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# Frequency-temperature response of a new multiferroic

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## Abstract

The frequency dependence of the electrical properties of a new complex multiferroic  $Bi_4Pb_2Ti_3FeNbO_{18}$  at different temperatures was investigated by impedance spectroscopy technique. The impedance spectroscopic data were collected at different frequencies (100 Hz–1 MHz) and temperatures (25–500 °C). This study provides important information about the effect of grain and grain boundary on microstructures of the materials. The data are presented in the Nyquist plots, from which electrical resistivity is determined.

Keywords: bismuth titanate, lead iron niobate, dielectric properties, impedance spectroscopy

#### I. Introduction

Bismuth titanate,  $Bi_4Ti_3O_{12}$  (BTO), is a well-known ferroelectric with a layered perovskite structure of relatively high dielectric constant, Curie temperature, and breakdown strength [1]. BTO is useful for electro-optic, piezo-electric, optical memory, and display applications. Further, it is known that the titanates and niobates have large polarizability and structural distortions. The ferroelectric polarization of BTO is induced from the pseudo-perovskite blocks. The bismuth-oxygen layers act as the insulating layers and their net electric charge is self-regulated to compensate the space charges [2,3]. On the other hand, lead iron niobate,  $Pb(Fe_{1/2}Nb_{1/2})O_3$ (PFN) belongs to the perovskite family and possess interesting electric and magnetic properties [4,5]. PFN exhibits a broad ferroelectric transition (~385 K) and displays a high dielectric constant (>10,000). PFN is a multiferroic material, exhibiting phase transitions from the paraelectric to ferroelectric phase at 385 K, and paramagnetic to G-type anti-ferromagnetic transition at 143 K [6]. Though individually, the materials cited above have their potentiality, it has some limitations also. Unfortunately, BTO has some problems because of its high  $T_C$ . Similarly, PFN exhibits a large dielectric loss around room temperature, and hence it in-

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creases rapidly with the increase of temperature, which is again undesirable for devices. It is very much required to develop materials with Curie temperature  $(T_C)$ close to the ambient temperature for devices. To meet the challenges, to solve the above problems and to enhance the properties of the materials, several attempts have been made by suitable substitutions at different atomic sites and/or fabricating solid solution or composites. In this attempt, we have combined these two ferroelectric/multiferroic compounds to get a new complex ferroelectric/multiferroic. The optimized fabrication conditions of the solid solution of the above compounds (i.e., BTO and PFN in 1:2 ratio, corresponding to Bi<sub>4</sub>Pb<sub>2</sub>Ti<sub>3</sub>FeNbO<sub>18</sub>) and its ferroelectric and magnetic properties have already been reported elsewhere [7]. In this paper, we report the frequency dependence of electrical impedance of this new multiferroic at different temperatures.

#### **II. Experimental**

The polycrystalline sample or solid solution of  $Bi_4Pb_2Ti_3FeNbO_{18}$  was fabricated using high-purity ( $\geq 99.9\%$ ) oxides;  $Bi_2O_3$ , PbO, Nb<sub>2</sub>O<sub>5</sub>, TiO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> (M/S Loba chemicals) by a high-temperature solid-state reaction method. The reactive/ingredient powders were taken in a stoichiometric amount (with 3% excess PbO and  $Bi_2O_3$  to compensate the lead/bismuth loss or evaporation at elevated temperatures) and mixed them thoroughly in an agate-mortar in a wet medium (methanol)

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for 3 h, and calcined at 800 °C in a high-purity alumina crucible in air for 8 h. The crystalline structure of the calcined powder was examined by X-ray diffraction (XRD) technique using X-ray powder diffractometer (PW3373 XPERTPRO, PHILIPS). The calcined powder was used to make cylindrical pellets of diameter 10 mm and thickness 0.5-2 mm under a pressure of about  $6 \times 10^6 \,\text{N/m^2}$  using a hydraulic press. Polyvinyl alcohol (PVA) was used as a binder to reduce the brittleness of the pellets. The binder was burnt out during the sintering process. The pellets were sintered in a covered alumina crucible at 750 °C in air. The sintering temperature was optimized to get maximum density of the sample (~95% of the theoretical density). The X-ray diffraction data were used to evaluate the theoretical density ( $\rho$ ,  $g/cm^3$ ) of the sample using the formula:

$$\rho = \frac{\sum A/N}{V}n\tag{1}$$

where  $\sum A$  is the sum of the atomic weights of all the atoms in the unit cell, *N* is the Avogadro's number, *n* is the number of atoms per unit cell and *V* is the volume of the unit cell (cm<sup>3</sup>). The evaluated density was compared with measured density (experimental density):

$$\rho = \frac{\text{mass of the pellet sample}}{\text{volume of the pellet sample}}$$
(2)

For electrical characterization, high-purity silver paste was then painted on the flat and parallel surfaces of the sintered pellets (as an electrode), and then dried at  $150 \,^{\circ}$ C in an oven for 4 h. The electrical parameters were obtained as a function of frequency (100 Hz–1 MHz) using an impedance analyser (N4L PSM, 1735) in conjunction with a laboratory-made sample holder in a wide temperature range from 25 to 500  $^{\circ}$ C.

#### III. Complex impedance studies

Impedance measurement is a flexible and widely employed tool for the electrical and dielectric characterization of ceramic materials [8-10] over a wide range of frequency and temperature. The grain, grain boundary, and material-electrode contributions towards the electrical properties of the materials are easily separated by this technique. The electrical response of the material can be studied by using the basic formalisms via the complex permittivity ( $\varepsilon^*$ ), complex impedance  $(Z^*)$ , complex admittance  $(Y^*)$ , complex electric modulus ( $M^*$ ) and dielectric loss or dissipation factor (tan  $\delta$ ), which are interrelated to each other [11]. These relations offer a wide scope for a structure-property analysis of the various parameters under different conditions (temperature or frequency), to be studied through graphs. In the case of multiferroic materials, a combination of all the impedance formalisms is the best strategy to distinguish the ferroelectric and non-ferroelectric properties of the materials [12,13].

The following formalisms of impedance spectroscopy have been used to study the frequency dependence of electrical properties of the material:

• complex impedance,

$$Z^*(\omega) = Z' - jZ'' = R_s - j/\omega \cdot C_s \qquad (3.a)$$

• complex admittance,

$$Y^{*}(\omega) = Y' - jY'' = 1/R_{p} - j\omega \cdot C_{p}$$
 (3.b)

• complex permittivity,

$$\varepsilon^*(\omega) = \varepsilon' - j\varepsilon'' \tag{3.c}$$

• complex modulus,

$$M^*(\omega) = M' + jM'' = 1/\varepsilon = j\omega C_0 Z^* =$$
  
=  $j\omega C_0 (1/Y^*)$  (3.d)

• loss tangent,

$$\tan \delta = Z'/Z'' = \varepsilon''/\varepsilon' = M''/M'$$
(3.e)



Figure 1. Variation of Z" with frequency of Bi<sub>4</sub>Pb<sub>2</sub>Ti<sub>3</sub>FeNbO<sub>18</sub> in temperature range: a) 250–375 °C and b) 400–500 °C

• relaxation frequency,

$$\omega_{max} = \frac{1}{2}\pi \cdot f_{max}$$
 and  $\omega_{max}RC = \omega_{max}\tau = 1$  (3.f)

Here  $R_s$  and  $C_s$  are the series resistance and capacitance;  $R_p$  and  $C_p$  are the parallel resistance and capacitance, respectively.

Figures 1a and 1b show the variation of the imaginary part of the impedance Z'' with frequency at different temperatures for  $Bi_4Pb_2Ti_3FeNbO_{18}$ . The impedance plots exhibit some important features of the material, such as: (i) a monotonous decrease in Z'' with a rise in frequency (without any peak) in said frequency and temperature range, (ii) appearance of a peak at a particular frequency (relaxation frequency), (iii) decrease in the magnitude of Z'' with a shift in the peak-frequency towards higher frequency, and (iv) peak broadening with a rise in temperature. The peak location gives the relaxation time from the relation  $\omega_{max} \cdot \tau = 1$ , where  $\omega_{max}$  is the angular frequency at the maximum of Z''-frequency patterns and  $\tau$  is the relaxation time. The broadening and the height of the peaks in proportion to the bulk resistance  $(R_b)$  indicate a temperature dependent electrical relaxation phenomenon in the material and the actuation of a hopping type mechanism of electron-lattice coupling [14].



Figure 2. Comparison between the variation of M'' and Z''with frequency of Bi<sub>4</sub>Pb<sub>2</sub>Ti<sub>3</sub>FeNbO<sub>18</sub>

The electrical modulus was analysed to monitor the effect of the experimental conditions (i.e., temperature and frequency) on the relaxation process in the sample. A combined plot (Fig. 2) of imaginary modulus M'' and impedance Z'' as a function of frequency is useful to detect the effect of the smallest capacitance and the largest resistance [9]. This plot helps to distinguish whether the relaxation process is due to short range or long-range movement of charge carriers. Thus, as the peak of M'' and Z'' versus frequency (Fig. 2) slightly departed, this indicates a slight departure from the ideal Debye-like behaviour of charge carriers [15,16].

For detailed analysis of the electric modulus, the following formalisms are used:

$$M^{*}(\omega) = \frac{1}{\varepsilon^{*}} = \frac{\varepsilon'(\omega)}{|\varepsilon^{*}(\omega)|^{2}} - i\frac{\varepsilon''(\omega)}{|\varepsilon^{*}(\omega)|}$$
  
$$\equiv M'(\omega) + iM''(\omega) \qquad (4)$$
  
$$= M_{\infty} \left[ 1 - \int_{0}^{\infty} \exp(-i\omega t) \frac{\mathrm{d}\varphi(t)}{\mathrm{d}t} \mathrm{d}t \right]$$

where  $M_{\infty} = 1/\varepsilon_{\infty}$ ,  $\varepsilon_{\infty}$  is the limiting high frequency real part of the permittivity, and the function  $\varphi(t)$  is a relaxation function. The peak position of frequency in loss modulus spectra gives the most probable relaxation time which is obtained from the condition  $\omega_m \cdot \tau_m = 1$ . The most probable relaxation time  $(\tau_m)$  also obeys the Arrhenius relation:

$$\omega_m = \omega_0 \exp\left[-\frac{E_a}{k_{\rm B}T}\right] \tag{5}$$



Figure 3. Variation of *M*<sup>''</sup> with frequency of Bi<sub>4</sub>Pb<sub>2</sub>Ti<sub>3</sub>FeNbO<sub>18</sub>

Figure 3 shows the variation of imaginary part of electrical modulus (M'') of  $Bi_4Pb_2Ti_3FeNbO_{18}$  with frequency at different temperatures. The frequency region below peak frequency  $(f_{max})$ , in Fig. 3, determines the range in which charge carriers are mobile over long distances. These plots also show that a well-defined relaxation mechanism is in operation from temperatures as low as 275 °C up to about 500 °C. The peaks shift systematically towards higher frequencies with increasing temperatures. A shift in  $f_{max}$  at constant  $M''_{max}$  (modulus peak) would imply variation in resistance (R) but not in capacitance (C). On the contrary, the change in the value of  $M''_{max}$  with no variation in  $f_{max}$  would suggest a change in R and C. However, the variations in both  $M''_{max}$  and  $f_{max}$  of our data indicate a variation in C. Further, the steady increase in the values of M'' as a function of temperature is a direct indication of decreasing capacitance [16]. It is observed that the peak  $M''_{max}$ 

Temperature [°C]	$C_{h}$ [F]	0	п	$R_{h}\left[\Omega\right]$	$C_{sh}$ [F]	$R_{gh}[\Omega]$
250	5.47E-010	4.56E-009	0.7275	4.52E+005	2.97E-010	1.03E+007
275	3.25E-010	4.41E-009	0.6282	1.55E+006	5.64E-010	4.32E+006
300	2.71E-010	4.96E-009	0.5985	1.28E+006	1.11E-009	1.18E+006
325	2.33E-010	9.93E-009	0.5141	9.12E+005	1.37E-008	5.47E+001
350	2.74E-010	2.82E-008	0.4799	2.66E+005	1.68E-009	4.31E+004
375	2.49E-010	1.02E-007	0.3471	9.40E+004	6.16E-009	2.37E+002
400	2.45E-010	2.21E-007	0.3214	4.15E+004	6.00E-009	1.89E+002
425	2.30E-010	3.27E-007	0.3155	2.22E+004	5.82E-009	3.66E+001
450	2.28E-010	9.97E-007	0.2526	1.33E+004	4.83E-009	1.27E+002
475	2.08E-010	2.10E-006	0.2228	9.02E+003	4.45E-009	5.13E+001
500	1.92E-010	4.90E-006	0.1866	6.39E+003	2.92E-009	3.81E+001

Table 1. Comparison of electrical parameters of Bi<sub>4</sub>Pb<sub>2</sub>Ti<sub>3</sub>FeNbO<sub>18</sub> at different temperatures



Figure 4. Nyquist plots fitted with equivalent circuit of Bi<sub>4</sub>Pb<sub>2</sub>Ti<sub>3</sub>FeNbO<sub>18</sub> in temperature range: a) 250–375 °C and b) 400–500 °C (inset equivalent circuit)

shifts towards higher frequency with a rise in temperature. This is related to the conductivity relaxation of the materials. It has also been observed that the height and broadening of the modulus peak appear to increase with an increase in frequency. The increase in the modulus peak height on increasing frequency represents the decrease in the capacitance value at higher frequency range. At the low-frequency side (of the peak), the ions are capable of moving long distances (i.e., performing successful hopping from one site to the neighbouring site). For the high-frequency side of the peak, the ions are spatially confined to their potential wells, and can execute only localized motion within the well [16].

Figure 4 presents the fitted Nyquist plots of the material using ZSIMP WIN Version 2 software. For the ideal Debye-like response, an equivalent circuit consisting of a parallel combination of a resistor and capacitor is represented. It has been found that the Z" peaks are broadened in the low frequency region. The semicircular arcs obtained are depressed with their centres below the real axis. Generally, to represent the departures from the ideal Debye-like behaviour, a constant phase element (CPE) is included with the parallel RC element [16]. The CPEs describe the "power law" dependence of the impedance components on frequency. The values of all corresponding parameters and values of n are given in Table 1.

The CPE impedance is given by  $Z_{CPE} = [A_0(j\omega)^p]^{-1}$ , where  $A_0 = A/\cos(n\pi/2)$  and  $j = \sqrt{-1}$ . Here, A and p are frequency-independent parameters which are temperature dependent. The value of p lies between 0 and 1 (p = 1 for an ideal capacitor and p = 0 for an ideal resistor). Hence, an equivalent circuit (as shown on inset in Fig. 4b) has been modelled to analyse the above parameters. The values of resistance ( $R_b$ ) and capacitance ( $C_b$ ) from the bulk part, resistance ( $R_{gb}$ ) and capacitance ( $C_{gb}$ ) from the grain boundary and n were obtained from the fitting data. It can be seen from Table 1 that the grain resistance decreases with the increase in temperature. It suggests that the increase in the bulk conductivity with increase in temperature is a typical behaviour of semiconductors.

#### **IV.** Conclusions

To summarize, we have presented the structureproperty relationship of a new multiferroic composite formed from two potentially used materials. Complex impedance spectroscopy enables us to separate the grain and grain boundary contributions in the materials. The grain resistance decrease with a rise in temperature. We used an equivalent circuit to explain the electrical phenomena occurring inside the materials.

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### References

- 1. R.E. Newnham, R.W. Wolfe, J.F. Dorrian, "Structural basis of ferroelectricity in the bismuth titanate family", *Mater. Res. Bull.*, **6** (1971) 1029–1040.
- 2. S.K. Kim, M. Miyayama, H. Yanagida, "Electrical anisotropy and a plausible explanation for dielectric anomaly of  $Bi_4Ti_3O_{12}$  single crystal", *Mater. Res. Bull.*, **31** (1996)121–131.
- 3. Y. Goshima, Y. Noguchi, M. Miyayama, "Dielectric and ferroelectric anisotropy of intergrowth  $Bi_4Ti_3O_{12}$ -Pb $Bi_4Ti_4O_{15}$  single crystals", *Appl. Phys. Lett.*, **81** (2002) 2226–2228.
- L. Yan, J. Li, C. Suchicital, D. Viehland, "Multiferroic epitaxial Pb(Fe<sub>1/2</sub>Nb<sub>1/2</sub>)O<sub>3</sub> thin films: A relaxor ferroelectric/weak ferromagnet with a variable structure", *Appl. Phys. Lett.*, **89** (2006) 132913/1–3.
- R. Blinc, P. Cevc, A. Zorko, J. Holc, M. Kosec, Z. Trontelj, J. Pirna, N. Dalal, V. Ramachandran, J. Krzystek, "Electron paramagnetic resonance of magnetoelectric", *J. Appl. Phys.*, **101** (2007) 033901.
- Y. Yang, J.M. Liu, H.B. Huang, W.. Zou, P. Bao, Z.G. Liu, "Magnetoelectric coupling in ferroelectromagnet Pb(Fe<sub>1/2</sub>Nb<sub>1/2</sub>)O<sub>3</sub>", *Phys. Rev. B*, **70** (2004) 132101/1–4.
- N. Kumar, S.K. Patri, R.N.P. Choudhary, "Characterization of Bi<sub>4</sub>Pb<sub>2</sub>Ti<sub>3</sub>FeNbO<sub>18</sub> nanoplates", J. Alloys

Comp., 615 (2014) 456-460.

- S. Lanfredi, A.C.M. Rodrigues, "Impedance spectroscopy study of the electrical conductivity and dielectric constant of polycrystalline LiNbO<sub>3</sub>", *J. Appl. Phys.*, 86 (1999) 2215–2219.
- D.C. Sinclair, A.R. West, "Impedance and modulus spectroscopy of semiconducting BaTiO<sub>3</sub> showing positive temperature coefficient of resistance", *J. Appl. Phys.*, 66 (1989) 3850–3856.
- T.S. Irvine, D.C. Sinclair, A.R. West, "Electroceramics: Characterization by impedance spectroscopy", *Adv. Mater.*, 2 (1990) 132–138.
- I.M. Hodge, M.D. Ingram, A.R. West, "Impedance and modulus spectroscopy of polycrystalline solid electrolytes", *J. Electroanal. Chem.*, **74** (1976) 125– 143.
- A.R. West, D.C. Sinclair, N. Hirose, "Characterization of electrical materials, especially ferroelectrics by impedance spectroscopy", *J. Electroceram.*, 1 (1997) 65–71.
- R. Schmidt, W. Eerenstein, T. Winiecki, F.D. Morrrison, P.A. Modgley, "Impedance spectroscopy of epitaxial multiferroic thin films", *Phys. Rev. B*, **75** (2007) 245111/1–8.
- M.A.L. Nobre, S. Lanfredi, "Ferroelectric state analysis in grain boundary of Na<sub>0.85</sub>Li<sub>0.15</sub>NbO<sub>3</sub> ceramic", *J. Appl. Phys.*, **93** (2003) 5557–5562.
- D.K. Pradhan, R.N.P. Choudhary, C. Rinaldi, R.S. Katiyar, "Effect of Mn substitution on electrical and magnetic properties of Bi<sub>0.9</sub>La<sub>0.1</sub>FeO<sub>3</sub>", *J. Appl. Phys.*, **106** (2009) 024102.
- O. Raymond, R. Font, N. Suárez-Almodovar, J. Portelles, J.M. Siqueiros, "Frequency-temperature response of ferroelectromagnetic Pb(Fe<sub>1/2</sub>Nb<sub>1/2</sub>)O<sub>3</sub> ceramics obtained by different precursors. Part II. Impedance spectroscopy characterization", *J. Appl. Phys.*, **97** (2005) 084108/1–8.