

# Dielectric and Magnetic Properties of $\text{Cr}^{3+}$ , $\text{Mn}^{2+}$ & $\text{Fe}^{3+}$ Doped $\text{BiNbO}_4$ Ceramic Powders

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**ABSTRACT:** We report here on the preparation, dielectric and magnetic of  $\text{Bi}_{0.95}\text{TM}_{0.05}\text{NbO}_4$  (where  $\text{TM} = \text{Cr}^{3+}$ ,  $\text{Mn}^{2+}$  &  $\text{Fe}^{3+}$ ) ceramic powders with a sintering temperature of  $800^\circ\text{C}$  through solid state reaction method. Both SEM images and EDAX elemental profiles have been obtained to analyze their particle sizes and the chemical compositions. The XRD profiles of the samples are measured to understand their structure details. The dielectric properties of those samples have also been measured as function of frequency and their magnetic properties have also been studied to understand their magnetic nature. It is interesting to mention that the dielectric constant ( $\epsilon'$ ) and dielectric loss ( $\tan \delta$ ) of all the samples have been found to be decreasing while ac conductivity ( $\sigma_{ac}$ ) increases as a function of frequency. The Cole-Cole plots of all the materials studied show the bulk resistance ( $R_b$ ) decreasing with an increase in the order of  $\text{Mn} < \text{Cr} < \text{Fe}$  that are in accordance with the literature reports. The present work thus documents more useful and interesting results.

**KEYWORDS:**  $\text{BiNbO}_4$  Ceramic Powders, dielectric, conductivity and magnetic properties – Analysis.

## I. INTRODUCTION

Bismuth-based dielectric ceramics have been considered to be more attractive materials of great relevance because of their production temperature being relatively low ( $<1000^\circ\text{C}$ ) and having all encouraging and supportive dielectric properties [1].  $\text{BiNbO}_4$  ceramics with practical dielectric properties at microwave frequency was first developed by Kagata et al.[2] and they have reported that these ceramics have high Q values (reciprocal of dielectric loss), but the temperature coefficient of resonant frequency ( $\tau_f$ ) values are high for practical applications. In order to lower  $\tau_f$  values several researchers have attempted to modify the microwave dielectric properties of  $\text{BiNbO}_4$  ceramics using different chemical compositions.  $(\text{Bi}_{1-x}\text{Nd}_x)\text{NbO}_4$  compositions are developed by Choi et al. [3] whereas  $\text{Bi}(\text{Nb}_{1-x}\text{Ta}_x)\text{O}_4$  compositions have been developed by Weng et al.[4]. Both compositions have high (Q x f) values and low  $\tau_f$  values. Some modifications of the compositions by the addition of oxides [5-8] substituting for A or B site [9-13] have been studied broadly. Recently there is an interest in ferromagnetism as because those materials could find a wide range of new applications [14-17]. In our previous work, the thermal, structural and dielectric properties of pure  $\text{BiNbO}_4$  ceramic powder (host matrix) and later on we have studied emission analysis of  $\text{RE}^{3+}$  ( $= \text{Eu}^{3+}$ ,  $\text{Sm}^{3+}$ ,  $\text{Pr}^{3+}$ ) doped  $\text{BiNbO}_4$  ceramic powders. In the present study our objectives are to study both dielectric and magnetic properties of  $\text{BiNbO}_4$  containing  $\text{Cr}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{3+}$  ions separately each.

## II. MATERIALS AND METHODS

Three different transitions metal ions such as  $\text{Cr}^{3+}$ ,  $\text{Mn}^{2+}$  and  $\text{Fe}^{3+}$  doped each of them separately in bismuth niobate ceramics were synthesized by a solid state reaction method. High pure and analytical reagent grade chemicals such as  $\text{Bi}_2\text{O}_3$ ,  $\text{Nb}_2\text{O}_5$ ,  $\text{TM}_2\text{O}_3$  ( $=\text{Cr}_2\text{O}_3$ ,  $\text{MnO}$ ,  $\text{Fe}_2\text{O}_3$ ) were used as the starting chemicals and were weighed based on the calculated compositions and each time it was finely powdered using agate mortar and a pestle for 2 h to obtain homogeneous precursor. The chemical mix was then put into silica crucible(s) and sintered at  $800^\circ\text{C}$  and it was kept at the same temperature for 6 h in an electrical tubular furnace. The same procedure was followed to prepare all three  $\text{Cr}^{3+}$ ,  $\text{Mn}^{2+}$  &  $\text{Fe}^{3+}$  ions each separately doped in  $\text{BiNbO}_4$  ceramic powders. Finally, those sintered samples were allowed to cool down to the room temperature. Each of these powders was again powdered in an agate mortar with a pestle for 30 min. The structures of the prepared ceramic powders were characterized based on the XRD profiles obtained from a

XRD 3003 TT Seifert diffractometer with  $\text{CuK}_\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$  at 40 KV and 20 mA and  $2\theta$  range from  $20^\circ$  to  $70^\circ$ , to identify the material nature and structure. To examine the morphology of the synthesized powders Scanning Electron Microscope (SEM) Photographs were taken by means of Philips XL 30 ESEM. The elemental analysis was carried out by Energy Dispersive X-ray Analysis (EDAX) using an X-ray detector attached to SEM system. The dielectric properties of the samples prepared were measured on a Phase Sensitive Multimeter (PSM) 1700 (LCR meter) with a frequency range of 1 Hz – 1 MHz. A Vibrating Sample Magnetometer (VSM, Lakeshore-7400, USA) was used for magnetization measurements with the variation of applied magnetic field on the prepared samples.

### III. RESULTS AND DISCUSSION

The diffraction peaks of all samples are in conformity with the standard card (JCPDS – 16-0295) of  $\text{BiNbO}_4$ , indicating that the all the prepared samples possess the same orthorhombic crystal structure as it is shown in Fig. 1(a), and in Fig.1(b) photographs of the samples in pellet forms.

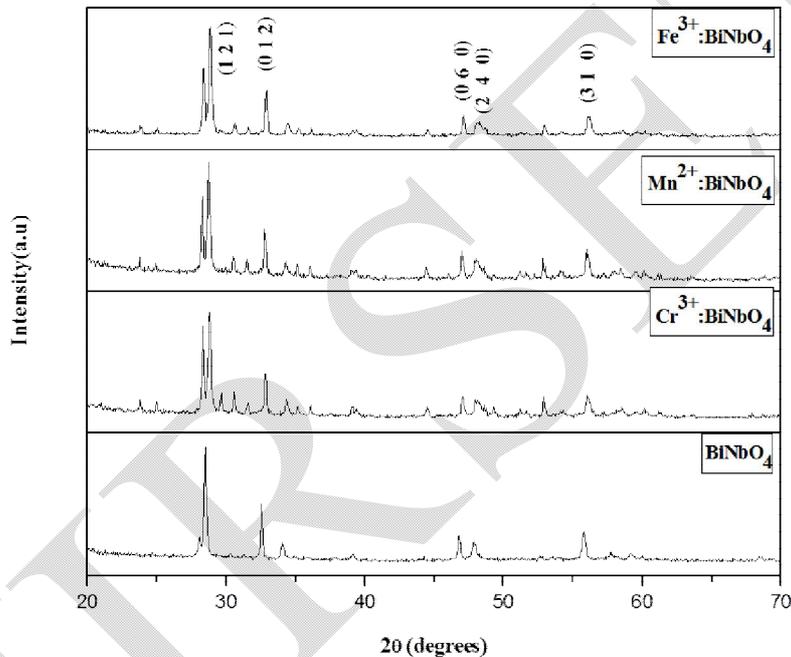


Fig. 1(a): XRD profiles of  $\text{BiNbO}_4$ ,  $\text{Cr}^{3+}:\text{BiNbO}_4$ ,  $\text{Mn}^{2+}:\text{BiNbO}_4$ ,  $\text{Fe}^{3+}:\text{BiNbO}_4$  ceramic powders

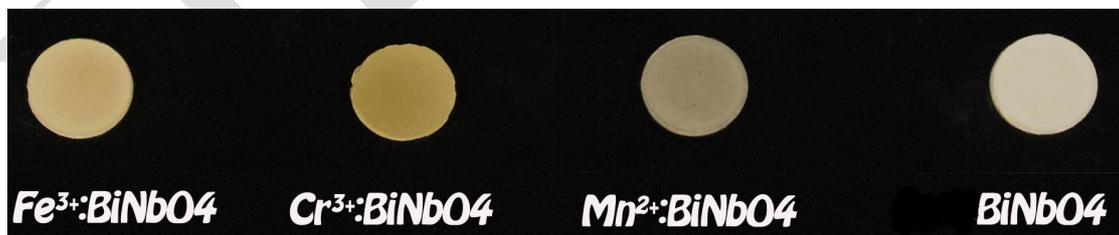


Fig. 1(b): photograph of  $\text{Cr}^{3+}:\text{BiNbO}_4$ ,  $\text{Mn}^{2+}:\text{BiNbO}_4$ ,  $\text{Fe}^{3+}:\text{BiNbO}_4$  and host  $\text{BiNbO}_4$  ceramic pellets.

The obtained XRD peaks have appropriately been labeled to the concerned ( $h, k, l$ ) values in order to validate their structures with the standard data. The crystallite size ‘ $t$ ’ was calculated by using the standard Scherrer’s formula  $t = K\lambda/(\beta \cos \theta)$ , where  $\beta$  is full width half maximum (FWHM) of the diffracted peak,  $\lambda$  is the wavelength of X-ray radiation,  $\theta$  is the angle of diffraction and constant  $K = 0.89$  [14]. The calculated crystallite sizes for  $\text{Cr}^{3+}$ ,  $\text{Mn}^{2+}$  and

Fe<sup>3+</sup>: BiNbO<sub>4</sub> ceramic powder samples are in 58.84 nm, 66.83 nm and 58.21 nm respectively. It is clear that there exist little changes in the crystallite sizes.

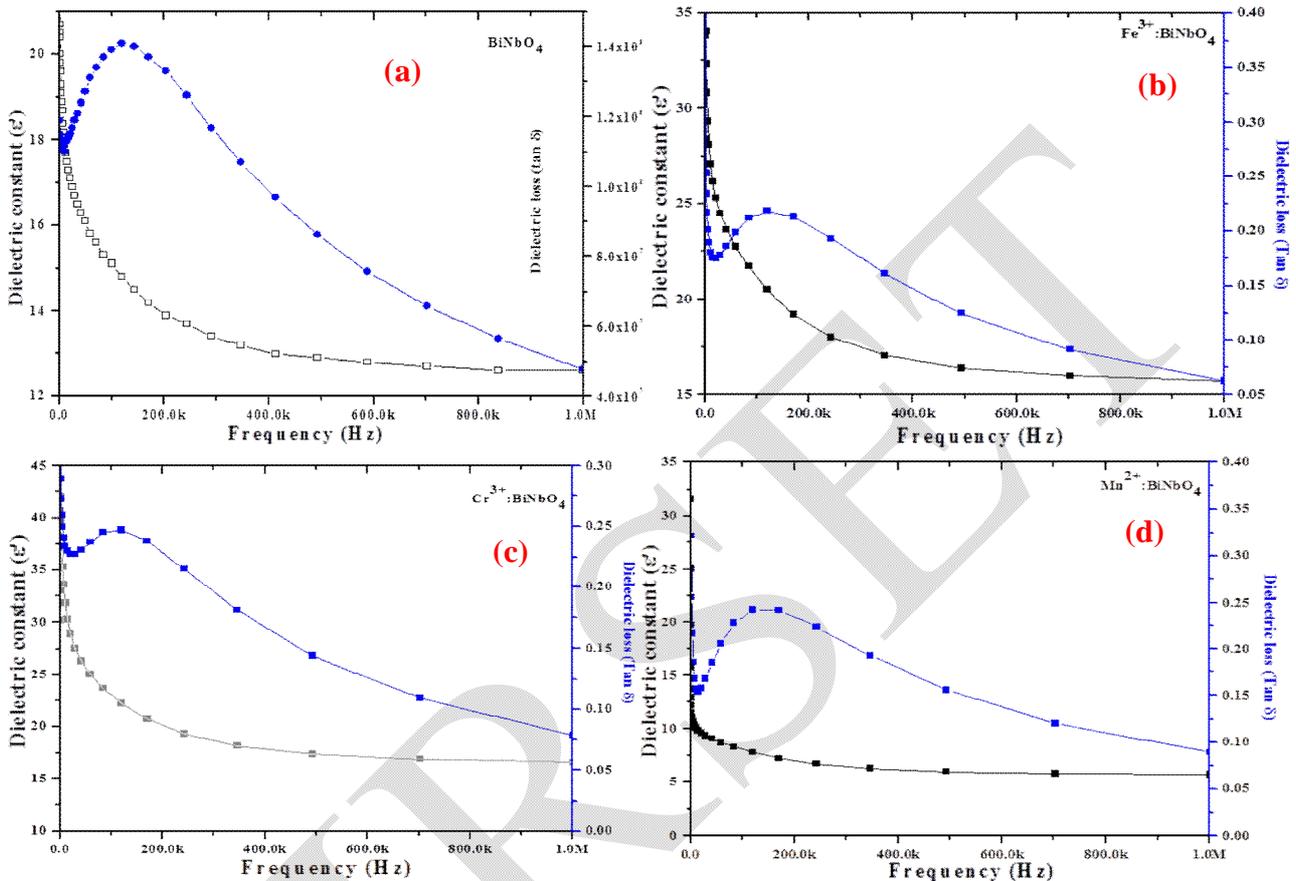


Fig. 2: Variation Dielectric constant ( $\epsilon'$ ), and Dielectric loss ( $\tan \delta$ ) as a function of frequency for host (a) BiNbO<sub>4</sub>, (b) Fe<sup>3+</sup>: BiNbO<sub>4</sub>, (c) Cr<sup>3+</sup>: BiNbO<sub>4</sub>, (d) Mn<sup>2+</sup>: BiNbO<sub>4</sub> ceramic powders

Fig. 2(a-d) shows the variation of dielectric constant ( $\epsilon'$ ) and dielectric loss ( $\tan \delta$ ) of host BiNbO<sub>4</sub> ceramic powder with the change of frequency at the room temperature. From the profiles it is clear that the dielectric constant decreases with an increase in the frequency. From these profiles it is observed that as frequency increases both dielectric constant ( $\epsilon'$ ) and dielectric loss ( $\tan \delta$ ) of BiNbO<sub>4</sub>, Fe<sup>3+</sup>: BiNbO<sub>4</sub>, Cr<sup>3+</sup>: BiNbO<sub>4</sub>, Mn<sup>2+</sup>: BiNbO<sub>4</sub> ceramic powder are found to decrease gradually with increasing of frequency. This is due to the phenomenon of frequency dispersion. The frequency of hopping between the ions could not follow the frequency of applied field and hence it lags behind, therefore the values of  $\epsilon'$  could normally decrease with increase in frequency. At higher frequencies,  $\epsilon'$  of all the samples have been found to be relatively constant with frequency. This is because periodic reversal of the field takes place so rapidly that the charge carriers will hardly be able to orient themselves in the field direction resulting in decrease of dielectric constant ( $\epsilon'$ ). It is evident from the figures the dielectric loss of all the prepared samples found to increase abruptly up to a particular frequency, beyond that it decreases gradually with increase in frequency, thus revealing the dielectric relaxation phenomenon of BiNbO<sub>4</sub> ceramic powder.

The dielectric loss tangent ( $\tan \delta$ ) is the phase difference due to the loss of energy within the sample. In the dielectric materials, defects, space charge formation, lattice distortions etc., in the boundaries could produce absorption current resulting in loss factor ( $\tan \delta$ ) and with high alternating frequency these could follow the field applied and then gradually come down to a low value. The contribution to the dielectric loss is mainly attributed to thermally activated

# International Journal of Innovative Research in Science, Engineering and Technology

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Vol. 3, Issue 12, December 2014

relaxation of freely rotating dipoles trying to align themselves in the applied field direction. dielectric loss of the four studied glass system decreases with an increase in frequency due to mobility of conducting species. The higher the mobility of conducting species, the higher would be the dielectric loss component.

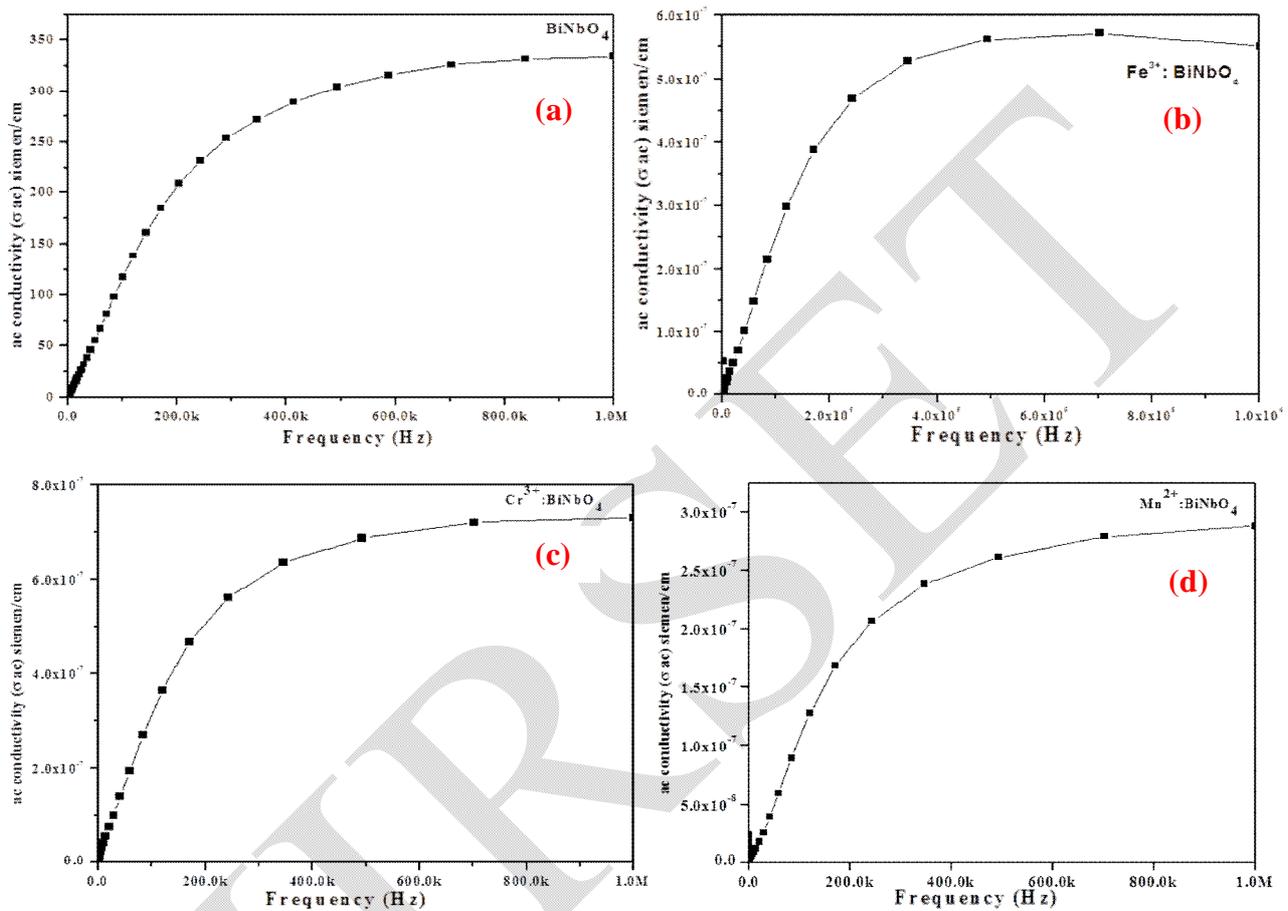
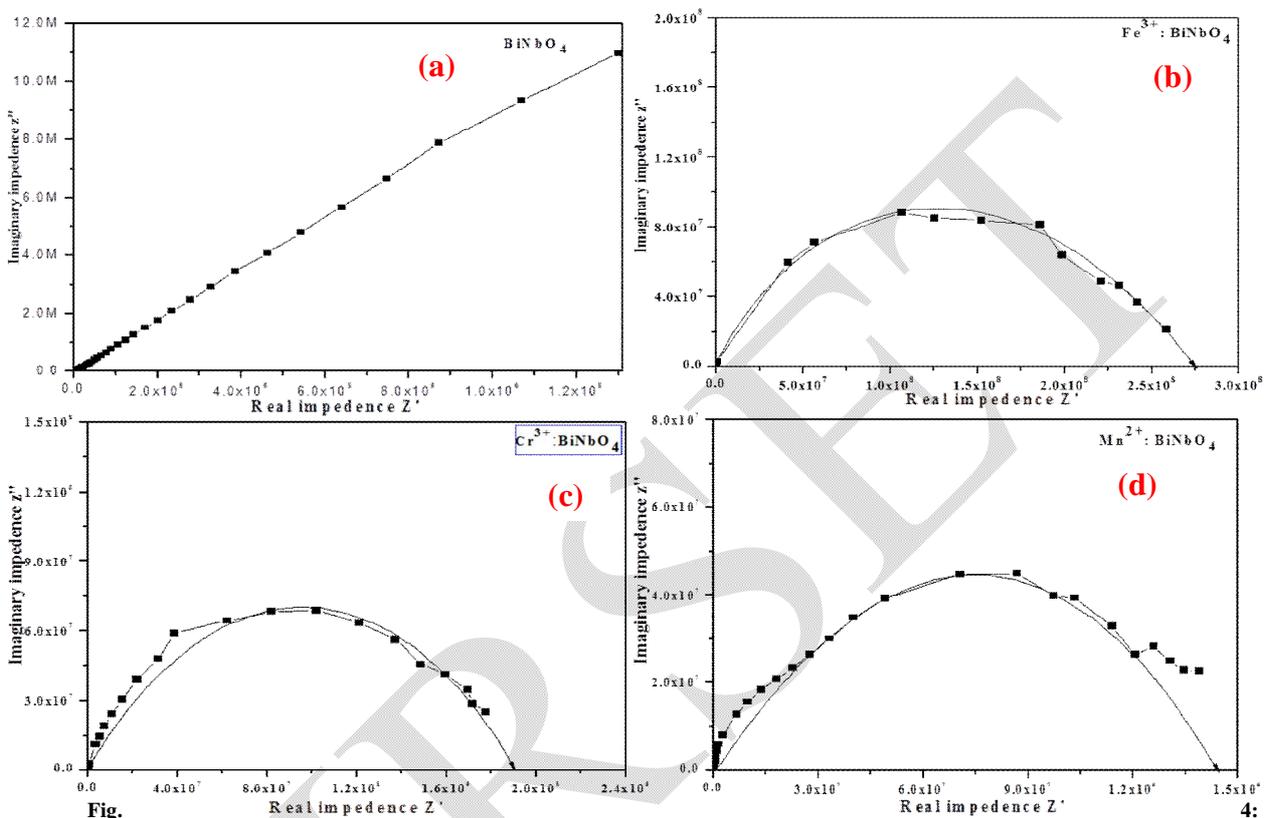


Fig. 3: Variation Dielectric constant ( $\epsilon'$ ), and Dielectric loss ( $\tan \delta$ ) as a function of frequency for host (a)  $\text{BiNbO}_4$ , (b)  $\text{Fe}^{3+}:\text{BiNbO}_4$ , (c)  $\text{Cr}^{3+}:\text{BiNbO}_4$ , (d)  $\text{Mn}^{2+}:\text{BiNbO}_4$  ceramic powders

Fig. 3(a-d) represents ac-conductivity ( $\sigma_{ac}$ ) profiles with dependence of frequency for  $\text{BiNbO}_4$ ,  $\text{Fe}^{3+}:\text{BiNbO}_4$ ,  $\text{Cr}^{3+}:\text{BiNbO}_4$ ,  $\text{Mn}^{2+}:\text{BiNbO}_4$  ceramic powder. These profiles are analyzed on the basis of Jonscher universal power law [18]:  $\sigma(\omega) = \sigma_{dc} + A\omega^s$   $0 < s < 1$ , where  $\sigma_{dc}$  is the dc conductivity of the samples, A is temperature dependent constant,  $\omega$  is the angular frequency of the applied field and s is the power law exponent in the range  $0 < s < 1$ , represents the degree of interaction between the mobile ions. The frequency dependence of conductivity is sum of the dc conductivity due to movements of free charges and polarization conductivity (ac conductivity) due to movements of bound charges. The nature of ac conductivity plots for the studied systems with and without dopant ions ( $\text{Fe}^{3+}$ ,  $\text{Cr}^{3+}$  &  $\text{Mn}^{2+}$ ) exhibit same trend of increasing in ac conductivity as a function of frequency. It is also observed that in the low frequency region, ion conductivity low and frequency independent, which could be attributed to the polarization effects at the electrode-electrolyte interface, the accumulation of ions due to slow periodic reversal of the electric field. In the intermediate frequency region, conductivity is a frequency independent due to a short range transport of ions in response to electric field. In the high frequency region, conductivity curves were exhibiting linear nature suggesting strong frequency dependence.

One of the most convenient ways of checking the polydisperse nature of dielectric relaxation is through complex Argand plane plots between  $z'$  and  $z''$ , which are usually called Nyquist Plots. Semicircular plots are expected with a centre located on  $z'$  axis. Where  $z'$  is real impedance (series resistance R) and  $z''$  is the imaginary impedance ( $1/(\omega C)$ ). Here  $\omega$  is the angular frequency ( $2\pi f$ ) and C is the series capacitance.



**Fig. 4:** Nyquist plots between  $z'$  and  $z''$  as a function of frequency for host (a)  $\text{BiNbO}_4$ , (b)  $\text{Fe}^{3+}:\text{BiNbO}_4$ , (c)  $\text{Cr}^{3+}:\text{BiNbO}_4$ , (d)  $\text{Mn}^{2+}:\text{BiNbO}_4$  ceramic powders

The Nyquist plots for host,  $\text{Cr}^{3+}$ ,  $\text{Mn}^{2+}$  and  $\text{Fe}^{3+}:\text{BiNbO}_4$  ceramic powder samples are shown in Fig.4 (a-d). The complex impedance plots show that the semicircle observed in the high frequency region, which is due to the bulk effect of the electrolytes. The bulk electrical resistance ( $R_b$ ) has been calculated from the low frequency intercept of the semicircle on the  $z'$  axis. The ionic conductivities of the samples are calculated by using the formula  $\sigma_{ac} = d/(R_b A)$  where 'd' is the thickness of the pellet of the samples prepared. The bulk resistances ( $R_b$ ) values of  $\text{Cr}^{3+}$ ,  $\text{Mn}^{2+}$  and  $\text{Fe}^{3+}:\text{BiNbO}_4$  ceramic powder samples obtained from Cole-Cole plots are  $1.90 \times 10^8$ ,  $1.44 \times 10^8$  and  $2.70 \times 10^8$  respectively. From these values the ionic conductivities of the samples are calculated and are found to be  $5.85 \times 10^{-7}$  Siemen/cm,  $6.54 \times 10^{-7}$  Siemen/cm and  $3.48 \times 10^{-7}$  respectively.

In Fig.5 (a-d), SEM micrographs and EDAX spectra of host  $\text{BiNbO}_4$ ,  $\text{Fe}^{3+}:\text{BiNbO}_4$ ,  $\text{Cr}^{3+}:\text{BiNbO}_4$  and  $\text{Mn}^{2+}:\text{BiNbO}_4$  ceramic powders are shown. The obtained micrographs show that the particles are agglomerated and the average diameter of the grain size is in the range of 400 nm ~ 500 nm. The elemental analysis of the synthesized products was performed using the energy dispersive x-ray analysis (EDAX) technique, which is attached to the SEM system. EDAX analysis was carried out mainly to confirm the presence of both host and dopant transition ions in the ceramics powders reported here and the results confirm their presence.

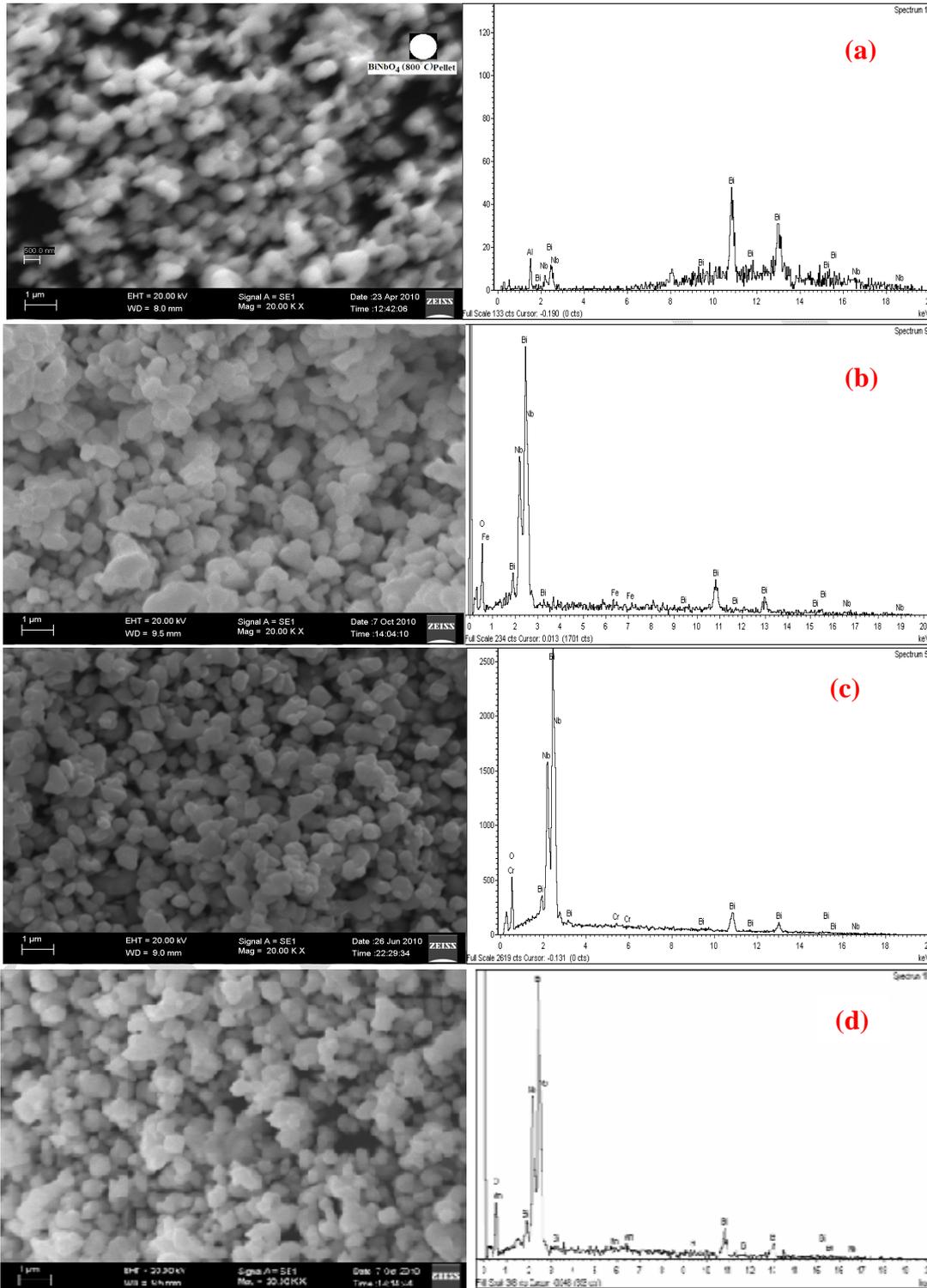
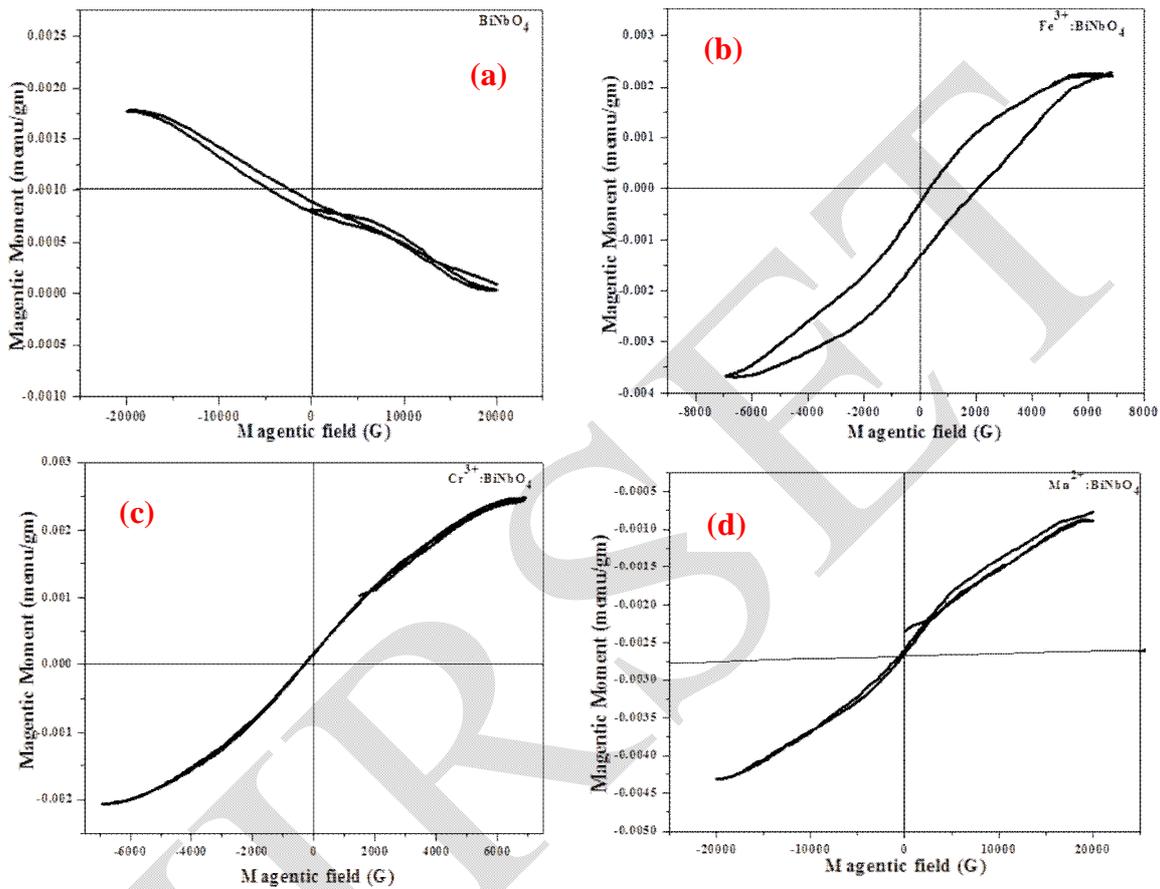


Fig. 5: SEM and EDAX profiles of host (a) BiNbO<sub>4</sub>, (b) Fe<sup>3+</sup>: BiNbO<sub>4</sub>, (c) Cr<sup>3+</sup>: BiNbO<sub>4</sub>, (d) Mn<sup>2+</sup>: BiNbO<sub>4</sub> ceramic powders

Fig.6 display the room temperature magnetic hysteresis (M-H) curves of the host BiNbO<sub>4</sub>, Fe<sup>3+</sup>: BiNbO<sub>4</sub>, Cr<sup>3+</sup>: BiNbO<sub>4</sub> and Mn<sup>2+</sup>: BiNbO<sub>4</sub> ceramic powders. The pure BiNbO<sub>4</sub> sample exhibits an anti-ferromagnetic behavior at the room temperature at the applied magnetic field of 25000 (G) in order to show hysteretic behavior. From the hysteresis curve of pure BiNbO<sub>4</sub> sample the magnetization saturation (MS) value is found to be in 0.0018 emu/g, coercivity is 336 gauss and retentivity is 9.3 emu/g.



**Fig. 6: Magnetization dependence of the applied magnetic field for host (a) BiNbO<sub>4</sub>, (b) Fe<sup>3+</sup>: BiNbO<sub>4</sub>, (c) Cr<sup>3+</sup>: BiNbO<sub>4</sub>, (d) Mn<sup>2+</sup>: BiNbO<sub>4</sub> ceramic powders**

From Fig 6 (b, c & d), it is clear that Cr<sup>3+</sup>-doped BiNbO<sub>4</sub> ceramic powder exhibits weak ferromagnetic behavior and Fe<sup>3+</sup>-doped BiNbO<sub>4</sub> ceramic powder exhibits strong ferromagnetic behavior at room temperature with the applied magnetic field of 8000 oersteds. For the Cr<sup>3+</sup>:BiNbO<sub>4</sub> sample the MS, coercivity and retentivity values are found to be 0.0024 emu/g, 336 oersteds and 1.6 emu/g respectively. For the sample Fe<sup>3+</sup>:BiNbO<sub>4</sub> ceramic powder the Ms, coercivity, retentivity values are found to be 0.0022 emu/g, 342 oersteds and 2.9 emu/g respectively. The Mn<sup>2+</sup> doped BiNbO<sub>4</sub> ceramic powder exhibits weak ferromagnetic behavior at room temperature with the applied magnetic field of 25000 gauss and is shown in Fig 6(d). The loop shows that the values of MS are -0.0043 emu/g, coercivity is 422 gauss and retentivity is 0.0025 emu/g.

**IV. CONCLUSION**

We conclude that Cr<sup>3+</sup> or Mn<sup>2+</sup> or Fe<sup>3+</sup>: BiNbO<sub>4</sub> ceramic powders have successfully been developed by a conventional solid state reaction method upon sintering those powders at 800°C. From the XRD profiles of these samples, the orthorhombic phase has been identified (JCPDS- 16-0295) and the crystallite sizes are found to be in the range of 58-66

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(An ISO 3297: 2007 Certified Organization)

Vol. 3, Issue 12, December 2014

nm. SEM investigations have revealed that the grain sizes of transition metal ions doped BiNbO<sub>4</sub> ceramic powders are in the range of 400nm ~ 500 nm. The dielectric constant  $\epsilon'$  and dielectric loss ( $\tan \delta$ ) values of all the samples decrease with an increase in frequency and such trends have been attributed to the existence of dispersion and dielectric relaxations. From Cole-Cole plots, the bulk resistance ( $R_b$ ) and dc-conductivity ( $\sigma_{dc}$ ) of these samples are evaluated. From the obtained hysteresis curves, we observed anti-ferromagnetic behavior from the host matrix and ferromagnetic behaviors from the transition metal ions ( $Cr^{3+}$ ,  $Mn^{2+}$  &  $Fe^{3+}$ ) doped: BiNbO<sub>4</sub> ceramic powders. From these profiles, the magnetization saturation, coercivity and remanence values are obtained for the samples studied. Based on the results documented here, we suggest these ceramic powders are considered to more important dielectric and magnetic materials for various potential applications.

## REFERENCES

- [1] Ling H C, Yan M F, Rhodes, "High dielectric constant and small temperature coefficient bismuth-based dielectric compositions", *Mater. Res.* 5, 1752-1762, 1990.
- [2] Katagata H, Inoue T, Kato J, Kameyama I, "Low fire bismuth-based dielectric ceramics for microwave use", *Jpn. J. Appl. Phys.* 31, 3152-3155, 1992.
- [3] Choi W, Kim K Y, "Effects of Nd<sub>2</sub>O<sub>3</sub> on the microwave dielectric properties of BiNbO<sub>4</sub> ceramics", *J. Mater. Res.* 13, 2945-2949, 1998.
- [4] Weng M H, Huang C L, "The microwave dielectric properties and the microstructures of Bi(Nb,Ta)O<sub>4</sub> ceramics", *Jpn. J. Appl. Phys.* 38, 5949-5952, 1999.
- [5] Yang Ch F, "Improvement of the dielectric properties of BiNbO<sub>4</sub> ceramics by the addition of CuO-V<sub>2</sub>O<sub>5</sub> mixtures", *J. Mater. Sci. Lett.* 18, 805-807, 1999.
- [6] Yang Ch F, "Improvement of quality value and shift of  $\tau f$  value of BiNbO<sub>4</sub> ceramics with addition of CuO-V<sub>2</sub>O<sub>5</sub> mixtures", *Jpn. J. Appl. Phys.* 38, 6797-6800, 1999.
- [7] Huang Ch L, Weng, M H, Shan G M, "Effect of V<sub>2</sub>O<sub>5</sub> and CuO additives on sintering behavior and microwave dielectric properties of BiNbO<sub>4</sub> ceramics", *J. Mater. Sci.* 35, 5443-5447, 2000.
- [8] Tzou W Ch, Yang Ch F, Chen Y Ch, Cheng P Sh, "Improvements in the sintering and microwave properties of BiNbO<sub>4</sub> microwave ceramics by V<sub>2</sub>O<sub>5</sub> addition", *J. Eur. Ceram. Soc.* 20, 991-996, 2000.
- [9] Chen Y Ch, Tzou W Ch, Yang Ch F, Chang P Sh, "The effect of the crystalline phase on the sintering and microwave dielectric properties of Cu-doped (Bi<sub>0.95</sub>Sm<sub>0.05</sub>)NbO<sub>4</sub> ceramics", *Jpn. J. Appl. Phys.* 40, 3225-3255 2001.
- [10] Zhou D, H. Wang, X. Yao, "Microwave dielectric properties and co-firing of BiNbO<sub>4</sub> ceramics with CuO substitution", *Mater. Chem. Phys.* 104, 397-402, 2007.
- [11] Huang Ch L, Weng M H, "The microwave dielectric properties and the microstructures of Bi (Nb, Ta) O<sub>4</sub> ceramics", *Jpn. J. Appl. Phys.* 38, 5949-5952, 1999.
- [12] Wang N, Zhao M Y, Li W, Yin Zh W, "The sintering behavior and microwave dielectric properties of Bi (Nb, Sb) O<sub>4</sub> ceramics", *Ceram. Int.* 30, 1017-1022, 2004.
- [13] Zhou D, Wang H, Yao X, Liu Y, "Microwave dielectric properties of low-firing BiNbO<sub>4</sub> ceramics with V<sub>2</sub>O<sub>5</sub> substitution", *J. Electro Ceram.*, doi : 10, 1007/s10832 - 007 - 9223 - 2 (online published).
- [14] Scherrer, Cottin P. *Nachricht.* 2, 98-99, 1918.
- [15] Fiebig M, Lottermoser T, Frohlich D, Goltsev A V & Pisarev R V, *Nature*, 419, 818, 2000.
- [16] Spaldin N A & Fiebig, *M. Science*, 309, 391, 2005.
- [17] Hill N A, *J. Phys. Chem. B*, 104, 6694, 2000.
- [18] A.K. Jonscher, The 'universal' dielectric response, *Nature* 267, 673-679, 1997.