Structural, Dielectric and Electrical Properties of BiFeW₂O₉ Ceramics

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Abstract

The polycrystalline sample of BiFeW₂O₉ was synthesized using a high-temperature (770°C) solid-state reaction method. The formation of a single-phase compound was confirmed by preliminary X-ray structural studies of the material. The SEM micrograph of the compound showed uniform growth of grains with some small number and size of voids suggesting the formation of high-densification homogeneous sample. Detailed studies of dielectric and electrical impedance (impedance, electric modulus and conductivity) properties of the system in a range of frequency (1 kHz -1 MHz) and temperature showed that these properties are strongly dependent on temperature and frequency. The nature of frequency dependence of ac conductivity follows the Jonscher’s power law. The temperature dependence of dc conductivity pattern follows the Arrhenius behavior. The J-E characteristic shows the non ohmic conductivity of the sample.

Keywords: X-ray diffraction, SEM micrographs, Dielectric properties, Electrical impedance

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1. Introduction

In recent years, multiferroics comprising of ferroelectric and ferromagnetic ordering in elastically distorted systems have drawn a considerable attention of researchers due to their potential properties for fabrication of magnetic and ferroelectric devices. In view of some unique properties of materials much more interest have been generated to design and develop single-phase materials with high dielectric constant, low dielectric loss, small structural distortion and high temperature phase transition for multifunctional applications. These parameters occur mainly due to the electric, magnetic and stress field applied on the materials. In the process of development of new materials, many novel materials with interesting and useful properties have been discovered for different purposes. Nowadays, a sizable number of multiferroic materials are available with variety of physical properties. Out of these, some important multiferroic materials, such as BiMnO₃, BiCoO₃, TbMnO₃, BiFeO₃ (BFO) etc, have been discovered with variety of interesting and unique characteristics. Among all these multiferroic materials studied so far, bismuth ferrite (BiFeO₃) has special place in the multiferroic series because of its high transition temperature (i.e., Curie temperature ~ 1083K and Neel temperature ~ 657K) [1-3] with reasonably high order parameters and coupling coefficient. To enhance these parameters by solving inherent problems such as, high leakage current, structural distortion, formation of multiphase system etc., lots of efforts have been made that includes substitution of suitable elements at different sites [4,5], particle size reduction [6,7], formation of solid-solution or composites [8,9], as required for different applications. Tungsten trioxide (WO₃) is a very good ferroelectric material with lots of structural modifications depending on experimental conditions [10]. In anticipation of getting very good physical properties, we have tailored the above properties of BiFeO₃ with addition of WO₃ in different ratios; BiFeO₃: xWO₃ (x= 1, 2, 3, 4...). In this paper, we report the structural, dielectric and electrical properties of a new system BiFeW₂O₉ of which not much is known.

2. Experimental

The polycrystalline sample of BiFeW₂O₉ (BFWO) was prepared by a high-temperature solid-state reaction method using stoichiometric proportions of high-purity (AR grade) precursors: Bi₂O₃, Fe₂O₃ and WO₃ (all from M/S Loba Chemie, Pvt. Ltd, India). These oxides were thoroughly mixed in dry (air) medium for 1 h, and then in wet medium (methanol) for another 2 h using agate mortar. The calcination of the above mixture was carried out at an optimized temperature (770°C) and time (4 h)
based on repeated firing. The calcined powder was mixed with binder (polyvinyl alcohol (PVA)) and compacted by a hydraulic press to form pellets of 10 mm diameter and 1–2 mm thickness at a pressure of $5 \times 10^6$ N/m$^2$. The sintering of the pellets was carried out at 800°C for 4 h.

In order to confirm the formation of compound through preliminary structural analysis, X-ray diffraction (XRD) pattern of calcined powder was recorded using an X-ray powder diffractometer (Rigaku Mini flex, Japan) with CuK$_\alpha$ radiation ($\lambda=1.5405$ Å) in a wide range of Bragg’s angle ($\theta$) ($20^0 \leq \theta \leq 80^0$) at a scanning rate of 3 deg./min. The surface morphology and grain size of the sample were recorded using scanning electron microscope (SEM) (JEOL-JSM, model-5800) at room temperature on a gold-coated pellets. One of the sintered pellets was first polished, then coated with silver paste on both surfaces and dried at 150°C for 8 h before electrical measurements. The capacitance (in parallel mode) ($C_p$), dissipation factor (D), impedance (Z) and phase angle (Φ) of a pellet was obtained as a function of frequency (1kHz-1MHz) at different temperatures using a computer controlled-LCR/phase sensitive meter (PSM - 1735, N4L, UK) along with a laboratory-designed and fabricated-sample holder and furnace. The dc conductivity was measured (in a range of applied voltage) at an interval of 25°C starting from room temperature (25°C) up to 500°C using a computer controlled electrometer (KEITHLEY, 6517 B).

3. Results and discussion

3.1. Structural analysis

The room temperature XRD pattern of BFWO (Fig. 1) consisting of sharp and single diffraction peaks is different from those of ingredients suggesting the formation of single-phase compound [11]. To index all the observed peaks (in different crystal systems with different unit cell configuration), a standard computer program package “POWD” [12] was used. An orthorhombic crystal system with a particular unit cell was found to be a suitable system because of the good agreement between observed (obs.) and calculated (cal) inter-planar spacing (d). The lattice parameters of unit cell (a, b and c) so obtained were refined using least-squares refinement sub-routine of POWD. The least-squares refined unit cell parameters are: $a=9.0441$ (24) Å, $b=8.4922$ (24) Å and $c=23.2897$ (24) Å (estimated standard deviation in parenthesis). Using refined lattice parameters, each peak was indexed and inter-planar spacing (d) of reflection planes of the compound was calculated.

Fig. 1 (inset) shows the surface micrograph of the pellet sample of BFWO. The uniform distribution of nearly same dimension of grains with small number and dimension of voids clearly suggests the formation of high-density sample. Most of
the particles are spherical. The nature of micrograph shows the polycrystalline nature of the sample.

3.2. Dielectric study

Fig. 2 shows the frequency dependence plot of dielectric constant ($\varepsilon_r$) and loss tangent (tan $\delta$) in the frequency range of 1 kHz-1 MHz. It is observed that the value of $\varepsilon_r$ decreases with increase in frequency. The dielectric constant is associated with different types of polarization of the material under the influence of electric field. We can find out the contribution of polarization in a particular frequency range [13] from the nature of variation of dielectric constant with frequency. The value of dielectric constant increases with increase in space charge polarization due to a large concentration of defects at higher temperatures [14]. The dipolar polarization, which is present in the lower frequency region, is very important for applications in capacitive and insulating properties of ceramics [15]. The electronic and ionic polarizations always exist at higher frequencies. The value of dielectric constant depends on other factors such as voids, grain boundaries, purity and other defects too, which are present in the sample, and due to those factors the sample have lower values of dielectric constant [16].

Dielectric or tangent loss is nothing but the wastage of energy. Fig. 2 shows the variation of tangent loss (tan $\delta$) with frequency and temperature. It decreases first with rise in frequency. After a certain limit of frequency, it remains almost constant. The frequency dependence of tangent loss is mainly attributed to the conductive process. The conduction process may be associated with the space charges and probably arises from trapped charges in the ceramic/electrode interfaces [17]. The sudden increase of tan$\delta$ in the high-temperature region could be associated with free charge carrier conductivity. Since the concentration of free charge carriers depends on temperature, the rate of loss is also high in the higher temperature region. As the loss factor is inversely proportional to frequency, it is related to disappearance of space charges at higher frequencies.

3.3. Impedance and Modulus Spectroscopy Study

The complex impedance (CI) technique is used to analyze the electrical response or transport properties of the materials in a wide range of frequencies. It enables us to evaluate and separate the contributions of electrical properties in the electrical parameters in the wide frequency range due the grains, grain boundaries and electrode/sample interface in a polycrystalline materials. The complex impedance interrelated parameters are expressed as, relative permittivity $\varepsilon^* = 1/M^* = \varepsilon' - j\varepsilon''$, complex modulus $M^* = 1/\varepsilon^* = M' + jM'' = j\omega C_0 Z$, complex impedance $Z^* = Z' - jZ'' = R_s - j/\omega C_s$. 
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complex admittance $Y^* = Y' + jY'' = 1/R_p + j\omega C_p,$
and $\tan\delta = \epsilon''/\epsilon' = M''/M' = -Z''/Z' = Y''/Y' .
Where $R_p = R_s (1 + 1/\tan^2\delta), C_p = C_s/(1 + \tan^2\delta)$ and
$j = \sqrt{-1}$ is the imaginary factor. $C_0$ is the geometrical capacitance and $\omega = 2\pi f$ = angular frequency. ($Z'$, $M'$, $\epsilon'$, $Y'$) and ($Z''$, $M''$, $\epsilon''$, $Y''$) are the real and imaginary components of the complex impedance, electrical modulus, permittivity and admittance respectively.

Fig. 3 shows the variation of $Z'$ and $Z''$ with frequency at different temperatures. Here, the value of $Z'$ decreases with the rise in both frequency and temperature. Therefore, the conducting property of the material increases with rise of temperature and frequency. At high frequency $Z'$ values coincide with each other at all temperatures suggesting the release of space charge [18]. The value of $Z''$ first increases with frequency and attains a maximum value $(Z''_{\text{max}})$ at a particular frequency known as relaxation frequency $(f_r)$. The value of $Z''$ then decreases with rise of temperature which implies the presence of relaxation in the material [19]. The relaxation process occurs due to the presence of immobile charges at lower temperatures, and due to defects and vacancies at higher temperatures [20]. It is observed that the peaks $(Z''_{\text{max}})$ shift towards higher frequencies side on increasing temperature. The change in the peak position and broadening on change in temperature suggests the presence of temperature dependent relaxation processes in the compound [21]. The relaxation effect and asymmetric broadening of the peak exhibit presence of non-Debye type of relaxation [22]. The solid line corresponds to a theoretical fitting of the experimental data (non-linear curve fitting), and is evaluated by $Z'' = \frac{R_0}{\omega^m} + \frac{\omega^n}{(\omega^2)}$ where $\omega_1 = 2\pi f_1$ and $\omega_2 = 2\pi f_2$ are the first and second characteristic angular frequencies $\omega$, $R_0$ is the bulk resistance, $m$ and $n$ are the temperature-independent and temperature-dependent parameters respectively. A good agreement between experimental and calculated values of both real and imaginary parts of impedance is found from the above fitting. At higher frequency, the value of $Z''$ coincides with each other for different temperatures implying release of space charge [23].

Fig. 4 shows the temperature dependence of complex impedance spectra (Nyquist plot) of BFWO. The complex impedance plots consist of semi-circular arcs that are gradually resolved on increasing temperature. A clear semicircle with tendency to form a second semicircle is observed at high temperatures. As the arcs seem to be asymmetric, depressed semicircles are observed with their centers just below the real axis (not shown) rather than on the real axis. This confirms the existence of non-Debye type of relaxation in the sample [24]. The nature of plot suggests that the electrical response consist of two semicircles; first one due to bulk (grain) property of material and second one due to the presence of grain boundary [25]. The impedance
data (with symbols) have been fitted (solid line) with the model by the commercially available software ZSIMPWIN Version2 (Fig. 4) [26]. A good agreement between the experimental data and fitting curves has been observed. On increasing temperature the intercept of the semicircles (at the Z’ axis) shifts towards lower side of Z’, indicating the reduction of the bulk resistance (R_g). With rise in temperature, the fitted value of R_g decreases and bulk capacitance (C_g) increases. This nature indicates the presence of negative-temperature coefficient of resistance (NTCR) as normally observed in semiconductors [27, 28].

Fig. 5 shows the variation of imaginary electrical modulus and imaginary impedance with frequency of BFWO at different temperatures. This plot gives the correlation between imaginary components of impedance and modulus, and also detects presence of the smallest capacitance and the largest resistance [29]. This plot also helps to distinguish whether relaxation process is due to short range or long range motion of charge carriers.

3.4. Electrical conductivity

3.4.1. ac conductivity

Study of ac electrical conductivity is normally carried out to get better understanding of the frequency dependence of electrical transport properties of the material. Using dielectric data the ac electrical conductivity (σ_ac) of the material was calculated with an empirical formula: σ_ac = ωε_rε_0 tanδ (ω= angular frequency, ε_0= vacuum permittivity). Jonscher’s power law [19] can explain the frequency dependence of ac conductivity. The relation is given by the equation σ_ac(ω) = σ_dc + Aω^n, where σ_dc=frequency independent conductivity (frequency independent plateau in the low frequency region), A is the temperature dependent pre-exponential factor and n is the frequency exponent. The exponent n can have a value between zero to one. This parameter is frequency independent but temperature and material dependent.

The experimental σ_ac values fit well Jonscher’s power law as shown in Fig. 6. The conductivity curves show dispersion in the low frequency region. The value of σ_ac increases with rise in frequency but it is nearly independent in the low frequency region. This type of trend in conductivity is very similar to that of previous reports in the literature for ionic conducting ceramics [30, 31]. The increasing trend of σ_ac with rise in frequency may be attributed to the disordering of cations between neighboring sites, and presence of space charge [21]. The dispersion is narrowed at high frequencies.

3.4.2. dc conductivity

Fig. 7 shows the variation of σ_dc as a function of inverse of the absolute temperature. The dc conductivity increases with rise in temperature, which exhibits the negative temperature coefficient of resistance (NCTR) behavior of the material. This behaviour can be explained by thermally activated transport processes, governed by
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an empirical Arrhenius relation $\sigma = \sigma_0 \exp (-E_a/kT)$, where $k$= Boltzmann constant, $\sigma_0$ = pre-exponential factor and $E_a$= activation energy. The activation energy ($E_a$) value in the temperature range of 100-325$^0$C is calculated from the slope and found to be 0.33eV. The $E_a$ value is much less compared to the reported compound [32]. The small value of activation energy may be due to the single ionized oxygen vacancies and from vacancies, charge carriers are generated. So, the collective motion of the mutual jumps of oxygen ions and vacancies leading to the ionic-polaronic conductivity mechanism, which plays an important role in conduction process [33, 34]. For this electrical conductivity is considered as a thermally activated process.

4. Conclusion

The polycrystalline sample of BFWO was prepared by a high-temperature solid-state reaction technique. The formation of the material in the orthorhombic phase was determined by preliminary X-ray diffraction analysis. The dielectric constant and tangent loss are found to be decreased on increasing frequency. The impedance study shows the existence of a negative temperature coefficient of resistance (NTCR) behaviour in the material. The variation of ac conductivity with frequency obeys Jonscher power law. The experimental results on electrical properties indicate that in the material, conductivity is possible due to the mobility of the oxide ions.

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Fig. 1 The indexed XRD pattern and SEM micrograph (inset) of BiFeW$_2$O$_9$. 
Fig. 2 Variation of relative dielectric constant & loss tangent as a function of frequency at different temperatures of BiFeWO$_9$.

Fig. 3 Variation of real and imaginary part of impedance with frequency at different temperatures of BiFeWO$_9$. 
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Fig. 4 Complex impedance plot at different temperatures of BiFeW₂O₉.

Fig. 5 Variation of imaginary electrical modulus and imaginary impedance with frequency at different temperatures of BiFeW₂O₉.
Fig. 6 Variation of ac conductivity (σ_{ac}) with frequency at selected temperatures of BiFeW_{2}O_{9}.

Fig. 7 Variation of dc conductivity (σ_{dc}) of BFWO as a function of inverse the absolute temperature of BiFeW_{2}O_{9}.

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