1), Nd-rich phase (point 2) and pyrochlore grains (point 3).

Nb (15.7 of Nb and 8.4 of Fe, 10^{-24} cm^3). However, there was a minima in dielectric constant at $x = 0.05$ for Sm and $x = 0.09$ for Nd. The decrease in dielectric constant at $x = 0.05$ and 0.09 could be due to substitution of Sm and Nd cations with Zn instead of Bi. The diminution in dielectric constant is probably to be due to unbalanced charge distribution in the lattice caused by the partial substitution of Zn with Sm and Nd.

The variation of dielectric properties of Sm, Nd and Fe doped BZN samples with frequency and temperature was identical (Fig. 6). The dielectric constant was nearly stable with frequency but the temperature had significant negative effect on dielectric constant which decreased with an increase in temperature. The dielectric loss was high at low frequencies and after an abrupt change just above 1 kHz a gradual decrease was observed with

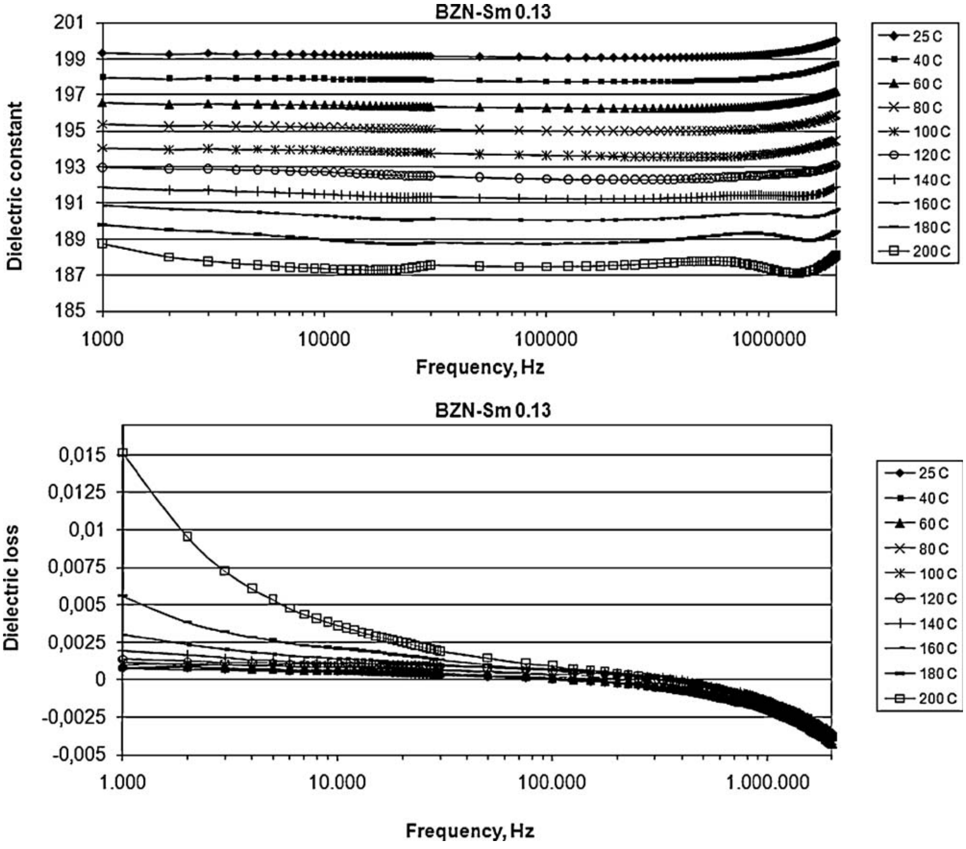

Fig. 6. Frequency and temperature dependence of (a) dielectric constant and (b) dielectric loss of Sm doped sample for $x = 0.13$ in $Bi_{1.5-x}Sm_xZn_{0.92}Nb_{1.5}O_{6.92}$ composition ($Bi_{1.37}Sm_{0.13}Zn_{0.92}Nb_{1.5}O_{6.92}$).

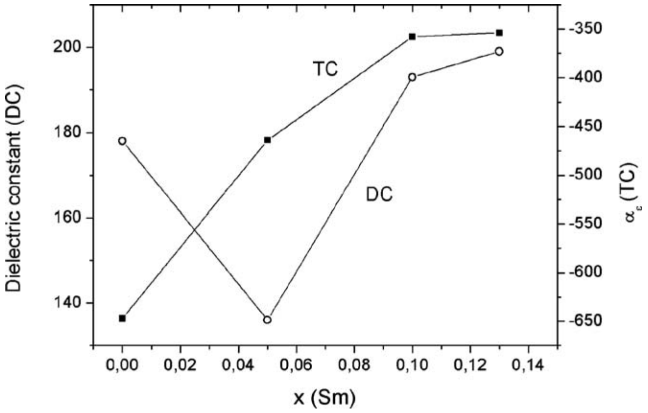

Fig. 7. Variation in dielectric properties as a function of Sm doping in $Bi_{1.5-x}Sm_xZn_{0.92}Nb_{1.5}O_{6.92}$ composition.

frequency. The decrease in dielectric loss with frequency is due to leakage conduction [17,18]. The dielectric loss also increased with temperature possibly due to increase in the number of charge carriers [16] but the dielectric loss above 40 kHz almost remained unchanged with temperature.

The dielectric properties of Sm doped samples were significantly effected by Sm concentration that the dielectric constant of pure BZN ($\varepsilon = 178$) increased with Sm additions reaching a value of $\varepsilon = 199$ at $x = 0.13$ (Fig. 7). The dielectric loss of Sm doped samples was below 0.0003. The temperature coefficient of dielectric constant decreased with x value from −647 ppm/°C (for $x = 0$) to −354 ppm/°C (for $x = 0.13$).

The dielectric properties of $Bi_{1.5-x}Nd_xZn_{0.92}Nb_{1.5}O_{6.92}$ solid solutions with $x = 0$, 0.1, 0.15 and 0.18 are shown in Fig. 8. The dielectric constant increased from $\varepsilon = 179$ at $x = 0$ to $\varepsilon = 219$ at $x = 0.18$. The dielectric loss of Nd doped BZN varied between 0.00016 and 0.00129. The increase in dielectric loss with x could be due to secondary phases which could not be detected within XRD limits [5]. The temperature coefficient of dielectric constant decreased with x from −647 ppm/°C (for $x = 0$) to −418 ppm/°C (for $x = 0.15$) but after $x = 0.15$, it rises with x ending with a value of −538 ppm/°C at $x = 0.18$.

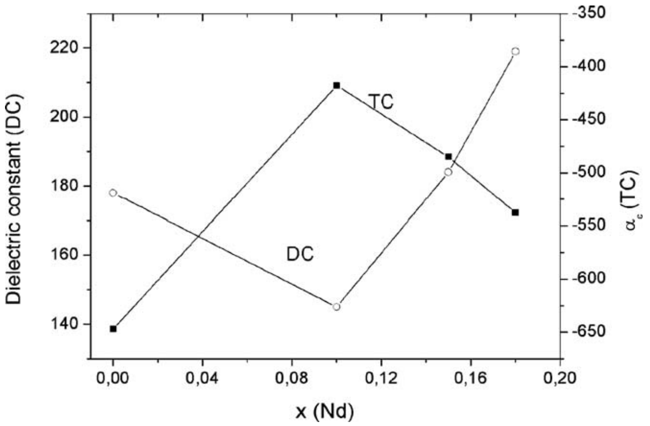

Fig. 8. Variation in dielectric properties as a function of Nd doping in $Bi_{1.5-x}Nd_xZn_{0.92}Nb_{1.5}O_{6.92}$ composition.

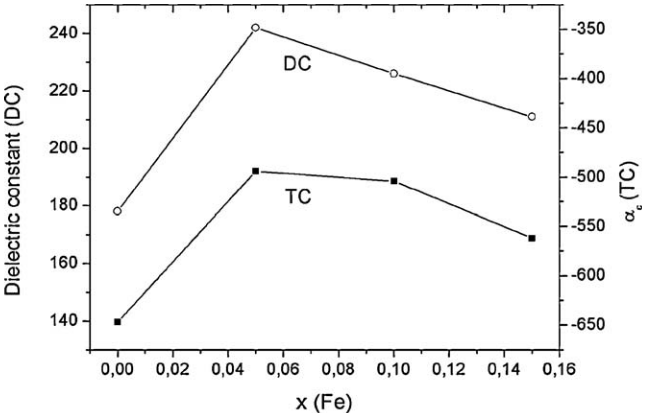

Fig. 9. Variation in dielectric properties as a function of Fe doping in $Bi_{1.5}Zn_{0.92}Nb_{1.5-x}Fe_xO_{6.92-x}$ composition.

The dielectric constant of Fe doped BZN ($Bi_{1.5}Zn_{0.92}Nb_{1.5-x}Fe_xO_{6.92-x}$) increased from 178 at $x = 0$ to 242 at $x = 0.05$ but then declined gradually with x attaining a value of 211 at maximum solubility limit ($x = 0.15$) (Fig. 9). The dielectric loss was quite high for all Fe dopings varying between 0.00622 and 0.00716. There was no consistent increase or decrease in temperature coefficient with iron doping. The α_ε value was −494, −504 and −565 ppm/°C for iron dopings of $x = 0.05$, 0.10 and 0.15, respectively.

4. Conclusions

Dielectric ceramics with Sm_2O_3, Nd_2O_3 and Fe_2O_3 doped compositions in the system of Bi_2O_3–ZnO–Nb_2O_5 were investigated in order to enhance the dielectric properties of BZN pyrochlore. XRD analysis indicated that the solubility of Sm, Nd and Fe in BZN was $x = 0.13$, 0.18 and 0.15 along the compositions of $Bi_{1.5-x}M_xZn_{0.92}Nb_{1.5}O_{6.92}$ (where M = Sm and Nd) and $Bi_{1.5}Zn_{0.92}Nb_{1.5-x}Fe_xO_{6.92-x}$. As the dopant content increased, second phases were observed in the XRD. Although Sm and Nd dopings generally led to an increase in dielectric constant ($\varepsilon = 199$ at $x = 0.13$ for Sm and $\varepsilon = 219$ at $x = 0.18$ for Nd), high Fe dopings caused a decrease in ε. The dielectric loss of Sm, Nd and Fe doped BZN varied between 0.0003 and 0.006. Temperature coefficient of doped BZN ceramics was between −647 and −354 ppm/°C. The dielectric properties of doped pyrochlores were nearly independent of frequency between 1 kHz and 2 MHz but the dielectric constants decreased significantly with temperature in the range of 20–200 °C. Temperature coefficient of dielectric constant of doped BZN pyrochlores was relatively very high.

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