Study of multiferroic properties of $\text{Bi}_2\text{Fe}_2\text{WO}_9$ ceramic for devices application

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Received 22 March 2016; Revised 4 August 2016; Accepted 6 August 2016; Published 26 September 2016

The $\text{Bi}_2\text{Fe}_2\text{WO}_9$ ceramic was prepared using a standard solid-state reaction technique. Preliminary analysis of X-ray diffraction pattern revealed the formation of single-phase compound with orthorhombic crystal symmetry. The surface morphology of the material captured using scanning electron microscope (SEM) exhibits formation of a densely packed microstructure. Comprehensive study of dielectric properties showed two anomalies at 200°C and 450°C: first one may be related to magnetic whereas second one may be related to ferroelectric phase transition. The field dependent magnetic study of the material shows the existence of small remnant magnetization (M_r) of 0.052 emu/g at room temperature. The existence of magneto-electric (ME) coupling coefficient along with above properties confirms multi-ferroic characteristics of the compound. Selected range temperature and frequency dependent electrical parameters (impedance, modulus, conductivity) of the compound shows that electric properties are correlated to its microstructure. Detailed studies of frequency dependence of ac conductivity suggest that the material obeys Jonscher's universal power law.

Keywords: X-ray diffraction; magnetism; ferroelectric properties; magneto-electric coupling; impedance; modulus.

1. Introduction

Multiferroic materials exhibit spontaneous polarization and magnetization in deformed system, whose direction can be reversed by an application of external electric, magnetic and stress fields. In this type of materials, ferroelectric and magnetic order parameters (i.e., charge and spin) not only coexist, but are also coupled with each other in order that the magnetic order parameter can be manipulated by an electric field and vice versa.¹ Reasonably a large magneto-electric (ME) coupling coefficient of multiferroics yields some technological applications such as data storage, spintronics, information storage, sensing and actuation etc.^{2,3} Though a sizeable number of multiferroics are available today, the most widely studied multi-ferroic is BiFeO_3 (BFO). It has a high ferroelectric Curie temperature ($T_c \sim 1103$ K) and a high anti-ferromagnetic Néel temperature ($T_N \sim 643$ K). It shows a rhombohedrally distorted perovskite crystal structure with space group $R3c$ and G-type anti-ferromagnetism at room temperature.⁴ Unfortunately, the performance of BFO for the technological applications is disappointing due to some inherent problems such as (i) easy formation of secondary phase during synthesis, (ii) low resistivity, (iii) low dielectric constant, (iv) high tangent loss and (v) high leakage current.^{5,6} In order to get higher coupling coefficient, tireless attempts carried out to solve these inherent tribulations by appropriate modification in its composition or fabricating its composites with another ferroelectrics. Recently, lots of

interesting work on synthesis and characterization of BFO have been reported by various workers. For example, BiFeO_3 was prepared by (a) rapid liquid phase sintering^{7,8} method, (b) doping with rare earth elements^{9,10} and/or (c) fabricating solid-solutions or composites with other ferroelectric materials.^{11–14} In this approach, we have combined BFO with tungsten trioxide WO_3 (having ferroelectricity¹⁵ at low temperature (<230 K)) in different molar ratio in anticipation of getting enhanced properties with reduction of transition temperatures even in distorted or modified crystal structure. In this paper, we report basic structure, electric and magnetic properties of a new system $\text{Bi}_2\text{Fe}_2\text{WO}_9$ (2BFO: WO_3 ratios).

2. Experimental Details

The standard and cost-effective solid-state reaction technique is adopted to synthesize $\text{Bi}_2\text{Fe}_2\text{WO}_9$ ceramic by use of high-purity ($\sim 99.9\%$) oxides (i.e., Bi_2O_3 , Fe_2O_3 and WO_3) in required stoichiometry. The details of fabrication and characterization techniques were described elsewhere.¹⁶ The magnetic hysteresis loop ($M-H$ curve) of the material was traced at 5 K and 300 K using a superconducting quantum interference device (SQUID) magnetometer. The ME coefficient of the sample was measured at room temperature as a function of magnetic field on a magnetically poled (for 1 h) sample using a ME set-up (M/s Marine India, New Delhi).¹⁷

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3. Results and Discussion

Figure 1 depicts the XRD pattern of the calcined powder of $\text{Bi}_2\text{Fe}_2\text{WO}_9$. The presences of sharp and distinct XRD peaks which are different from that of ingredients clearly suggest the formation of single-phase new compound. The peak position (2θ), full width at half maximum (FWHM), and relative intensity of each peak were calculated using commercially available software (JANDEL PEAK FIT). As the XRD pattern of the material is different from that of ingredients and/or basic compounds, indexing of all the XRD peaks was carried out using diffraction angle (2θ) and intensity of each peak using a standard computer software or program package "POWD"¹⁸ in different crystal systems. An orthorhombic crystal symmetry was concluded based on the finest agreement between the observed and calculated inter planar spacing (d). The selected values of lattice parameters of orthorhombic unit cell (a , b and c) were refined using least-squares refinement sub-routine of POWD. The least-squares refined unit cell parameters of the material are: $a = 17.0083$ (38) Å, $b = 6.3644$ (38) Å, and $c = 9.3563$ (38) Å and volume = 1012.79 Å³ (estimated standard deviation in parenthesis). Further, the crystallite size (P) was calculated from some strong peaks using Scherrer's equation,¹⁹ $P_{hkl} = k\lambda/\beta_{1/2}\cos\theta_{hkl}$, where k is constant = 0.89, $\beta_{1/2}$ is the FWHM and $\lambda = 1.5405$ Å. The average value of crystallite size was found to be 31 nm.

Figure 1(insert) shows the surface micrograph of the sample. The nature of micrograph (size, distribution of grains) exhibits the formation of a polycrystalline sample. The nature, distribution and size of the grains suggest that the crystallization has taken place with almost no formation of

secondary phases. However, the existence of some voids of irregular dimensions indicates that the pellet has certain degree of porosity that reduces its density. The smaller grains of different sizes ($1\text{--}5\text{ }\mu\text{m}$) are homogeneously distributed throughout the surface of sample.

Figure 2 shows temperature dependence of relative dielectric constant (ϵ_r) and loss tangent ($\tan\delta$) (inset) at different frequencies of $\text{Bi}_2\text{Fe}_2\text{WO}_9$. In ferroelectric materials, the value of dielectric constant increases with increase in temperature up to a certain temperature, called transition temperature (T_C) and then decreases. The dielectric anomaly is associated with the ferroelectric–paraelectric ($F\text{--}P$) phase transition at that particular temperature (T_C). In the temperature dependent dielectric study of the compound, two anomalies are observed. A small anomaly at 250°C may be related to the magnetic transition whereas a large and prominent anomaly at 460°C may be related to ferroelectric–paraelectric phase transition. This assumption can be drawn based on the combined effect of phase transition parameters of two compounds BFO and WO_3 . Therefore, origin and mechanism of the transition in $\text{Bi}_2\text{Fe}_2\text{WO}_9$ may be considered as the same as of these two compounds. However, detailed studies using various experimental techniques are very much required. From the figure, it is also clear that ϵ_r and $\tan\delta$ is temperature and frequency dependent; both the values generally increases monotonically with increase in temperature except two anomalies as mentioned above. In the low-temperature region ($< 250^\circ\text{C}$), ϵ_r is nearly constant. Above 250°C , the values of ϵ_r increase drastically with rise in temperature indicating the occurrence of high electrical conductivity and high dielectric loss in the high-temperature

Fig. 1. Room temperature XRD pattern and SEM micrograph (inset) of $\text{Bi}_2\text{Fe}_2\text{WO}_9$.

Fig. 2. Temperature dependence of dielectric constant ϵ_r and loss tangent $\tan\delta$ (inset) at different frequencies of $\text{Bi}_2\text{Fe}_2\text{WO}_9$.

region. The rapid increase in ϵ_r may be due to thermally activated transport property, presence of space charges and/or electrical dipoles.

Figure 2 (inset) shows the variation of tangent loss with temperature at different frequencies. The value of tangent loss ($\tan \delta$) is almost constant upto 400°C, and then increases abruptly at high temperatures that may be related to some thermal processes occurring in the material signifying maximum energy loss. However, the loss is frequency dependent, and increases on increasing frequency, which certainly indicates the slow dynamics relaxation phenomena like-space charge relaxation. The sudden increase in the value of $\tan \delta$ in the high-temperature region at all frequencies could be associated with conductivity due to free-charge carriers. The increasing value of $\tan \delta$ in the sample may be due to the presence of more number of defects produced in the sample during high temperature processing and existence of oxygen vacancies.²⁰

Fig. 3. P - E loop of $\text{Bi}_2\text{Fe}_2\text{WO}_9$ at room temperature.

Figure 3 shows the electric field dependence of electric polarization (hysteresis loop) of $\text{Bi}_2\text{Fe}_2\text{WO}_9$ at room temperature. From the figure, the loop has remnant polarization of $0.85 \mu\text{C}/\text{cm}^2$ even at small applied field, and thus reduces electrical leakage current or dielectric loss. Above value of P_r clearly suggests the existence of weak polarization due to bismuth ferrite even with its modification by WO_3 . Even with the small value of remnant polarization, the existence of ferroelectric properties in the material can be confirmed. The occurrence of hysteresis loop at room temperature supports the assumption of ferroelectric properties in the material up to 460°C.

Figure 4 shows field depend magnetic moment (magnetic hysteresis loops) of $\text{Bi}_2\text{Fe}_2\text{WO}_9$ at low (5 K) and room temperatures (300 K). It is clear from the figure that saturated magnetization/moment at low temperature is significantly

Fig. 4. Magnetization hysteresis loops of $\text{Bi}_2\text{Fe}_2\text{WO}_9$ at 5 K and 300 K. The inset shows magnified parts of the loops.

higher as compared to that of room temperature. As the splitting of loop for the two temperatures at low field could not be observed, the magnified central part of it has been shown in the inset of the figure. The slim magnetic loops with non-zero remnant magnetization (M_r) for the sample are observed, reflecting the presence of a weak ferromagnetism both at 5 K and 300 K. The coercive fields are 5.42 kOe and 4.8 kOe at 5 K and 300 K respectively, and the corresponding values of M_r are 0.056 emu/g and 0.052 emu/g . The M - H pattern also shows a field induced spin alignment at low field which may be due to canted spin responsible for the ferromagnetic component of the system.²¹

The temperature dependence of magnetization behavior of $\text{Bi}_2\text{Fe}_2\text{WO}_9$ sample are carried out at zero field cooled (ZFC) and field cooled (FC) from 300 K to 5 K applying a fixed field 100 Oe and shown in Fig. 5. The ZFC magnetization was obtained during sample heating after cooling from 300 K in zero field, while the FC magnetization was measured during heating after cooling in a magnetic field. The ZFC and FC curves of the sample start to split below 300 K and magnetization decreases with the decrease in temperature upto 210 K and thereafter a steep increase is observed. The splitting between ZFC and FC curve is attributed to spin glass like behavior as reported for other compounds²²; and the steep rise in magnetization value of the sample suggests the development of incommensurate magnetic structure in the sample.²³

The value of magneto-electric (ME) coupling coefficient can be obtained using the ME voltage of open circuit as a function of the applied ac magnetic field. The ME coupling coefficient of the material was obtained based on an equation; $\alpha = (dV/dH_{ac})/t$, where H_{ac} is the applied ac magnetic field, α is the ME coupling coefficient and t is the thickness of the sample.¹⁷ Figure 6 shows the variation of the induced voltage as a function of ac magnetic field (H_{ac}) (500 Gauss dc

Fig. 5. Variation of magnetization (ZFC and FC) with temperature of $\text{Bi}_2\text{Fe}_2\text{WO}_9$.

Fig. 6. Induced voltage as a function of ac magnetic field at 500 Gauss dc magnetic field of $\text{Bi}_2\text{Fe}_2\text{WO}_9$.

bias magnetic field) of $\text{Bi}_2\text{Fe}_2\text{WO}_9$. The studied material has notable ME coefficient for a particular field (500 Gauss) and the ME coefficient of the sample was found to be $5.77 \text{ mVcm}^{-1}\text{Oe}^{-1}$.

Complex impedance spectroscopy (CIS) is now a well-established standard experimental technique to study the electrical properties of ionic and ceramic materials as a function of frequency and temperature.¹⁶ The impedance measurement gives both real (resistive) and imaginary (reactant) components. Some formulism of CIS technique

used here is given below:

$$\begin{aligned}\text{Complex modulus } M^* &= M' + jM'' = j\omega C_0 Z^*, \\ \text{Complex impedance } Z^* &= Z' - jZ'' = 1/j\omega C_0 \varepsilon^*, \\ \text{Complex permittivity } \varepsilon^* &= \varepsilon' - j\varepsilon'',\end{aligned}$$

where $j = \sqrt{-1}$ = the imaginary factor. C_0 is the geometrical capacitance and $\omega = 2\pi f$ = angular frequency. (Z', M', ε') and $(Z'', M'', \varepsilon'')$ are the real and imaginary parts of the complex impedance electrical modulus and complex permittivity, respectively.

Figure 7 shows the frequency dependence of Z' and Z'' at different temperatures of $\text{Bi}_2\text{Fe}_2\text{WO}_9$. The value of Z' decreases on incremental temperature in lower frequency region which shows a tendency of merging with each other in the higher frequency region irrespective of temperature. This tendency of merging specifies the release of the space charge as a result of lowering in the barrier properties of the material.²⁴ In very low-frequency region, Z' value remains independent of frequency, because the electric field treats like a dc field so there is no frequency dependent characteristics of the compound.²⁴ The Z' value attains a constant value and this trend appears to be shifting gradually towards high-frequency side with increasing temperature. The decrease in value of Z' with rise in frequency as well as temperature, indicate the increase in ac conductivity of the ceramic.²⁵ At high-frequency, the space charge has lesser time to relax and the recombination would be faster. Hence, the space charge polarization is reduced at higher frequency leading to a merge of curves at higher frequency.²⁶ The decrease in magnitude of Z' in the low-frequency region with rise in temperature shows

Fig. 7. Variation of Z' and Z'' with frequency at selected temperatures of $\text{Bi}_2\text{Fe}_2\text{WO}_9$.

negative temperature coefficient of resistance (NTCR) behavior. Similarly Z'' value decreases with increasing temperature and at higher frequency, the curves coincide with each other giving rise to a constant value. These curves exhibit a characteristic peak at a particular frequency, resulting from the contribution of dipolar polarization and the appearance of peak indicates the presence of relaxation process of the material.²⁷

The impedance analysis of the compound is characterized by the formation of semicircular arcs whose pattern of evolution changes with change in temperature.²⁸ The extent of intercept of semicircles on the real axis (Z' -axis) provides the information on the kind of electrical processes occurring within the material. An equivalent electrical circuit can correlate the semicircles and microstructure of the material. Each semicircle is considered as a parallel combination of resistance and capacitance.²⁸ This semicircular behavior can be explained by the mathematical equation: $(Z'' - R/2)^2 + Z'^2 = R^2/4$.²⁵

Figure 8 shows complex impedance plots for some selected temperatures (200°C–525°C) of $\text{Bi}_2\text{Fe}_2\text{WO}_9$. The intercept of the depressed semicircular arcs along Z' -axis

provides the values of respective grain and grain boundary resistance of the sample. Up to 375°C (Figs. 8(a) and 8(b)) a single semicircle is observed, which confirms only bulk or grain contribution to the impedance data. Above the said temperature, two clear semicircular arcs are observed in the high- and low-frequency regions (shown in Figs. 8(c) and 8(d)). The presence of two semicircular arcs indicates the existence of two different relaxation processes and distribution of relaxation time instead of a single relaxation time. In ideal Debye-type relaxation, a semicircle with its center at Z' -axis should be observed,²⁹ but depressed semi-circles of non-Debye type of relaxation are observed. The nature of plots suggest that the overall electrical processes in the compound arise mainly due to the contribution from grain and grain boundary,²⁹ and thus can be modeled as an equivalent electrical circuit. This figure compares the impedance data with fitted data using commercially available software ZSIMP WIN version 2.³⁰ This type of electrical process are modeled using an equivalent circuit according to the “Brick layer model”,¹⁷ comprising of two parallel $R-C$ circuits of both grain and grain boundary effects connected in series. For ideal Debye-type response, it is considered that

Fig. 8. Nyquist plot at selected temperatures of $\text{Bi}_2\text{Fe}_2\text{WO}_9$ with the corresponding equivalent circuit (inset).

Fig. 9. Variation of M' and M'' with frequency at selected temperatures of $\text{Bi}_2\text{Fe}_2\text{WO}_9$.

an equivalent circuit consists of parallel combination of (CQR), where Q is known as constant phase element (CPE) which represents departure from the ideal Debye-type response.³¹ It is also observed that the value of R_g and R_{gb} decreases with increasing temperature; which in turn, suggests the NTCR behavior of the compound.

Figure 9 shows frequency response of M' and M'' at selected temperatures of $\text{Bi}_2\text{Fe}_2\text{WO}_9$. The M' value approaches to zero on lowering frequency with a monotonic dispersion, whereas with rise in frequency the M' values coincide with each other. This may be due to presence of conduction phenomenon and short-range mobility of charge carriers.³² From the figure, the value of M'' first increases, attains a maxima value (M''_{max}) and then decreases. The M''_{max} peak shifts to higher-frequency side with the rise in temperature. This nature of dielectric relaxation suggests that the hopping mechanism of charge carriers dominates intrinsically at higher temperatures in thermally activated process.²⁸ The asymmetric broadening of the peaks indicate the spread of relaxation with different time constants, suggesting occurrence of non-Debye type relaxation in the material.²⁸

Figure 10 depicts the variation of ac conductivity (σ_{ac}) with frequency at some selected temperatures of $\text{Bi}_2\text{Fe}_2\text{WO}_9$. The value of σ_{ac} increases with increasing frequency but it is nearly independent at low frequency showing dispersion phenomena obeying the Jonscher's power law equation³³; $\sigma_{\text{ac}} = \sigma_{\text{dc}} + A\omega^n$ where σ_{dc} is the dc conductivity at a particular temperature, A is temperature dependent constant, and n is temperature dependent exponent in the range of $0 < n < 1$. The n represents the degree of interaction between mobile ions with the lattices around them, and A determines the strength of polarizability. The increasing trend

Fig. 10. Variation of ac conductivity with frequency at selected temperatures of $\text{Bi}_2\text{Fe}_2\text{WO}_9$.

of σ_{ac} with rise in frequency and temperature may be attributed to the disordering of cations between neighboring sites, and presence of space charge.

Figure 11 shows the variation of current density with electric field of $\text{Bi}_2\text{Fe}_2\text{WO}_9$. The value of current density (J) increases on increasing electric field (E) for some selected temperatures. It can also be observed that leakage current increases abruptly with increasing electric field. The increase in the slope of the curves on increasing temperature suggests an increase in dc conductivity of the materials with temperature and thus confirms the NTCR-type behavior. The

Fig. 11. Variation of current density (J) with electric field (E) at selected temperatures of $\text{Bi}_2\text{Fe}_2\text{WO}_9$.

curves also reveal that the material allows a very small leakage current to pass through them. The nonlinear nature of these plots at different temperatures indicates non-ohmic nature of the system.

4. Conclusion

The polycrystalline $\text{Bi}_2\text{Fe}_2\text{WO}_9$ was prepared by a solid-state reaction technique. X-ray analysis exhibits the orthorhombic crystal structure of the compound at room temperature. The detailed dielectric and electrical studies indicate that the material has — (a) NTCR-type behavior, (b) electrical transport (conduction) due to bulk and grain boundary contribution and (c) temperature-dependent relaxation phenomena. Modulus analysis indicates nonexponential type of conductivity relaxation in the material. The frequency dependence of ac conductivity obeys Jonscher's power law. The occurrence of ferroelectric and magnetic anomalies and ME co-efficient confirm multiferroicity of $\text{Bi}_2\text{Fe}_2\text{WO}_9$ and can be promising candidate for magnetic sensor and magnetoelectric computer memory applications.

Acknowledgments

The author is thankful to Mr. B.B. Palei of IMMT, Bhubaneswar for his kind help in carrying out X-ray diffraction analysis.

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