Electrical and magnetic properties of $(\text{BiNa})_{1/2}(\text{FeV})_{1/2}\text{O}_3$

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Abstract. Potential multiferroic material, $(\text{BiNa})_{1/2}(\text{FeV})_{1/2}\text{O}_3$, synthesized using solid-state route is investigated. The phase formation was confirmed by X-ray diffraction and surface morphology by scanning electron microscopy (SEM). Structural data reveal the single phase formation corroborated by SEM. The grain distribution is uniform with an average grain size of $3\text{--}6\ \mu\text{m}$. Electrical properties were investigated in a frequency range (1 kHz–1 MHz) by complex impedance spectroscopy (CIS) technique. The material showed negative temperature coefficient of resistance (NTCR) reflecting semiconductor behaviour. A.C. conductivity was found to obey Johnson's law. Conductivity mechanism is discussed and activation energy estimated (1.17 eV) for the conduction process is associated with $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$ variable state. The M–H curve showed the presence of ferromagnetism in the studied material.

Keywords. Solid-state route; X-ray diffraction; complex impedance spectroscopy; a.c. conductivity.

1. Introduction

Multiferroic (magnetoelectric) materials with simultaneous ferroelectric and magnetic orders and coupling between them have recently attracted wide attention. The coupling produces various possibilities in the realization of mutual control and detection of electrical polarization and magnetism. As a potential candidate for practical applications (Khomchenko *et al* 2007; Yan *et al* 2007), single phase multiferroic material, BiFeO_3 (BFO), has been the focus of research, due to its multiferroic properties at room temperature ($T_C = 1103\ \text{K}$, $T_N = 643\ \text{K}$). The large magnetic moment and strong ferroelectric performance are required for any multiferroic material to be useful either as magnetoelectric device or ferroelectric memory chips. However, BFO has a small spontaneous polarization value due to its high electric leakage both in thin film and in bulk form. This is generally associated with the oxygen vacancies and variable valence iron ions (Fe^{+3} to Fe^{+2}) via the formation of shallow energy centres. Doping in BFO has been proved to be effective in enhancing the magnetic moment; La substitution for Bi can improve the magnetic moment in BFO polycrystalline bulks. Further, A/B-site doped BFO also exhibits interesting piezoelectric and relaxor properties useful in micro electromechanical systems, micro actuators, and transducers.

Owing to the fact that most of relaxors are lead-based systems, such as $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ (PZT) (Fernandez *et al* 1998), $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{--PbTiO}_3$ (Cross 1987) etc and considering the high toxicity of lead, there is an increasing interest in developing alternative piezoelectric materials, which are lead-free, environmental friendly, and biocompatible. As

a lead-free piezoelectric ceramics, bismuth sodium titanate $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ (BNT) (Hosono *et al* 2001) is considered to be one of the promising candidates because of its pronounced ferroelectricity. Recently, ferromagnetism behaviour has been explored in Co-doped BNT (Wang *et al* 2009) and solid solution, $\text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3\text{--LiSbO}_3\text{--BiFeO}_3$ (Jiang *et al* 2009), for applications in devices. Detailed literature survey revealed that BFO simultaneously substituted at A-site by Na and B-site by vanadium is not yet investigated for their possible multiferroic nature. Therefore, in this paper we report the electrical (impedance) and magnetic studies of $(\text{BiNa})_{1/2}(\text{FeV})_{1/2}\text{O}_3$ (BNFV).

2. Experimental

Polycrystalline samples of $(\text{BiNa})_{1/2}(\text{FeV})_{1/2}\text{O}_3$ were prepared by high-temperature solid-state reaction technique using high-purity carbonates and oxides in desired stoichiometry: Bi_2O_3 , Na_2CO_3 , Fe_2O_3 (99.9%, M/s Sarabhai M. Chemicals, India) and V_2O_5 (99%, M/s Koch Light Ltd., UK). These ingredients were thoroughly mixed in wet atmosphere (methanol) in an agate mortar for 2 h, and then dried by slow evaporation. The air-dried powder of the precursors was calcined at optimized temperatures and time (873 K for 4 h). The process of mixing and calcination was repeated until homogeneous fine powder of the ceramic was formed. The formation of the desired phase was studied by X-ray diffractometer (Rigaku Miniflex, Japan) at room temperature using CuK_α radiation ($\lambda = 0.15405\ \text{nm}$) over a wide range of Bragg angles, θ ($20^\circ \leq 2\theta \leq 70^\circ$) with a scanning speed of $3^\circ\ \text{min}^{-1}$. The calcined powders were used to make cylindrical pellets using a hydraulic press at a pressure of $5 \times 10^6\ \text{Nm}^{-2}$. Polyvinyl alcohol (PVA) was used as a binder.

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The pellets were sintered at 873 K for 4 h in an air atmosphere. The scanning electron micrograph (SEM) of the pellet sample was recorded with a high-resolution scanning electron microscope (JEOL-JSM, model: 5800 F) to study the surface morphology/microstructure of the material.

Impedance studies were carried out using a computer-controlled impedance analyser (HIOKI LCR Hi TESTER, Model: 3532) in the frequency range from 1 kHz to 1 MHz at different temperatures. The sintered pellets were polished by a fine emery paper to make both the faces flat and parallel. For electrical characterization, the flat surfaces of the pellet were electroded with high-purity air-drying conducting silver paste. The electrical conductivity of the material was evaluated from the a.c. impedance data of the symmetrical cell, Ag/BNFV/Ag. The magnetic measurements were carried out by vibrating sample magnetometer (Lake Shore, USA) with a maximum field up to 16 kOe.

3. Results and discussion

Figure 1 shows X-ray diffraction pattern of the calcined powder of BNFV recorded at room temperature. All the observed diffraction peaks were carefully indexed and the lattice parameters were evaluated in various crystal systems using a standard computer program 'POWDMULT'. The best agreement between the observed (d_{obs}) and calculated (d_{cal}) inter-planar spacing using the criteria ($\Sigma(d_{\text{obs}} - d_{\text{cal}}) = \text{minimum}$) resulted into the orthorhombic crystal system with $a = 3.2688 \text{ \AA}$, $b = 32.8196 \text{ \AA}$ and $c = 5.9779 \text{ \AA}$ having ± 0.003 standard deviation. Figure 1 (inset) shows room temperature scanning electron micrograph of the sintered pellet at 2.5 K magnification exhibiting surface morphology and microstructure. The pellet was gold coated by sputtering technique. The grains are uniformly distributed

Figure 1. Room temperature XRD pattern of calcined powder of BNFV and (inset) SEM micrograph of sintered pellet.

throughout the surface showing dense grain packing, polycrystalline nature and single-phase. The average grain size of the material obtained using linear intercept method was found to be $\sim 3.6 \mu\text{m}$.

Complex impedance spectroscopy (CIS) technique is widely used to study the electrical properties and structure–property relationship of ionic solids and electro-ceramics. The variation of imaginary and real parts of the impedance (i.e. Z' and Z'') with frequency at selected temperatures is shown in figure 2. It is observed that the values of Z' and Z'' decrease with increase in both frequency and temperature. This decrease in Z' suggests an increase in a.c. conductivity of the material with increase in temperature and frequency. Also both the Z' and Z'' values for all temperatures merges at/above 100 kHz. This behaviour may be due to (i) the release of space charges and (ii) reduction in the barrier potential of the material with rise in temperatures (Macdonald 1987).

Figure 3 shows temperature dependence of complex impedance spectrum (Nyquist plot) of BNFV (500–694 K). It is observed that at low temperatures, the intrinsic impedance response shows single semicircular arc (not shown) up to 500 K, indicating electrical properties of the material arising due to the bulk (intra-grain) effect mainly. With increasing temperature ($> 500 \text{ K}$, figure 3), the single semicircular arc appears flat reflecting the overlap of two semicircular arcs; the grain boundary starts contributing at higher temperatures. The data were fitted using an equivalent circuit comprising of a parallel combination of a resistor and capacitor (grain response) coupled in series with another R–C–Q equivalent circuit (modeling the typical grain boundary response) showing that both grains and grain boundary contribute to the impedance. The presence of constant phase element (CPE) is supported by the fact that the frequency dependence of dielectric response shows large dielectric dispersion at low frequencies that change with temperature. Thus it is a material with low frequency dielectric dispersion

Figure 2. Frequency variation of (i) real (Z') and (ii) imaginary part (Z'') of impedance (inset) at selected temperatures.

Figure 3. Complex impedance spectrum of BNFV as compared to fitted data at selected temperatures.

associated with significantly non-zero conductivity. Therefore, a constant phase element (CPE) is introduced in the equivalent circuit to incorporate leaky capacitor. The values of the electrical or transport parameters corresponding to the equivalent circuit (grain parameters) modeled by fitting process of the measured data at different temperatures are given in table 1. It has been observed that the bulk resistance (R_b) decreases with increase in temperature, which may be due to the increase in interaction between the mobile ions with the lattice around them. The point of intercept on the real axis shifts towards the origin of the complex impedance spectrum indicating decrease in the resistive property of the material. The increased value of Q with temperature also supports that grain boundaries trapped the charges released by grains at higher temperature. Thus, up to a very high temperature (<622 K) conduction is mainly through grains. The results also indicate the presence of negative temperature coefficient of resistance (NTCR) type behaviour in the material (Barik *et al* 2008).

Figure 4a shows variation of real part (M') of the complex electrical modulus with frequency for $(\text{BiNa})_{1/2}(\text{FeV})_{1/2}\text{O}_3$

Figure 4. Frequency variation of (i) real part (M') and (ii) imaginary part (M'') of complex modulus at selected temperatures.

Table 1. Equivalent circuit parameters of materials (for grain response).

Temperature ($^{\circ}\text{C}$)	$R_b (\times 10^4 \Omega)$	C_b (in Farad)	CPE (Q)
500	250.5	1.222E-10	8.333E-008
525	173.1	1.280E-10	2.179E-7
549	149.8	1.357E-10	5.454E-6
598	35.14	1.187E-10	1.403E-6
622	15.17	1.165E-10	1.297E-6
670	3.08	1.345E-10	1.05E-8
694	2.15	9.782E-11	2.247E-6

at selected temperatures. At low temperatures and low frequencies, M' value is not zero. As the temperature increases, a very low value ($\sim$ zero) of M' was approached indicating that the electrode polarization effect is significant at lower temperature – space charge accumulation at interface. A continuous increase in the value of M' on increasing frequency with a tendency to appear saturated in the high frequency region at all the temperatures is observed. Such observation may be related to the lack of restoring force governing the mobility of the charge carriers under the action of an induced electric field. This behaviour supports the long-range mobility of charge carriers. Further, a sigmoidal increase in the value of M' with frequency may be attributed to the conduction phenomena due to short-range mobility of charge carriers. Figure 4b shows variation of imaginary component of the complex electric modulus (M'') with frequency over a wide range of temperature and

frequency. The variation of (M'') with frequency at different temperatures provides useful information about charge transport processes (i.e. mechanism of electrical transport, conductivity relaxation and ion dynamics). The modulus spectra are characterized by well-resolved asymmetric peaks which shift towards high frequency side on increasing temperature. These peaks indicate the transition from short range to long range mobility on decreasing frequency. The low frequency side of the peaks provide the range of frequencies in which the ions are capable of moving long distances (i.e. performing successful hopping from one site to the neighbouring site) whereas high frequency side of peaks represent spatial confinement of mobile ions to their potential wells, where they can execute only localized motion. The peak shifts towards higher frequency side on rise in temperature indicating the presence of temperature dependent relaxation process in the material. The peak maxima ($M''_{\max}$) increases as the temperature increased. This shift to the higher frequency side may be due to polaron hopping resulting due to the decrease in capacitance value as the temperature rises (Ahmad *et al* 2007; Arbi *et al* 2007).

Figure 5 shows variation of σ_{dc} with $10^3/T$. At higher temperatures, the conductivity vs temperature response is more or less a straight line, and can be explained by a thermally activated transport of Arrhenius type:

$$\sigma_{dc} = \sigma_0 \exp(-E_a/K_B T),$$

where σ_0 , E_a and K_B represent the pre-exponential term, the activation energy of the mobile charge carriers and Boltzmann's constant, respectively. At lower temperature, a small deviation from the linear behaviour of conductivity has been noticed and can be attributed to hopping type phenomena (Mott 1990). The activation energy associated with conduction process has been estimated to be 1.17 eV in the temperature range 500–694 K. Relatively high value of activation energy reflects ionic conduction as the dominant process.

Figure 5. Variation of d.c. conductivity of BNFV with temperature.

The frequency dependence of a.c. conductivity (σ_{ac}) at various temperatures is shown in figure 6. At low temperatures the conductivity increases with increase in frequency which is a characteristic of ω^n (n = exponential) dependence. At high temperatures and low frequencies, conductivity shows a flat response while it has $a\omega^n$ dependence at high frequencies. The phenomenon of the conductivity dispersion in solids is generally analysed using Jonscher's (1977) power law:

$$\sigma_{ac} = \sigma_0 + A\omega^n,$$

where σ_0 is the d.c. conductivity, A the temperature dependent constant and ' n ' the temperature dependent (power law) exponent ($0 \leq n \leq 1$). The exponent ' n ' represents the degree of interaction between mobile ions with the lattices around them, and A determines the strength of polarizability. The material obeys the universal power law, and is confirmed by a typical fit of the above equation to the experimental data (figure 6 (inset)). The estimated value of n is 0.30 at 598 K showing strongly interacting dipolar system. The low frequency dispersion is attributed to the a.c. conductivity whereas the frequency independent plateau region of the conductivity pattern corresponds to d.c. conductivity of the material. The variation of σ_{ac} involves a power exponent, which indicates that the conduction process is a thermally activated process (Macdonald 1987).

Figure 7 shows magnetic hysteresis loop of $(\text{BiNa})_{1/2}(\text{FeV})_{1/2}\text{O}_3$ at room temperature. The value of remanent (mass) magnetization is 0.03 emu/g and coercive magnetic field is 0.72 kOe. The nature of the loop indicates the presence of an ordered ferromagnetic structure. The magnetic response of this material may be due to the presence of magnetically ordered Fe^{+3} ions in the material. Relatively small value of magnetization also reflects Fe^{3+} valence state hopping into Fe^{2+} .

Figure 6. Frequency-temperature dependence of a.c. conductivity (σ_{ac}) and its nonlinear fitting at 598 K.

Figure 7. Variation of magnetization, M , with magnetic field, H (i.e. M - H curve) of BNFV at room temperature.

4. Conclusions

Polycrystalline $(\text{BiNa})_{1/2}(\text{FeV})_{1/2}\text{O}_3$ is prepared by a solid-state reaction technique, stabilized in single-phase as confirmed by XRD. The material has densely packed grains homogeneously distributed as revealed by scanning electron micrograph. The enhancement of a.c. conductivity of the material with temperature at higher frequencies is observed from the impedance plot. The Nyquist plot shows the contribution arising mainly due to bulk (intra-grain) behaviour at lower temperatures and grain boundaries contributing only at higher temperatures. The material shows negative

temperature coefficient of resistance (NTCR) type behaviour. The d.c. conductivity follows Arrhenius law, and the activation energy is estimated to be ≈ 1.17 eV. The conduction process is thermally activated. The M - H curve confirmed the ferromagnetic property of the studied material. The conduction process is associated with variable state of iron and thus material can be optimized for possible multiferroic behaviour by stabilizing iron in Fe^{3+} state.

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