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Sol–gel synthesized $BiFeO_3$ nanoparticles: Enhanced magnetoelelctric coupling with reduced particle size

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ABSTRACT

The present study reports the effect of particle size on magnetic, electrical and magnetoelectric properties of $BiFeO_3$ nanoparticles prepared by the sol–gel method. Structural analysis revealed rhombohedral phase of $BiFeO_3$ nanoparticles. Varying calcination temperature successfully tailored their size in the range 27–153 nm. The magnetic measurement confirmed enhanced ferromagnetism with reduced particle size, thereby revealing increase in suppression of spin spiral structure. Increasing density of uncompensated spins with reduced particle size enhances exchange bias. Electrical analyses-dielectric and ferroelectric-reveal decreasing losses with particle size, which results in enhanced dielectric constant and polarization values. Magnetic field dependent polarization substantiates the presence of magnetoelectric coupling. More the particle size reduction more the spin spiral suppression, and magnetic moments being oriented perpendicular to the ferroelectric axis [111], there results maximum polarization and subsequently, maximum magnetoelectric coupling.

1. Introduction

Ferroelectricity and magnetism-the base of existing technology-are two unrelated phenomena which co-exist in a unique class of materials known as multiferroics [1–5]. Inspite of the flurry of research in multiferroics, no profound results representing device realization has been observed. The unique phenomenon of multifunctional materials: 'magnetoelectric effect (ME)', which allows magnetic control of electric field and vise versa, is an inherent property of $BiFeO_3$[2]. It is of immense interest from two point of views [2]: (i) understanding physical fundamentals involved in coupling of various order parameters, and (ii) realization of devices having extra degree of freedom such as electrical control of magnetization, exchange bias, magnetocrystalline anisotropy etc. $BiFeO_3$, a rare multiferroic material, possesses magnetism originating from unpaired d-shell electrons of Fe^{3+} (B-site) while polarization exists due to displacement of $6s^2$ lone pair of Bi^{3+} with respect to FeO_6 octahedral [3]. The ferroelectric (T_C ~1103 K) and magnetic (T_N~647 K) orders co-existing in single phase, well above room temperature, make it unique [4]. However, it suffers many constraints, viz. high leakage current density, weak magnetism, and low magnetoelectric coupling values [4,5]. Reduction of size to nano scale has proven to be quite efficient in enhancement of its multiferroism [4–11]. Park et al. reported strong dependence of magnetism of single crystalline $BiFeO_3$ nanoparticles [4]. Increasing magnetism with decreasing particle size is correlated to increasing suppression of its spin cycloid and uncompensated spins on particle size. Mazumder et al. studied particle size dependence of magnetization and phase transition at Néel temperature [6]. High saturation magnetization (0.4 μ_B/Fe) along with calorimetric and dielectric anomalies at magnetic transition points, which indicate strong coupling of electric and magnetic order parameters in nanoscale $BiFeO_3$ nanoparticles (4–40 nm) [7] were reported. The influence of particle size on lattice parameters and polar displacement of atoms was reported by Selbach et al. [5]. It has been shown by rietveld refinement that rhombohedral distortion, reduced with decreasing particle size, is accompanied with decaying polarization. Significantly high photocatalytic activity in nanoscale $BiFeO_3$, as compared to bulk, is owed to high surface to volume ratio of nanoparticles [8]. These studies unveils crucial role of particle size. Despite these studies, influence of size on the heart of the multiferroic $BiFeO_3$ i.e. ME coupling has not yet been much explored [9] and also, a few studies report on tunability of electrical properties [9,10].

The present paper reports size dependent investigations of magnetic, dielectric, ferroelectric, and magnetoelectric coupling properties of $BiFeO_3$ nanoparticles synthesized by the sol–gel

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method.

2. Experiment

$BiFeO_3$ nanoparticles were prepared by the sol–gel method, described elsewhere [11]. The so-obtained powder were calcined at different temperatures viz. 450 °C (Bi4), 550 °C (Bi5), and 650 °C (Bi6) for 4 h.

Structure, morphology, and size were determined by X-ray diffractometer (XRD: PANalytical X'Pert PRO MRD ML), scanning electron microscope (FEG SEM: JSM-7600F), and transmission electron microscopy (TEM: Philips-CM200), respectively. Magnetic (M-H) measurements were done using vibrating sample magnetometer (VSM: Princeton Applied Research Model 151/155). The electrical i.e. dielectric (HIOKI 3522-50 LCR Hi-Tester) and polarization (P-E: Marine India) measurements were performed on Ag-Pellet-Ag capacitor arrangement. The powder was pelletized by uniaxial press at a pressure of 10 t/cm^2.

3. Results and discussion

3.1. Structural and phase analyses

Fig. 1(a) shows XRD patterns of the synthesized nanoparticles, where all diffraction peaks characterize rhombohedral structure (JCPDS Card No. 86-1518). Peaks denoted by (⁎) are attributed to $Bi_{24}Fe_2O_{39}$ (JCPDS file no. 42-0201). Typical broadened peaks in XRD patterns illustrate formation of nanocrystallites. The average crystallite size (d) of the synthesized nanoparticles has been calculated using the Debye-Scherrer equation [12]:

$$d = \frac{0.9\lambda}{\beta \cos\theta} \quad (1)$$

where β is the full width at half maximum (FWHM) of the most intense peak, λ is the Cu target wavelength (1.5406 Å) and θ is the glancing angle. The values obtained are given in Table 1.

Rhombohedral phase remains consistent with increasing calcination temperature. Enlarged (Fig. 1(b)) view of XRD patterns reveal broadening of peaks with decreasing calcination temperature, indicating decreasing crystallite size. This observation corroborates well with crystallite size, determined from Eq. (1); this may be attributed to the merging of smaller grains via diffusion through grain boundaries, which enlarge crystallite size [11].

3.2. Morphological analysis

Topographical investigations, carried out using TEM, revealed agglomerated nanoparticles (Fig. 2(a) and (b)). Agglomeration is an inherent property of nanoparticles owing to their high surface to volume ratio. Similar observations, reported earlier, are

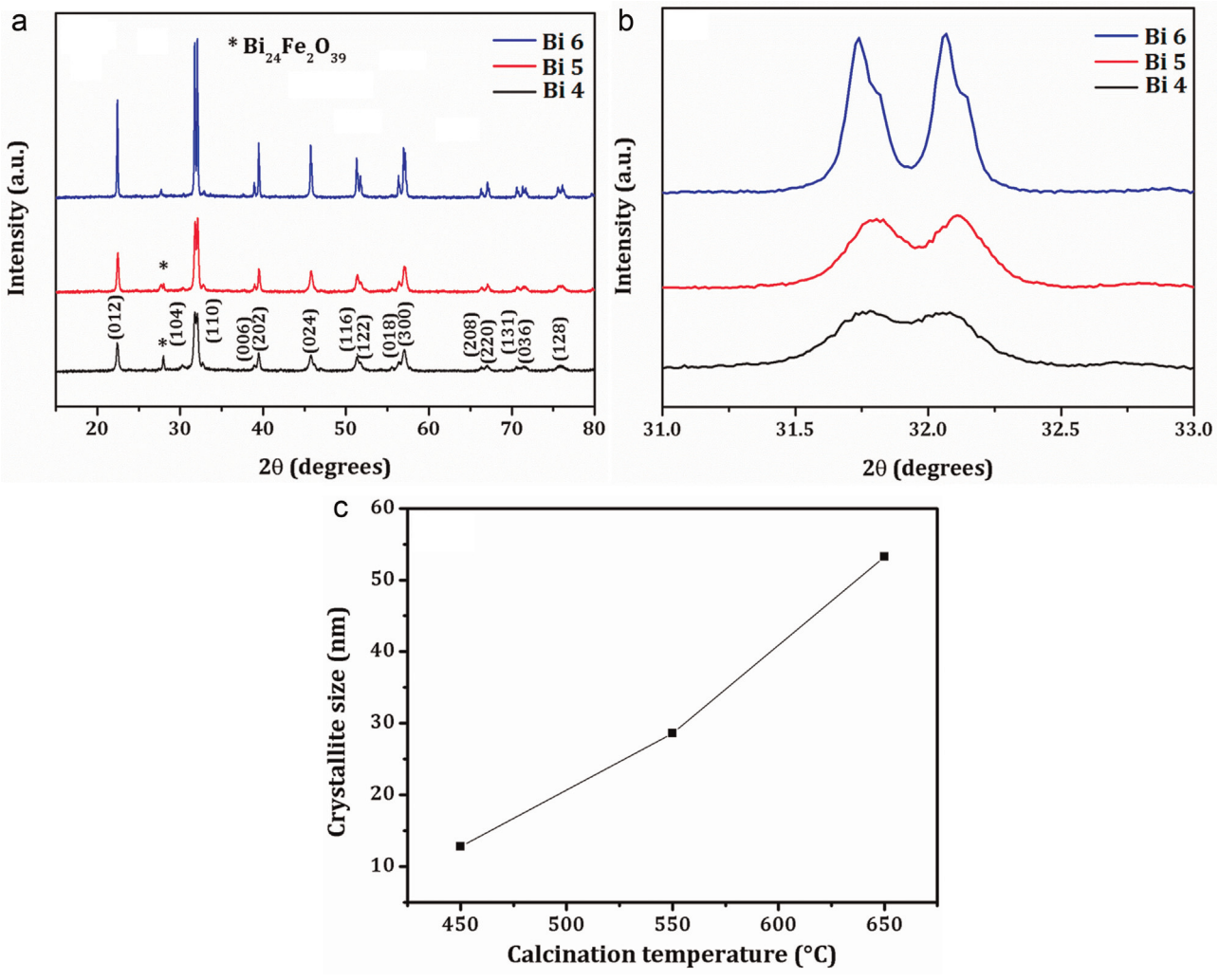

Fig. 1. (a) XRD patterns of Bi4, Bi5 and Bi6 nanoparticles, (b) their enlarged XRD patterns at around 2θ–32° and (c) variation of crystallite size with calcination temperature.