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Structural – Electrical property correlation in defect induced nanostructured off-stoichiometric bismuth ferrite: A defect analysis

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HIGHLIGHTS

- Dielectric analysis has been carried out to analyse the defect mechanism.
- RBS and EdX study confirm the elemental constituents.
- Correlation between observed J-V-f behaviour and defects has been established.
- HRTEM, SAED pattern and impedance analysis supports the defect analysis.

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ABSTRACT

In order to increase magnetization, an attempt has been made to synthesize nanostructured bismuth ferrite using high energy planetary ball milling (HEPBM). In this process local heating in HEPBM and Bi-volatility has eventually led to the formation of $BiFe_5O_{12}$ (off stoichiometric bismuth iron garnet (BIG)). Electrical characterization has been done in order to identify the nature of defects and diffusion mechanism which has been supported by high resolution transmission electron microscopy and selected area electron diffraction images. The simultaneous analysis of current density-applied voltage (J–V) and current density-frequency (J–ν) curves gives insight mechanism for defect formation and how surface charge density depends on relaxation time and frequency of field applied.

1. Introduction

Polycrystalline ceramics particularly oxides contain large number of defects, their structure and chemistry are governed by kinetics of defect movements. These defects can be charged or neutral and can be classified into various categories such as vacancies, interstitials and defect clusters etc. In ceramics, defect associates are very important because of columbian interactions which may be strong as well as long range. In addition to this, non stoichiometry increases the concentration of defects. Various properties of oxides are dependent on the concentration of defects present in the sample. Bismuth ferrite is one of such materials in which stoichiometric problem exists due to Bi volatilization and it makes an impact on electrical and magnetic properties.

In order to increase magnetization, an attempt has been made to synthesize nanostructured bismuth ferrite using high energy planetary ball milling (HEPBM). In this process local heating in HEPBM and Bi-volatility has eventually led to the formation of $Bi_{3-\delta}Fe_5O_{12}$ (off stoichiometric bismuth iron garnet (BIG)). Garnets have been mostly studied for their magnetic and magneto-optical properties [1]. There have been far fewer studies on the dielectric/electrical properties of bismuth iron garnet or other garnets [2]. In a few recent reports, giant increase in dielectric permittivity with temperature has been reported showing the potential for new applications [3]. Effect of milling and milling duration on sintered sample and thermodynamics of phase transition are reported elsewhere [4,5].

In this work, effect of sintering on the microstructure and structural imperfections for 40 h milled (N40) sample has been studied in detail. The electrical conductivity depends on the type,

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concentration and the mobility of defects. The parameters for the type and concentration of defects have been calculated using the relation between current density, applied voltage and frequency. How does interplay between time period of ac electric field applied and relaxation time, generate the surface charge has been analytically discussed. Further these defects have been visualized using HRTEM and SAED images.

2. Experimental

Highly pure powders of Bi_2O_3 and Fe_2O_3 (Sigma Aldrich) were mixed in stoichiometric (with 5 mol.% extra Bi_2O_3) proportions to form $BiFeO_3$ by two synthesizing routes. First by conventional solid state route (SSR) and second route, mechanochemical treatment was performed in a planetary ball mill (RetschPM100) with milling speed 400 rpm. Milling was carried out in toluene medium with high wear resistant 10 mm steel balls in a steel vial for effective 40 h. The milling vessels were stopped for 30 min after each hour of milling for removing the water vapor overpressure. The dielectric measurements were carried out using a precision LCR meter (Agilent 4284A) and impedance analysis has been done with NOVOCONTROL Alpha- AT impedance analyzer, having a frequency range from 20 Hz to 1 MHz, operating at oscillation amplitude of 0.2 V. The J–V measurements are done as a function of frequency at room temperature for different bias voltage (0.001–10 V). High resolution transmission electron microscopy images were analyzed using ImageJ software.

3. Results and discussions

3.1. Structural and microstructural studies using XRD

Fig. 1(a) compares the XRD pattern of milled and sintered N40 sample. There is a shift in the maximum intensity peak (400) indicating the reduction in lattice parameters on sintering. This is attributed to the homogeneous strain developed in the sample during sintering. Fig. 1(b) shows the indexing of the XRD data on matching with JCPDS file No. 01-086-0367 and other phases are also marked.

As the constituent powders were added stoichiometrically the resulting compound should be stoichiometric. In order to verify the stoichiometry, RBS study has been done. It is revealing that Bi, Fe and O are elemental constituents and the intensity of respective elements shows the difference in stoichiometry (see Fig. 2(a)). It has again been confirmed through EDAX analysis (Fig. 2(b)).

As shown in Fig. 1(a), sintering has produced thermal stress in the milled sample. To analyse the broadening of peaks and reduction of lattice parameters, microstrain has been calculated and plotted as a function of angle for the milled and sintered sample. It is well known that the structural imperfections are mainly caused by the displacement of atoms from their lattice positions and contribute to the microstructural effect in addition to crystal size. Microstrain, $\in = \Delta d/d_0$ (where, Δd is displacement in lattice spacing from its ideal crystal value d_0) measures the relative mean variation of displacement. The strain broadening of diffraction reflection at scattering angle $\theta(\beta_d(\theta))$, is proportional to deformation in the crystal ($tan\theta$) and dislocation (δ); and mathematically equal to $-2\,\delta\,tan\theta$ [6].

The microstrain and strain broadening have been plotted as a function of scattering angle θ for the milled and sintered N40 sample(not shown here). The microstrain displaces the atom on either side of lattice but unique feature is that $\in_{sintered} - \in_{milled}$ is nearly constant (see Fig. 3) as both polynomial and linear fitting shows negative slope. It implies microstrain for milled sample is higher than the sintered sample at the same position and $\in_{sintered} - \in_{milled}$ will become more negative. Thus, sintering has

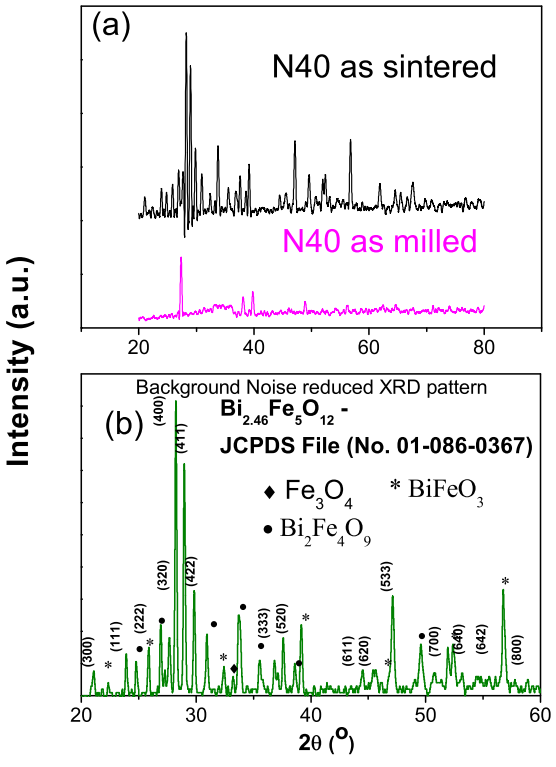

Fig. 1. (a) XRD pattern of milled and sintered N40 sample and (b) background noise reduced indexed XRD for sintered N40 sample.

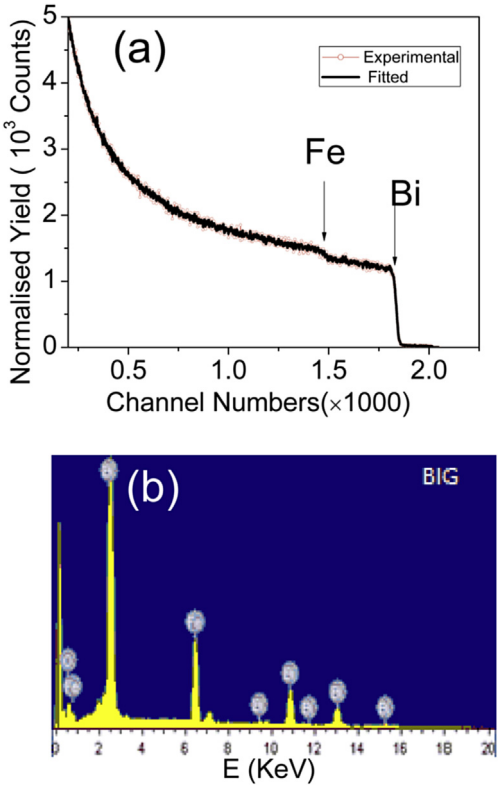

Fig. 2. (a) RBS yield and (b) EDX for N40 sample.