PREPARATION AND DIELECTRIC PROPERTIES OF $Bi_{1.5}Zn_{1.0}Nb_{1.5}O_7$ AND $Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$ PYROCHLORE CERAMICS

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 $Bi_{1.5}Zn_{1.0}Nb_{1.5}O_7$ and $Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$ pyrochlore compositions were prepared and investigated by X-ray diffraction (XRD) and scanning electron microscopy (SEM) and their dielectric properties were measured. XRD of $Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$ gave only single phase pyrochlore but second phases were observed in the XRD of $Bi_{1.5}Zn_{1.0}Nb_{1.5}O_7$. SEM supported X-ray results but in the microstructure of $Bi_{1.5}Zn_{1.0}Nb_{1.5}O_7$ composition a Zn-rich phase was also observed in additon to pyrochlore and ZnO. $Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$ pyrochlore had higher dielectric constant and lower loss values than $Bi_{1.5}ZnNb_{1.5}O_7$ composition between 25-200 °C in the frequency range of 10 kHz-2 MHz, possibly due to presence of second phases in $Bi_{1.5}ZnNb_{1.5}O_7$.

INTRODUCTION

Pyrochlore compounds have general formula of $A_2B_2O_7$ where A cations are eight-coordinated and located within scalenohedra, and the B cations are sixcoordinated and located within trigonal antiprisms. The simple pyrochlore structure is face centered cubic with space group Fd3m (No. 227). There are eight molecules per unit cell (Z = 8) and for a stoichiometric pyrochlore structure ($A_2B_2O_7$) there are 88 atoms in a unit cell that 16 A and 16 B cations are found in position d and c, and 56 O anions exist in position f and b.

In Bi₂O₃–ZnO–Nb₂O₅ (BZN) system, two different ternary compounds form with different compositions and crystal structures: Bi₂Zn_{2/3}Nb_{4/3}O₇ and Bi_{1.5}Zn_{1.0}Nb_{1.5}O₇ or $(Bi_{15}Zn_{05})(Zn_{05}Nb_{15})O_7$ (BZN) [1]. While $Bi_2Zn_{2/3}$ Nb_{4/3}O₇ compound is monoclinic, Bi_{1.5}Zn_{1.0}Nb_{1.5}O₇ pyrochlore is cubic [2, 3]. The structure of $Bi_{1.5}Zn_{1.0}Nb_{1.5}O_7$ belongs to a typical pyrochlore with face centered cubic cell, space group Fd3m (No:227) and a lattice parameter of a = 10.5560 Å [3, 4]. In $(Bi_{1.5}Zn_{0.5})(Zn_{0.5}Nb_{1.5})O_7$ pyrochlore compound while Bi and Nb ions occupy A- and B-sites, respectively, Zn ions occupy both Aand B-sites [5]. The Bi₂Zn_{2/3}Nb_{4/3}O₇ compound has a monoclinic zirconolite-like structure with space group C2/c (No.15) and a lattice parameter of a = 13.1037(9) Å, b = 7.6735(3) Å, c = 12.1584(6) Å and $\beta = 101.318(5)^{\circ}$ [2]. The formation of $Bi_2Zn_{2/3}Nb_{4/3}O_7$ phase belongs to diffusion controlled reaction with zero nucleation rate but $Bi_{15}Zn_{10}Nb_{15}O_7$ phase is diffusion controlled reaction with a constant nucleation rate [6]. $Bi_{15}Zn_{10}Nb_{15}O_7$ has a lower activation energy and formation temperature than Bi₂Zn_{2/3}Nb_{4/3}O₇ [6].

The dielectric properties of two compounds are also significantly different [1, 7, 8, 9]. While cubic Bi_{1.5}Zn_{1.0}Nb_{1.5}O₇ pyrochlore has a dielectric constant of 145, dielectric loss of < 0.0002 and temperature coefficient of dielectric constant of -360 ppm/°C, monoclinic Bi₂Zn_{2/3}Nb_{4/3}O₇ has lower dielectric constant of 80, identical dielectric loss of < 0.0002 and positive temperature coefficient of dielectric constant of 200 ppm/°C.

BZN pyrochlores are attractive materials for capacitors and wireless communications technology as microwave resonators, high frequency filter applications in multilayer structures due to their high and tunable dielectric constant, low dielectric loss, small and close to zero values of the temperature coefficient of dielectric constant, low sintering temperature and lower cost of electrode materials.

For the cubic BZN pyrochlore structure two different formulas have been given in the literature: Bi_{1.5}Zn_{1.0}Nb_{1.5}O₇ and Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}. [5, 10, 11, 12]. Hong et al. [11] determined the crystal chemical formula of BZN pyrochlore as Bi_{1.5}Zn_{0.5}Nb_{1.5}Zn_{0.5}O₇ by comparing the calculated theoretical x-ray diffraction intensities with the observed ones. Levin et al. [5] studied $Bi_{15}Zn_{10}Nb_{15}O_7$ and $Bi_{15}Zn_{092}Nb_{15}O_{692}$ phases using x-ray and neutron powder diffraction techniques. They reported that Bi1.5Zn1.0Nb1.5O7 consisted of a cubic pyrochlore phase and small amount of ZnO but Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92} phase contained only a single phase pyrochlore. Wu et al. [10] prepared both Bi_{1.5}Zn_{1.0}Nb_{1.5}O₇ and Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92} phases and studied structure and dielectric behaviour of these phases. They concluded that Bi₁₅Zn₁₀Nb₁₅O₇ didn't only contain a single phase pyrochlore but also small amount of ZnO which was

distributed evenly within the grain and at the grain boundaries of pyrochlore. But $Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$ gave only single phase pyrochlore [10].

High frequency dielectric properties of $Bi_{1.5}Zn$ Nb_{1.5}O₇ and $Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$ ceramics were measured by several authors (Table 1). Wu et al. [10] determined that both $Bi_{1.5}ZnNb_{1.5}O_7$ and $Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$ reveal high dielectric constant (> 120) and low Q × f (< 600) at 2.2 GHz but $Bi_{1.5}ZnNb_{1.5}O_7$ has slightly higher Q × f due to presence of ZnO second phase which produces interstitial defects. The low Q × f value was attributed to the dielectric relaxation and voids present in the samples. In addition, $Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$ pyrochlore indicates a broad dielectric relaxation at around 230 K similar to $Bi_{1.5}ZnNb_{1.5}O_7$.

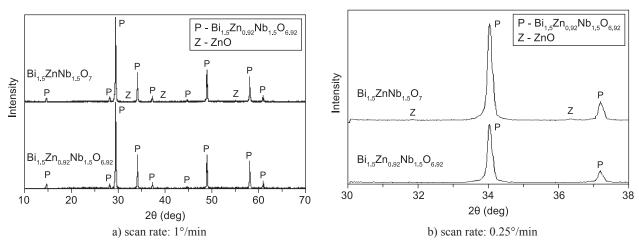
Although in the Bi_2O_3 –ZnO– Nb_2O_5 system the proper BZN pyrochlore composition is $Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$, $Bi_{1.5}Zn_{1.0}Nb_{1.5}O_7$ composition has been used as the pyrochlore composition in various studies [16, 17, 18, 19]. Therefore, in the present study, two of these compositions, $Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$ and $Bi_{1.5}Zn_{1.0}Nb_{1.5}O_7$, were produced and detailed X-ray analysis and microstructural study were performed to reveal the second phases. In addition, the dielectric properties of $Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$ and $Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{7}$ pyrochlores were investigated at various frequencies and temperatures.

EXPERIMENTAL

Two different pyrochlore compositions, Bi₁₅Zn Nb_{1.5}O₇ and Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92} were synthesized by conventional powder processing technique. The starting materials were reagent grade oxide powders of Bi₂O₃, ZnO and Nb₂O₅ (99.9 % purity each, Merck Chemicals). Stoichiometric mixtures were milled for 4 h in ethanol with zirconia balls. After drying, powders were calcined in a closed alumina crucible at 800 °C for 4 h. The calcined powders were milled in an agate mortar and they were pressed into pellets with 10 mm in diameter and 2 mm in thickness at 2 MPa. Then the pellets were sintered between 900-1200 °C for 4 h in a closed alumina crucible. The densities of the samples were measured by Archimedes method. X-ray diffraction analysis was performed using an X-ray diffractometer (Rigaku, CuKα radiation, 1°/min) using powdered sample. The microstructures of sintered specimens were examined using a scanning electron microscope equipped with energy dispersive spectrometer (JEOL 5910LV). Fracture surfaces and also surface pores were examined to investigate the second phases. The dielectric measurements of Bi1.5ZnNb1.5O7 and Bi1.5Zn0.92Nb1.5O6.92 pyrochlores were performed at frequencies from 1 kHz

Table 1. Comparison of dielectric properties of $Bi_{1.5}ZnNb_{1.5}O_7$ and $Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$ pyrochlores produced in this study with data in the literature.

	Frequency	Dielectric Constant	Dielectric Loss	Sintering Temperature and Time	Ref.
Bi _{1.5} Zn _{0.92} Nb _{1.5} O _{6.92}	1 MHz	178	0.0002	1000 °C−4 h	Present Study
(Bi1.5Zn0.5)(Zn0.5Nb1.5)O7	1 MHz	150	0.0006	1000 °C−4 h	Present Study
(Bi _{1.5} Zn _{0.5})(Zn _{0.5} Nb _{1.5})O ₇	1 MHz	170	$\le 4 \times 10^{-4}$		[13]
(Bi _{1.5} Zn _{0.5})(Zn _{0.5} Nb _{1.5})O ₇	1 MHz	152	3×10 ⁻⁴		[8]
$(Bi_{15}Zn_{05})(Zn_{05}Nb_{15})O_7$	2.24 GHz	121.2		1000 °C − 4 h	[10]
$(Bi_{15}Zn_{05})(Zn_{05}Nb_{15})O_7$	1 MHz	148	6.5×10 ⁻⁴	1000 °C − 3 h	[14]
$(Bi_{15}Zn_{05})(Zn_{05}Nb_{15})O_7$	1 MHz	130	4×10 ⁻⁴	1000 °C	[15]
$Bi_{15}Zn_{0.92}Nb_{1.5}O_{6.92}$	2.40 GHz	126.2		1050 °C − 4 h	[12]
Bi _{1.5} Zn _{0.92} Nb _{1.5} O _{6.92}	2.27 GHz	121.3		1000 °C - 4 h	[10]





to 2 MHz on silver-plated discs using a high precision LCR meter (HP 4284A). The temperature dependence of the dielectric properties in the range from room temperature to 200 °C was measured using an automated measurement systems consisting of a PC, a HP 4284 LCR meter and a temperature chamber.

RESULTS AND DISCUSSION

$Comparison \ of \ Bi_{1.5}ZnNb_{1.5}O_7 \ and \\ Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92} \ pyrochlore \ compositions$

After calcination at 800 °C for 4 h although $Bi_{1.5}Zn$ Nb_{1.5}O₇ powder contained Bi_2O_3 and ZnO phases in addition to pyrochlore, $Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$ gave only pyrochlore and Bi_2O_3 phases and no ZnO phase was observed. Both $Bi_{1.5}ZnNb_{1.5}O_7$ and $Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$ powders (about 10 g) were weighed before and after calcination and the weight loss was below 1% for both ceramics.

Figure 1a indicates the XRD patterns of $Bi_{1.5}Zn$ Nb_{1.5}O₇ and $Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$ pellets sintered at 1000°C for 4 h. Although $Bi_{1.5}ZnNb_{1.5}O_7$ samples gave pyrochlore and a very small amount of ZnO phase, Bi₁₅Zn_{0.92} Nb_{1.5}O_{6.92} samples gave only single phase pyrochlore. Since XRD of Bi1.5Zn0.92Nb1.5O6.92 pyrochlore did not show any superlattice reflections, the cations are randomly distributed over the A and/or B sites in the $A_2B_2O_7$ pyrochlore. In the XRD of $Bi_{15}ZnNb_{15}O_7$ sample, ZnO peaks are more obvious at lower scan rates (Figure 1b). Same kind of results were also obtained by the others in the literature [5, 10]. Levin et al. [5] investigated the structure of Bi₁₅ZnNb₁₅O₇ pyrochlore and concluded that it consisted of a cubic pyrochloretype phase and small amount of ZnO. Wu et al. [10] investigated the microstructures of Bi1.5ZnNb1.5O7 and Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92} pyrochlores and indicated that Bi_{1.5}ZnNb_{1.5}O₇ was not composed of a single phase pyrochlore but instead, it consists of unusual structure of $Bi_{15}Zn_{0.92}Nb_{1.5}O_{6.92}$ and ZnO which is distributed evenly in the grain and at the boundaries.

XRD results were also confirmed by SEM. Although SEM investigation of $Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$ pyrochlore pellets sintered at 1000°C for 4 h revealed only single phase pyrochlore, $Bi_{1.5}ZnNb_{1.5}O_7$ pellets gave ZnO second phases in addition to pyrochlore (Figures 2 and 3).

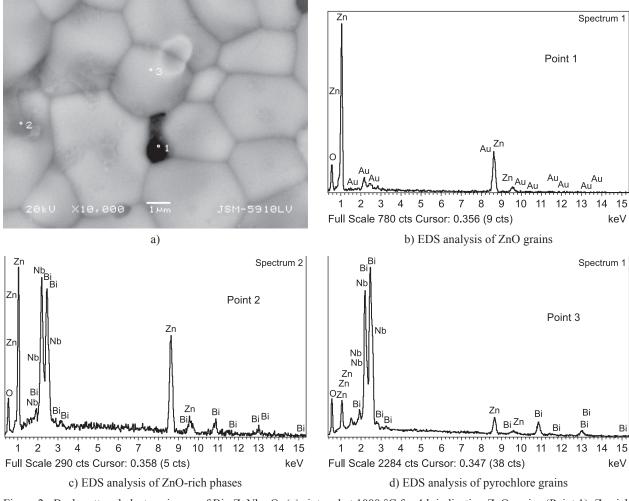


Figure 2. Backscattered electron image of $Bi_{1.5}ZnNb_{1.5}O_7$ (a) sintered at 1000 °C for 4 h indicating ZnO grains (Point 1), Zn-rich phases (Point 2) and pyrochlore grains (Point 3) (b).

Moreover, some ZnO rich phases were also observed in the microstructure of $Bi_{1.5}ZnNb_{1.5}O_7$ pyrochlore pellets (Figure 2).

Densities of Bi_{1.5}ZnNb_{1.5}O₇ and Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92} Pyrochlore Ceramics

The densities of $Bi_{1.5}ZnNb_{1.5}O_7$ and $Bi_{1.5}Zn_{0.92}$ Nb_{1.5}O_{6.92} ceramics sintered at different temperatures are shown in Figure 4. $Bi_{1.5}ZnNb_{1.5}O_7$ and $Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$ ceramics indicate identical sintering behaviors that density increases with the sintering temperature up to 1000 °C, then decreases above this temperature possibly due to evaporation. Although the melting temperature of $Bi_{1.5}ZnNb_{1.5}O_7$ pyrochlore is high enough ($T_m = 1190$ °C), evaporation losses may occur due to unreacted Bi_2O_3 ($T_m = 825$ °C). The theoretical densities were calculated as 7,11 g/cm³ for $Bi_{1.5}ZnNb_{1.5}O_7$ and 7.04 g/cm³ for $Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$ using lattice parameters of 10.556 Å and 10.5616 Å for $Bi_{1.5}ZnNb_{1.5}O_7$ and $Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$, respectively [5, 14]. Dielectric Properties of $Bi_{1.5}ZnNb_{1.5}O_7$ and $Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$ Pyrochlores

The variation of dielectric constant and dielectric loss of Bi_{1.5}ZnNb_{1.5}O₇ and Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92} ceramics with frequency at different temperatures is shown in Figures 5 and 6. Bi1.5Zn0.92Nb1.5O6.92 ceramic has higher dielectric constant and lower loss values than Bi₁₅ZnNb₁₅O₇. Although the dielectric constant of Bi_{1.5}Zn Nb_{1.5}O₇ varies between 137-150 at frequency range of 1 kHz - 2 MHz at temperatures of 25-200 °C, Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92} ceramic has higher dielectric constant values of 160-185 at the same frequency and temperature ranges. The lower dielectric constant of Bi_{1.5}ZnNb_{1.5}O₇ than Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92} ceramic could be due to presence of second phases in Bi_{1.5}ZnNb_{1.5}O₇. Comparison of dielectric properties of Bi_{1.5}ZnNb_{1.5}O₇ and $Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$ pyrochlores with other studies in the literature are given in Table 1. For both ceramics the dielectric constant rapidly decreases at lower frequencies and remain fairly constant at higher frequencies. The dielectric loss is also found to be decreasing with

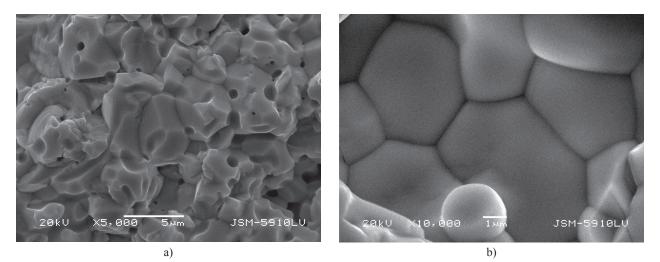


Figure 3. Backscattered electron images of Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92} pyrochlore ceramic sintered at 1000 °C for 4 h.

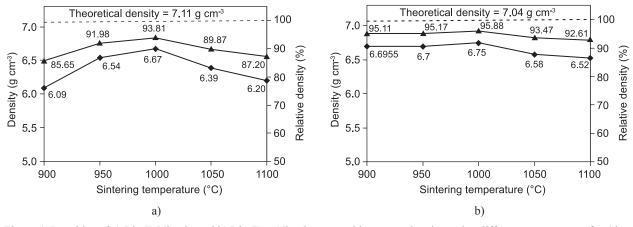


Figure 4. Densities of a) Bi_{1.5}ZnNb_{1.5}O₇ and b) Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92} pyrochlore ceramics sintered at different temperatures for 4 h.

frequency and remains almost constant at higher frequency region. $Bi_{1.5}ZnNb_{1.5}O_7$ pyrochlore ceramic has higher loss values than $Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$. The decrease in dielectric constant and dielectric loss with frequency is one of the features of normal dielectrics [20]. The higher value of dielectric constant at low frequency is due to the presence of all types of polarization (i.e., interface, dipolar, ionic and electronic, etc.) at room temperature, but at higher frequencies ($\geq 10^6$ Hz), electronic polarization is the main contributor for dielectric constant. At high frequencies, there is not much frequency dispersion of dielectric properties for both $Bi_{1.5}ZnNb_{1.5}O_7$ and $Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$ pyrochlores which is an important property for many applications. The dielectric loss values of $Bi_{1.5}ZnNb_{1.5}O_7$ pyrochlore is generally higher than $Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$ pyrochlore and this could be due to presence of minor amount of ZnO second phase in $Bi_{1.5}ZnNb_{1.5}O_7$.

CONCLUSION

 $Bi_{1.5}Zn_{1.0}Nb_{1.5}O_7$ and $Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$ pyrochlore compounds were produced from mixed oxide technique and their dielectric properties were investigated as a function of frequency and temperature. XRD patterns revealed that although $Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$ pyrochlore contained only single pyrochlore phase, $Bi_{1.5}Zn_{1.0}Nb_{1.5}O_7$

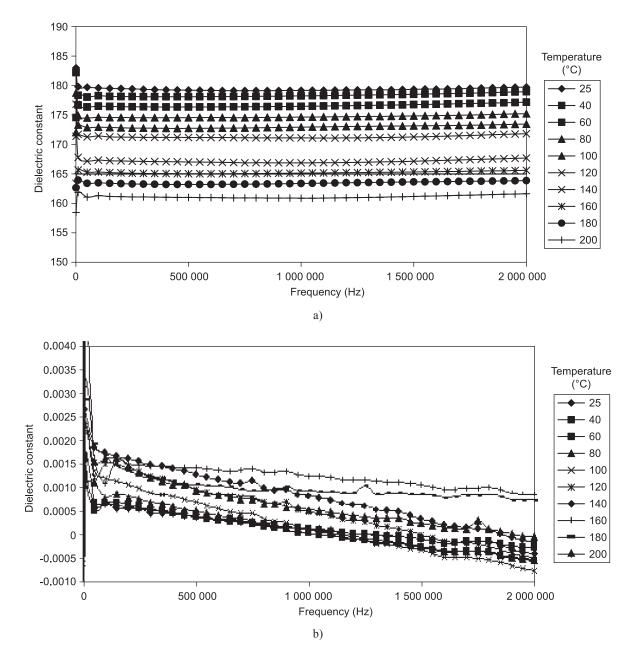


Figure 5. Frequency variation of a) dielectric constant b) dielectric loss of $Bi_{1,3}Zn_{0.92}Nb_{1,5}O_{6.92}$ ceramic at various temperatures.

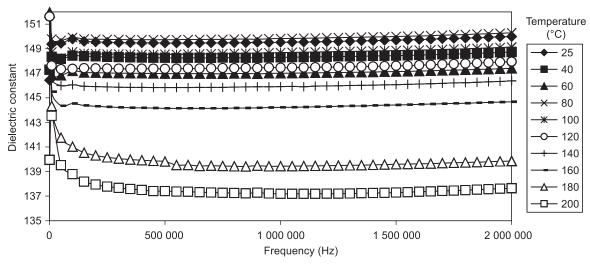
pyrochlore contained also small amounts of ZnO second phase. But SEM results of $Bi_{1.5}Zn_{1.0}Nb_{1.5}O_7$ revealed another Zn-rich phase in addition to pyrochlore and ZnO. $Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$ pyrochlore had higher dielectric constant and lower loss values than $Bi_{1.5}ZnNb_{1.5}O_7$ at temperature range of 25-200°C. $Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$ pyrochlore exhibits higher dielectric constant and lower loss (e = 179 and tan δ = 0.00008 at 1 MHz at 25°C) than $Bi_{1.5}Zn_{1.0}Nb_{1.5}O_7$ (e = 150 and tan δ = 0.0006 1 MHz at 25°C), possibly due to existence of second phases in $Bi_{1.5}Zn_{1.0}Nb_{1.5}O_7$.

Acknowledgements

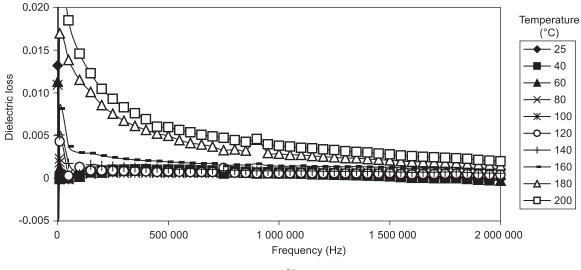
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References

- 1. Swartz S.L., Shrout T.R.: US Patent 5449652 (1995).
- Levin I., Amos T.G., Nino J.C., Vanderah T.A., Reaney I.M., Randall C.A., Lanagan M.T.: J. Mater. Res. 17, 1406 (2002).
- Nino J.C., Reaney I.M., Lanagan M.T., Randall C.A.: Mater. Lett. 57, 414 (2002).
- 4. Wang H., Wang X., Yao X.: J. Chin. Ceram. Soc. 23, 241 (1995).
- Levin I., Amos T.G., Nino J.C., Vanderah T.A., Randall C.A., Lanagan M.T.: J. Solid State Chem. 168, 69 (2002).
- Chen S.Y., Lee S.Y., Lin Y.J.: J. Eur. Ceram. Soc. 23, 873 (2003).
- Cann D.P., Randall C.A., Shrout T.R.: Solid State Commun. 100, 529 (1996).
- 8. Valant M., Davies P.K.: J. Am. Ceram. Soc. 83, 147 (2000).
- Nino J.C., Kanagan M.T., Randall C.A.: J. Appl. Phys. 89, 4512 (2001).



a)



b)

Figure 6. Frequency variation of a) dielectric constant b) dielectric loss of Bi_{1.5}ZnNb_{1.5}O₇ ceramic at various temperatures.

- Wu M.C., Kamba S., Bovtun V., Su W.F.: J. Eur. Ceram. Soc. 26, 1889 (2006).
- 11. Hong W., Huiling D., Xi Y.: Mater. Sci. and Eng. B 99, 20 (2003).
- Wang X., Wang H., Yao X.: J. Am. Ceram. Soc. 80, 2745 (1997).
- 13. Wu M.C., Huang Y.C., Su W.F.: Mater. Chem. and Phys. 100, 391 (2006).
- 14. Du H.L, Yao X.: Ferroelectrics 262, 83 (2001).

- 15. Wang Q., Wang H., Yao X.: Ceram. Int. 34, 901 (2008).
- 16. Wang Q., Wang H., Yao X.: Ceram. Int. 35, 143 (2009).
- Du H., Yao X., Zhang X., Weng H.: Appl. Surf. Sci. 253, 1856 (2006).
- 18. Su W.F., Lin S.C.: J. Eur. Ceram. Soc. 23, 2593 (2003).
- 19. Du H., Yao X.: Mater. Sci. and Eng. B 99, 437 (2003).
- Moulson A. J, Herbert J. M.: *Electroceramics*, Second ed., p. 53-70, John Wiley & Sons Ltd., England 2003.