



## ELECTRICAL PROPERTIES OF BISMUTH NICKEL TANTALATE PYROCHLORE, A NEW PYROCHLORE SOLID SOLUTION

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### ABSTRACT

$\text{Bi}_3\text{Ni}_2\text{Ta}_3\text{O}_{14}$  (BNT) pyrochlores and a series of its solid solutions  $\text{Bi}_3\text{Ni}_{2-x}\text{Ta}_3\text{O}_{14-x}$  ( $-0.2 \leq x \leq 1.0$ ) were prepared via conventional solid state method. The phase purity of BNT and its solid solutions was investigated by X-ray diffraction (XRD) method. Phase pure of BNT cubic pyrochlore was successfully synthesized at  $x = 0.6$  ( $\text{Bi}_3\text{Ni}_{1.4}\text{Ta}_3\text{O}_{13.4}$ ) with sintering temperature of 1050 °C over 24 hours. The single phase material crystallized in a cubic system, space group  $Fd\bar{3}m$  with  $a = b = c = 10.5134 \text{ \AA}$ ,  $\alpha = \beta = \gamma = 90^\circ$ , respectively. Detailed analysis was carried out on single phase material and the electrical properties was determined by ac impedance spectroscopy in the frequency of 5 Hz to 13 MHz. Conductivity revealed that the sample was in bulk properties and it had a high activation energy of 0.93eV and 0.95eV for heat and cool respectively. Ac impedance indicate that BNT exhibits dielectric properties with permittivity,  $\epsilon'$  of 44.85 and dielectric loss,  $\tan \delta$ , of 0.003 at room temperature in the frequency region  $1 \times 10^5 \text{ Hz}$  (100 kHz) respectively.

**Keywords:** bismuth, nickel, tantalum, pyrochlore, electrical properties.

### INTRODUCTION

Ceramics, by definition, comprise inorganic, non-metallic, non-water-soluble compounds that show ionic contributions in their chemical bonds. Along with the revolutionary development of electronics in the second half of the twentieth century, the huge potential of ceramic materials has been unfolded and introduced into a fascinatingly wide spectrum of electrical and microelectronic devices and applications. After the Second World War, the technical exploitation of ferroelectric ceramics began, because of their unique properties such as high dielectric permittivity, high piezoelectric constants and electromechanical coupling, high pyroelectric coefficients, and, under certain circumstances, high optical transparency and electro-optic coefficients [1].

Electroceramics are predominantly oxide-based materials that contain electro-active intra-granular (bulk) and inter-granular (grain boundary) regions whose properties depend on the close control of structure-stoichiometry relationships. The application of electroceramic powders depends on their fabrication and sintering processes to yield monolithic components. Electroceramic powders are derived from highly refined materials or specific chemical synthesis which include conventional synthesis (powder mixing, coprecipitation and fusion) and wet chemical techniques (sol gel processing, hydrothermal, aerosol generation and spray roasting) [2].

Stoichiometric pyrochlores, whose general formula is  $\text{A}_2\text{B}_2\text{O}_7$ , have a structure composed of two different types of cation coordination polyhedral, in which the A-site positions typically occupied by larger cations are eight-coordinated and B-site positions favored by smaller sized cations are six-coordinated with different anions [3]. Pyrochlore compounds can accommodate various cations in the A- and B-sites due to their large stability field which impart various properties to the pyrochlores. Pyrochlore materials demonstrate a wide spectrum of electrical properties ranging from insulating to

metallic of which few compounds exhibiting semiconductor-to-metal transition. The applications of these materials are found in capacitors, thermistors, resistors, switching elements and microwave communication [4].

Recently, Bi-based pyrochlore ternary system have triggered great research interests owing to their relatively low sintering temperatures and excellent dielectric properties [5-7].  $\text{Bi}_2\text{O}_3\text{-ZnO-Nb}_2\text{O}_5$  ternary system have been reported to has a low sintering temperature below 1000 °C, high dielectric permittivity, low dielectric loss and temperature stability [8-9]. In the case of Ta analogue, ideal nominal composition,  $\text{Bi}_2\text{Zn}_2\text{Ta}_3\text{O}_{14}$  was reported in the  $\text{Bi}_2\text{O}_3\text{-ZnO-Ta}_2\text{O}_5$  system as confirmed by detailed phase diagram study [7]. It existed as cubic pyrochlore with  $\epsilon'$  of 58,  $\tan \delta$  of 0.0023 at 30 °C and 1 MHz [10].

Enormous attempts are made to reduce the dielectric loss and to fine-tune the dielectric constant of dielectric materials, making them suitable candidates for various electrical applications. The low dielectric loss of NiO and comparable ionic radii between  $\text{Ni}^{2+}$ , 0.70 Å and  $\text{Zn}^{2+}$ , 0.74 Å have shed new idea to study the Ni-substituted pyrochlore phases. There appears limited literature available on pyrochlores in the  $\text{Bi}_2\text{O}_3\text{-NiO-Ta}_2\text{O}_5$  (BNT) ternary system and the actual stoichiometry of different phases is still remained unclear. In this research, the pyrochlore materials of  $\text{Bi}_2\text{O}_3\text{-NiO-Ta}_2\text{O}_5$  (BNT) ternary system was synthesized using conventional solid state method and the electrical properties of its single phase material was investigated for its potential application.

### EXPERIMENTATION

Samples of nominal compositions,  $\text{Bi}_3\text{Ni}_{2-x}\text{Ta}_3\text{O}_{14-x}$  ( $-0.2 \leq x \leq 1.0$ ) were prepared by conventional solid state method. The starting materials were reagent grade oxide powders,  $\text{Bi}_2\text{O}_3$  (Aldrich, 99.9 %), NiO (Aldrich, 99.9%) and  $\text{Ta}_2\text{O}_5$  (Alfa Aesar, 99.9%). In order



to remove moisture, NiO and Ta<sub>2</sub>O<sub>5</sub> were dried at 600 °C and Bi<sub>2</sub>O<sub>3</sub> was at 300 °C, respectively for 3 hours before weighing.

The powders were weighed according to the stoichiometric quantities of the oxides ~ 3 – 4 g with accuracy of ± 0.0002 g and mixed with sufficient acetone in an agate mortar, to ensure the homogeneity of the mixture. The resulting powder was transferred into a Pt foil and pre-fired at 800 °C for 24 hours. Subsequently, the mixture was fired at temperatures of 900 °C and 1050 °C for 24 hours with intermediate regrinding. Regrinding was carried out in order to increase the contact area and to refresh contact surfaces. Weight loss is checked and it is showed that no significant loss through volatilization of the materials used. The synthesis process is illustrated as follows :

Oxides weighed → ground with acetone\* → 900 °C (24h)\* → 1050 °C (24h)

\* with intermediate regrinding

The powders were pressed into pellet of 8 mm in diameter and ~1.5 mm in thickness prior to sintering at 1050 °C for 24 h. The phase purity of the samples were characterized by X-ray powder diffraction using an automated Shimadzu diffractometer XRD 6000, Cu K $\alpha$  radiation in  $2\theta$  range of 10–70° at the scan speed of 2°/min. Data for lattice parameter determination were collected at a scan rate of 0.1°/min and the refinement was performed by *Chekkcell* software.

The electrical behaviours of the single phase sample was measured using HP4192A ac impedance analyser in the frequency range of 5 Hz–13 MHz. Gold coated pellet was attached to conductivity jig prior to electrical measurement in temperature controlled horizontal tube furnace. The electrical data were collected in heat-cool cycle in the temperature range of 28–800 °C after 30 min equilibration time.

## RESULTS AND DISCUSSION

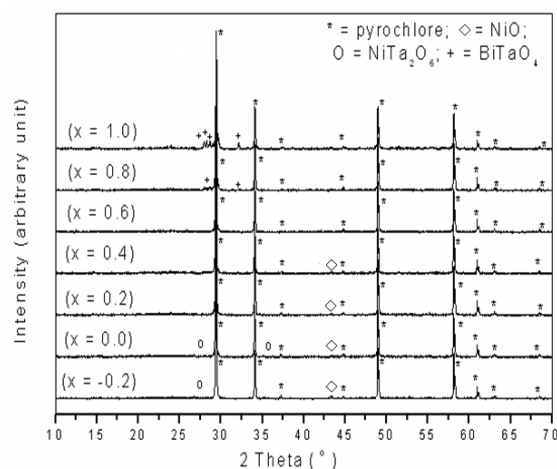
### Phase purity

Samples with different compositions in the Bi<sub>2</sub>O<sub>3</sub>-NiO-Ta<sub>2</sub>O<sub>5</sub> system were prepared by conventional solid state method. Refinement process was carried out using *Chekkcell* programme in accordance with cubic Bi<sub>3</sub>Zn<sub>2</sub>Ta<sub>3</sub>O<sub>14</sub> (BZT) analogue. After several heatings with an incremental step of 50 °C starting from 900 °C to 1150 °C, the formation of Bi<sub>3</sub>Ni<sub>2</sub>Ta<sub>3</sub>O<sub>14</sub> was investigated and it was observed that the composition of Bi<sub>3</sub>Ni<sub>2</sub>Ta<sub>3</sub>O<sub>14</sub> appeared to contain extra NiO. The extra peak of unreacted NiO was discernable around the Bragg angle  $2\theta$ , 43.32°.

The components of the Bi<sub>2</sub>O<sub>3</sub>-NiO-Ta<sub>2</sub>O<sub>5</sub> system are two unreactive oxides, Ta<sub>2</sub>O<sub>5</sub> and NiO, together with one volatile, reactive oxide Bi<sub>2</sub>O<sub>3</sub>. It is necessary, therefore, to find appropriate heat-treatment conditions such that the temperature is high enough for the Ta<sub>2</sub>O<sub>5</sub> and NiO to react, but not too high that volatilization of Bi<sub>2</sub>O<sub>3</sub> occurs before it can combined chemically. Numerous

studies on the related BZN system have shown that temperatures of the order of 950 °C are required to achieve equilibrium, but based on the more refractory nature of Ta<sub>2</sub>O<sub>5</sub> compared with Nb<sub>2</sub>O<sub>5</sub>, it was understood that temperatures of at least 1000 °C would be required to ensure that equilibrium had been reached.

The Bi<sub>3</sub>Cu<sub>2</sub>Ta<sub>3</sub>O<sub>14</sub> solid solutions were proposed with a general formula of Bi<sub>3</sub>Ni<sub>2-x</sub>Ta<sub>3</sub>O<sub>14-x</sub>, in which deficiency in Ni was compensated by creation of oxygen vacancy O<sup>2-</sup>. Different samples with x ranging from -0.2 to 1.0 were prepared and their XRD diffraction patterns are shown in Figure-1.



**Figure-1.** XRD diffraction pattern of Bi<sub>3</sub>Ni<sub>2-x</sub>Ta<sub>3</sub>O<sub>14-x</sub> with compositions ranging from x = -0.2 to 1.0 prepared at 1050 °C for 24 hours.

It was observed that the single phase cubic pyrochlore formed only at x = 0.6 (Bi<sub>3</sub>Ni<sub>1.4</sub>Ta<sub>3</sub>O<sub>13.4</sub>) after heating at 1050 °C for 24 h. The XRD pattern for Bi<sub>3</sub>Ni<sub>1.4</sub>Ta<sub>3</sub>O<sub>13.4</sub> was shown in Figure-2. It was refined using the parameter information from ICDD number 73-132 with a = b = c = 1.5400 Å,  $\alpha = \beta = \gamma = 90^\circ$ , space group *Fd3m*, respectively. Bi<sub>3</sub>Ni<sub>1.4</sub>Ta<sub>3</sub>O<sub>13.4</sub> was confirmed as single phase material as all the diffraction peaks could be fully indexed. This material crystallized in a cubic system, space group *Fd3m* with a = b = c = 10.5134 Å,  $\alpha = \beta = \gamma = 90^\circ$ , respectively.

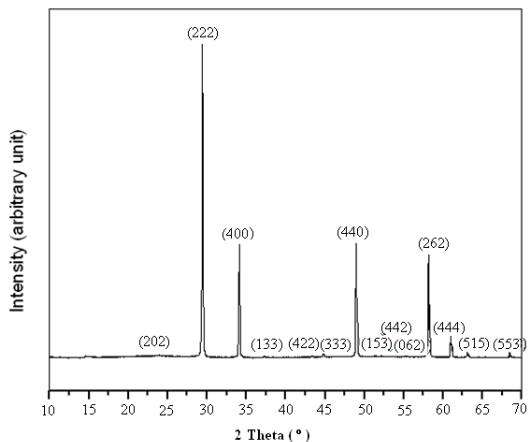


Figure-2. XRD diffraction pattern of  $\text{Bi}_3\text{Ni}_{1.4}\text{Ta}_3\text{O}_{13.4}$  prepared at 1050 °C for 24 hours.

**Electrical properties**

The electrical properties of single phase  $\text{Bi}_3\text{Ni}_{1.4}\text{Ta}_3\text{O}_{13.4}$  was determined by a.c impedance spectroscopy. The impedance data are normalized by the geometric factor. Measurement was made starting from room temperature to 800 °C by increment steps of 50 °C. In cole-cole plot, perfect single semicircles were observed above temperature of 450 °C (Figure-3). The impedance data can be represented by the equivalent circuit consists of parallel R and C elements of the bulk material (Figure-4).

The corresponding bulk resistivities,  $R_b$  can be obtained from the intercept on the real part of impedance  $Z'$ . The results shows that there is a decrease in resistance that may be associated with intra-granular (bulk) and inter-granular (grain boundary) region of the sample when the temperature of measurement increased. An associated capacitance of  $7.99 \times 10^{-12}$  was obtained at 450 °C and this corresponded to the bulk properties of materials. This agreed reasonably with that obtained from the cole-cole plot where  $\omega RC_b = 1$ .

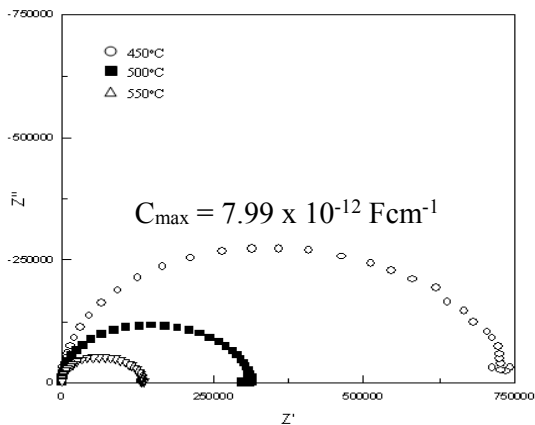


Figure-3. Cole-cole plot of  $\text{Bi}_3\text{Ni}_{1.4}\text{Ta}_3\text{O}_{13.4}$  measured at different temperature.

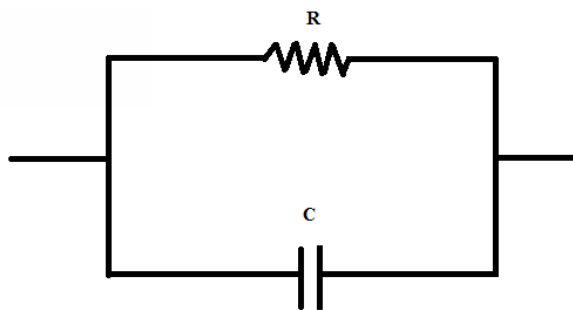


Figure-4. Circuit of parallel R and C elements.

In low frequency region, there is no sign of electrode effects (no spike at the intercept of the semicircle with  $Z'$  axis (real part of complex impedance)). Therefore the conducting species are of electronic conduction. The impedance data are therefore be represented by the equivalent circuit shown in Figure-4, which R and C elements of the bulk material,  $R_b$  (bulk resistance) and  $C_b$  (bulk capacitance), in parallel. This is confirmed by the combined spectroscopic plots shown in Figure-5. The plots show two coincident peaks of  $M''$  (imaginary part of complex modulus) and  $Z''$  (imaginary part of complex impedance). The half height width of the  $M''$  is approximately 1.33 decade, which is close to the perfect Debye which is 1.14 decade, indicating that the material is homogenous.

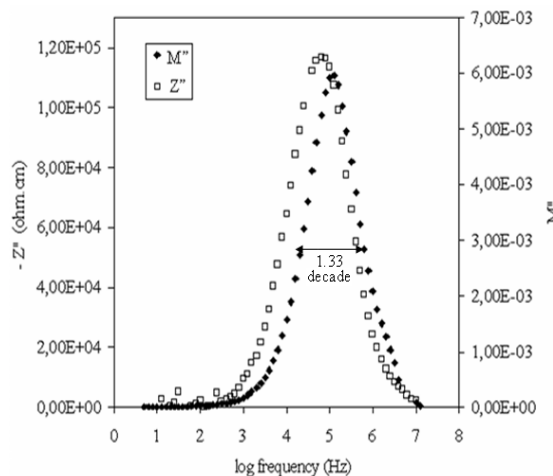
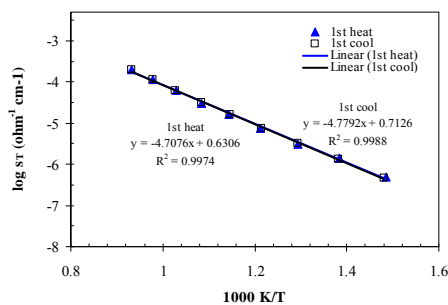


Figure-5. Combined spectroscopic plots of  $\text{Bi}_3\text{Ni}_{1.4}\text{Ta}_3\text{O}_{13.4}$  at 450 °C.

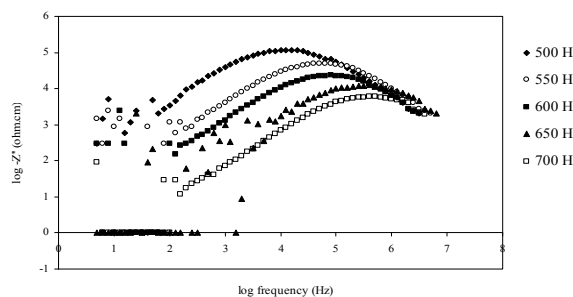
Conductivity values are extracted from cole-cole plots. Conductivity of this materials are reversible on heat-cool cycle. Figure-6 shows the Arrhenius plots in the logarithmic form of  $\text{Bi}_3\text{Ni}_{1.4}\text{Ta}_3\text{O}_{13.4}$  sintered at 1050 °C. The Arrhenius's law was applied to correlate the observed behaviour with a general relation,  $\sigma = \sigma_0 \exp(-E_a/RT)$  where  $\sigma_0$  represents a pre-exponential factor,  $E_a$  is the apparent activation energy of the conduction process,  $k$  is Boltzmann's constant and  $T$  is the absolute temperature.



**Figure-6.** Arrhenius plot of  $\text{Bi}_3\text{Ni}_{1.4}\text{Ta}_3\text{O}_{13.4}$  sintered at  $1050^\circ\text{C}$ .

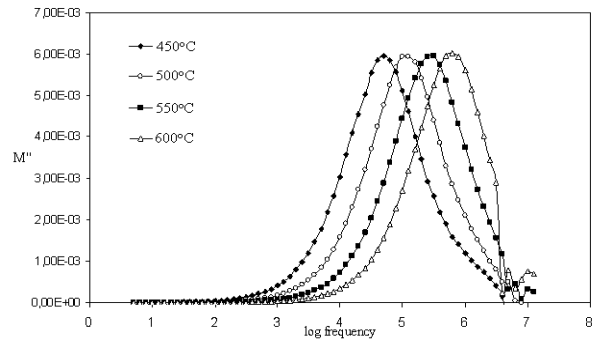
From the linear range of the plot, the activation energy,  $E_a$  can be calculated in which the activation energy of  $0.93\text{eV}$  and  $0.95\text{eV}$  were obtained for heat and cool respectively. For a.c impedance measurement, forming pellet with higher density is important for the charge carrier to move more easily with less porosity. The high activation energy for  $\text{Bi}_3\text{Ni}_{1.4}\text{Ta}_3\text{O}_{13.4}$ , when not linked to ionic conduction, are usually associated with a hopping type of electronic transport mechanism, which suggests the existence of defects such as oxygen vacancy for the hopping of electrons.

Figure-7 shows the imaginary part of impedance as a function of frequency on a logarithmic scale. Dispersion can be seen from the Figure and the maxima of the curve are displaced to higher frequency with the increase in measuring temperature. The presence of a maximum means the presence of a polarization process in the dielectric material.



**Figure-7.** Imaginary part of impedance of  $\text{Bi}_3\text{Ni}_{1.4}\text{Ta}_3\text{O}_{13.4}$  at different temperatures as a function of temperature.

Figure-8 shows the modulus spectra,  $M''$  versus frequency on logarithmic scale. Peak positions shifted toward higher relaxation frequencies with increase in temperature. This behavior suggest that the dielectric relaxation is thermally activated in which hopping mechanism of charge carriers dominates intrinsically. Peak heights are independent of temperature and it thus appears that  $\text{Bi}_3\text{Ni}_{1.4}\text{Ta}_3\text{O}_{13.4}$  is non ferroelectric.



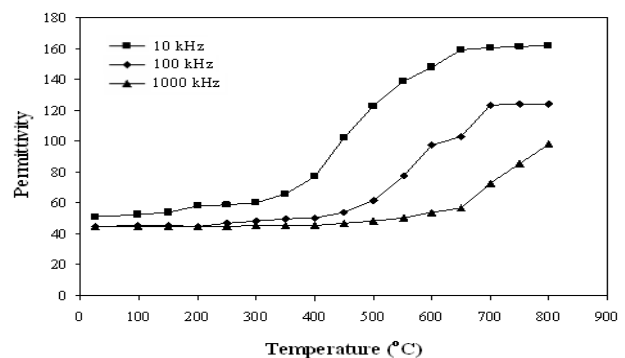
**Figure-8.** Imaginary part of electrical modulus of  $\text{Bi}_3\text{Ni}_{1.4}\text{Ta}_3\text{O}_{13.4}$  as a function of frequency.

The dielectric properties of  $\text{Bi}_3\text{Ni}_{1.4}\text{Ta}_3\text{O}_{13.4}$  was investigated at various frequencies and temperatures. The permittivity can be expressed as a complex number :

$$\epsilon^* = \epsilon' - j\epsilon'' \quad (1)$$

where  $\epsilon'$  and  $\epsilon''$  are the real and imaginary parts of the permittivity, respectively. Figure-9 shows the real of complex permittivity as a function of temperature at several frequencies. It is observed that permittivity,  $\epsilon'$  decrease with increasing frequency. The higher value of permittivity at lower frequencies is due to simultaneous presence of all types of polarizations (i.e. space charge, dipolar, ionic, electronic, etc.) in the compound. At higher frequencies, the main contribution to  $\epsilon'$  comes from electronic polarization, as some of the polarization become ineffective and thus, the value of  $\epsilon'$  decreases.

$\text{Bi}_3\text{Ni}_{1.4}\text{Ta}_3\text{O}_{13.4}$  exhibits permittivity,  $\epsilon'$  of 44.85 at room temperature in the frequency,  $f$ , region  $1 \times 10^5$  Hz (100 kHz) and it was found that this value is slightly lower than those reported in the  $\text{Bi}_2\text{O}_3\text{-ZnO-Ta}_2\text{O}_5$  ternary system. Cubic  $\text{Bi}_{1.5}\text{ZnTa}_{1.5}\text{O}_7$  ( $\alpha$ -BZT) has permittivity ( $\epsilon'$ ) of 58 at room temperature and 1 MHz [7]. The dielectric permittivities of BNN was also investigated by Nguyen *et al.* 2007 [11]. It was found that at room temperature, a permittivities of 116 which is quite high was obtained at 100 kHz.



**Figure-9.** Real part of complex permittivity as a function of temperature at several frequencies.



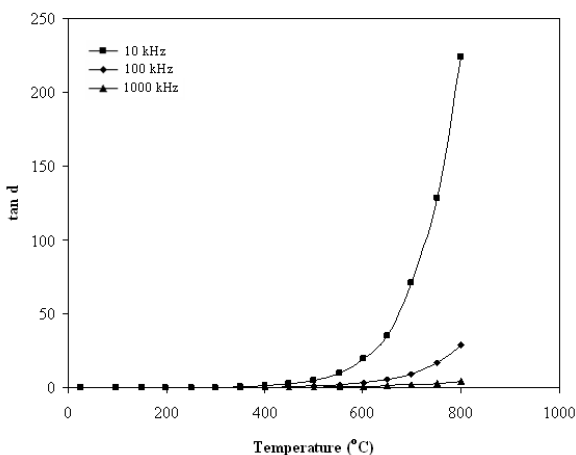
Fig.10 shows the dielectric loss,  $\tan \delta$ , as a function of temperature at several frequencies.

The dielectric loss can be expressed as:

$$\tan \delta = \epsilon'' / \epsilon' \quad (2)$$

At high frequencies, the losses are much lower than those occurred at low frequencies. This kind of dependence of  $\tan \delta$  with frequency is associated with losses due to the conduction mechanism. Dielectric loss decreases with frequencies when temperature is above 400 °C. On increasing the temperature, the electrical conductivity increases due to the increase in thermally activated drift mobility of electric charge carriers according to the hopping mechanism. Therefore the dielectric polarization increases causing a marked increase in  $\epsilon'$  and  $\tan \delta$  as temperature increases above 400 °C. Both  $\epsilon'$  and  $\tan \delta$  decrease with increasing frequency probably because the jumping frequency of electric charge carriers cannot follow the alternation of applied ac electric field beyond a certain critical frequency.

At room temperature,  $\text{Bi}_3\text{Ni}_{1.4}\text{Ta}_3\text{O}_{13.4}$  exhibits low dielectric loss,  $\tan \delta$ , of 0.003 in the frequency,  $f$ , region  $1 \times 10^5$  Hz (100 kHz). The dielectric loss tangents of BNN reported to be slightly lower than  $\text{Bi}_3\text{Ni}_{1.4}\text{Ta}_3\text{O}_{13.4}$ . This was investigated by Nguyen *et al.*, (2007) [11] and it was reported that at room temperature, dielectric loss tangents obtained is desirably low which is 0.00065 at 100 kHz. In the  $\text{Bi}_2\text{O}_3$ -ZnO- $\text{Ta}_2\text{O}_5$  ternary system, it was found that cubic  $\text{Bi}_{1.5}\text{ZnTa}_{1.5}\text{O}_7$  ( $\alpha$ -BZT) has dielectric loss ( $\tan \delta$ ) of 0.0023 at room temperature and 1 MHz which also found to be slightly lower than  $\text{Bi}_3\text{Ni}_{1.4}\text{Ta}_3\text{O}_{13.4}$ .



**Figure-10.** Dielectric losses,  $\tan \delta$ , as a function of temperatures at several frequencies.

## CONCLUSION

The pyrochlores provide great compositional variable and structural flexibility to form a wide range of solid solution which the BNT cubic pyrochlores are successfully prepared with the proposed mechanism  $\text{Bi}_3\text{Ni}_{2-x}\text{Ta}_3\text{O}_{14-x}$  ( $-0.2 \leq x \leq 1.0$ ). The phase purity of BNT and its solid solutions was investigated by X-ray diffraction (XRD) method. Phase pure BNT cubic

pyrochlore was successfully synthesized at  $x = 0.6$  ( $\text{Bi}_3\text{Ni}_{1.4}\text{Ta}_3\text{O}_{13.4}$ ) with sintering temperature of 1050 °C over 24 hours. Conductivity revealed that the sample was in bulk properties and it had a high activation energy of 0.93eV and 0.95eV for heat and cool respectively. Ac impedance indicate that BNT exhibits dielectric properties with permittivity,  $\epsilon'$  of 44.85 and dielectric loss,  $\tan \delta$ , of 0.003 at room temperature in the frequency region  $1 \times 10^5$  Hz (100 kHz) respectively.

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