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 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$_{7}$ 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$_2$B$_2$O$_7$ where A cations are eight-coordinated and located within scalenohedra, and the B cations are six-coordinated 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$_2$B$_2$O$_7$) 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 Bi$_2$O$_3$–ZnO–Nb$_2$O$_5$ (BZN) system, two different ternary compounds form with different compositions and crystal structures: Bi$_2$Zn$_{2/3}$Nb$_{4/3}$O$_7$ and Bi$_{1.5}$Zn$_{1.0}$Nb$_{1.5}$O$_{7}$ or (Bi$_{1.5}$Zn$_{0.5}$)(Zn$_{0.5}$Nb$_{1.5}$)O$_7$ (BZN) [1]. While Bi$_2$Zn$_{2/3}$Nb$_{4/3}$O$_7$ compound is monoclinic, Bi$_{1.5}$Zn$_{1.0}$Nb$_{1.5}$O$_{7}$ 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 A- and B-sites [5]. The Bi$_{1.5}$Zn$_{0.92}$Nb$_{1.5}$O$_{6.92}$ compound is monoclinic, Bi$_{1.5}$Zn$_{1.0}$Nb$_{1.5}$O$_{7}$ pyrochlore is also significantly different [1, 7, 8, 9]. While cubic Bi$_{1.5}$Zn$_{1.0}$Nb$_{1.5}$O$_{7}$ pyrochlore has a dielectric constant of 145, dielectric loss of < 0.0002 and temperature coefficient of dielectric constant of -360 ppm/°C, monoclinic Bi$_2$Zn$_{2/3}$Nb$_{4/3}$O$_7$ has lower dielectric constant of 80, identical dielectric constant 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.

The dielectric properties of two compounds are also significantly different [1, 7, 8, 9]. While cubic Bi$_{1.5}$Zn$_{1.0}$Nb$_{1.5}$O$_{7}$ pyrochlore has a dielectric constant of 145, dielectric loss of < 0.0002 and temperature coefficient of dielectric constant of -360 ppm/°C, monoclinic Bi$_2$Zn$_{2/3}$Nb$_{4/3}$O$_7$ has lower dielectric constant of 80, identical dielectric constant of < 0.0002 and positive temperature coefficient of dielectric constant of 200 ppm/°C.

For the cubic BZN pyrochlore structure two different formulas have been given in the literature: Bi$_{1.5}$Zn$_{1.0}$Nb$_{1.5}$O$_{7}$ and Bi$_{1.5}$Zn$_{0.92}$Nb$_{1.5}$O$_{6.92}$. Hong et al. [11] determined the crystal chemical formula of BZN pyrochlore as Bi$_{1.5}$Zn$_{0.5}$Nb$_{1.5}$Zn$_{0.5}$O$_7$ by comparing the calculated theoretical x-ray diffraction intensities with the observed ones. Levin et al. [5] studied Bi$_{1.5}$Zn$_{1.0}$Nb$_{1.5}$O$_{7}$ and Bi$_{1.5}$Zn$_{0.92}$Nb$_{1.5}$O$_{6.92}$ phases using x-ray and neutron powder diffraction techniques. They reported that Bi$_{1.5}$Zn$_{1.0}$Nb$_{1.5}$O$_{7}$ 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$_{1.5}$O$_{7}$ 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 Bi$_{1.5}$Zn$_{1.0}$Nb$_{1.5}$O$_{7}$ 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\(_{1.5}\)O\(_7\) 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\(_2\)O\(_3\)–ZnO–Nb\(_2\)O\(_5\) 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\(_{1.0}\)Nb\(_{1.5}\)O\(_7\) pyrochlores were investigated at various frequencies and temperatures.

### EXPERIMENTAL

Two different pyrochlore compositions, Bi\(_{1.5}\)Zn Nb\(_{1.5}\)O\(_7\) 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 Bi\(_2\)O\(_3\), ZnO and Nb\(_2\)O\(_5\) (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, CuK\(_\alpha\) 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 Bi\(_{1.5}\)ZnNb\(_{1.5}\)O\(_7\) and Bi\(_{1.5}\)Zn\(_{0.92}\)Nb\(_{1.5}\)O\(_{6.92}\) 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.

<table>
<thead>
<tr>
<th>Frequency</th>
<th>Dielectric Constant</th>
<th>Dielectric Loss</th>
<th>Sintering Temperature</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi(<em>{1.5})Zn(</em>{0.92})Nb(<em>{1.5})O(</em>{6.92})</td>
<td>1 MHz</td>
<td>178</td>
<td>1000 °C – 4 h</td>
<td>Present Study</td>
</tr>
<tr>
<td>Bi(<em>{1.5})Zn(</em>{0.92})Nb(<em>{1.5})O(</em>{6.92})</td>
<td>1 MHz</td>
<td>150</td>
<td>1000 °C – 4 h</td>
<td>Present Study</td>
</tr>
<tr>
<td>Bi(<em>{1.5})Zn(</em>{0.92})Nb(<em>{1.5})O(</em>{6.92})</td>
<td>1 MHz</td>
<td>170</td>
<td>≤ 4×10(^{-4})</td>
<td>[13]</td>
</tr>
<tr>
<td>Bi(<em>{1.5})Zn(</em>{0.92})Nb(<em>{1.5})O(</em>{6.92})</td>
<td>1 MHz</td>
<td>152</td>
<td>3×10(^{-4})</td>
<td>[8]</td>
</tr>
<tr>
<td>Bi(<em>{1.5})Zn(</em>{0.92})Nb(<em>{1.5})O(</em>{6.92})</td>
<td>2.24 GHz</td>
<td>121.2</td>
<td>1000 °C – 4 h</td>
<td>[10]</td>
</tr>
<tr>
<td>Bi(<em>{1.5})Zn(</em>{0.92})Nb(<em>{1.5})O(</em>{6.92})</td>
<td>1 MHz</td>
<td>148</td>
<td>6.5×10(^{-4})</td>
<td>[14]</td>
</tr>
<tr>
<td>Bi(<em>{1.5})Zn(</em>{0.92})Nb(<em>{1.5})O(</em>{6.92})</td>
<td>1 MHz</td>
<td>130</td>
<td>4×10(^{-4})</td>
<td>[15]</td>
</tr>
<tr>
<td>Bi(<em>{1.5})Zn(</em>{0.92})Nb(<em>{1.5})O(</em>{6.92})</td>
<td>2.40 GHz</td>
<td>120.2</td>
<td>1050 °C – 4 h</td>
<td>[12]</td>
</tr>
<tr>
<td>Bi(<em>{1.5})Zn(</em>{0.92})Nb(<em>{1.5})O(</em>{6.92})</td>
<td>2.3 GHz</td>
<td>121.3</td>
<td>1000 °C – 4 h</td>
<td>[10]</td>
</tr>
</tbody>
</table>

**Figure 1.** XRD patterns of Bi\(_{1.5}\)ZnNb\(_{1.5}\)O\(_7\) and Bi\(_{1.5}\)Zn\(_{0.92}\)Nb\(_{1.5}\)O\(_{6.92}\) pellets sintered at 1000 °C for 4 h.
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$_{1.5}$ZnNb$_{1.5}$O$_7$ powder contained Bi$_2$O$_3$ and ZnO phases in addition to pyrochlore, Bi$_{1.5}$Zn$_{0.92}$Nb$_{1.5}$O$_{6.92}$ gave only pyrochlore and Bi$_2$O$_3$ 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$_{1.5}$ZnNb$_{1.5}$O$_7$ 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, Bi$_{1.5}$Zn$_{0.92}$Nb$_{1.5}$O$_{6.92}$ samples gave only single phase pyrochlore. Since XRD of Bi$_{1.5}$Zn$_{0.92}$Nb$_{1.5}$O$_{6.92}$ pyrochlore did not show any superlattice reflections, the cations are randomly distributed over the A and/or B sites in the A$_2$B$_2$O$_7$ pyrochlore. In the XRD of Bi$_{1.5}$ZnNb$_{1.5}$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 Bi$_{1.5}$ZnNb$_{1.5}$O$_7$ pyrochlore and concluded that it consisted of a cubic pyrochloretype phase and small amount of ZnO. Wu et al. [10] investigated the microstructures of Bi$_{1.5}$ZnNb$_{1.5}$O$_7$ and Bi$_{1.5}$Zn$_{0.92}$Nb$_{1.5}$O$_{6.92}$ pyrochlores and indicated that Bi$_{1.5}$ZnNb$_{1.5}$O$_7$ was not composed of a single phase pyrochlore but instead, it consists of unusual structure of Bi$_{1.5}$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](image-url)
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$_{1.5}$O$_7$ 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 ($T_m = 1190^\circ$C), evaporation losses may occur due to unreacted Bi$_2$O$_3$ ($T_m = 825^\circ$C). The theoretical densities were calculated as 7.11 g/cm$^3$ for Bi$_{1.5}$ZnNb$_{1.5}$O$_7$ and 7.04 g/cm$^3$ 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$_{1.5}$O$_7$ 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. Bi$_{1.5}$Zn$_{0.92}$Nb$_{1.5}$O$_{6.92}$ ceramic has higher dielectric constant and lower loss values than Bi$_{1.5}$ZnNb$_{1.5}$O$_7$. Although the dielectric constant of Bi$_{1.5}$ZnNb$_{1.5}$O$_7$ 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$_{1.5}$O$_7$ 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$_{1.5}$O$_7$. 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 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
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$_7$

![Graph](image_url)

**Figure 5.** Frequency variation of a) dielectric constant b) dielectric loss of Bi$_{1.5}$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 $\delta = 0.00008$ at 1 MHz at 25°C) than Bi$_{1.5}$Zn$_{1.0}$Nb$_{1.5}$O$_{7}$ ($e = 150$ and tan $\delta = 0.0006$ 1 MHz at 25°C), possibly due to existence of second phases in Bi$_{1.5}$Zn$_{1.0}$Nb$_{1.5}$O$_{7}$.

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References


Figure 6. Frequency variation of a) dielectric constant b) dielectric loss of Bi$_{1.5}$ZnNb$_{1.5}$O$_{7}$ ceramic at various temperatures.
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