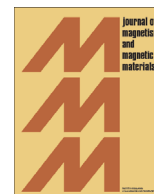




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Study of room temperature ferromagnetic and ferroelectric properties in α -Fe_{1.6}Ga_{0.4}O₃ alloy



Abdul Gaffar Lone, R.N. Bhowmik*

Department of Physics, Pondicherry University, R. Venkataraman Nagar, Kalapet, Pondicherry 605014, India

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ABSTRACT

The compound α -Fe_{1.6}Ga_{0.4}O₃ has been prepared by mechanical alloying and subsequent vacuum annealing at 800 °C. X-ray diffraction and Raman spectroscopy confirmed rhombohedral phase. The samples have shown enhanced ferromagnetic properties in comparison with α -Fe₂O₃ sample. The samples also exhibited good signature of ferroelectric polarization. Increase of alloying time has affected the variation of ferromagnetic and ferroelectric parameters. The samples with 50 h alloying time showed relatively large leakage of polarization, where as the samples at lower and higher alloying time showed better ferroelectric properties. Details of the ferroelectric loop have been studied at different applied voltages and frequencies. It has been found that leakage of polarization can be optimized by adjusting the frequency of the applied voltage. The ferroelectric properties have been understood by correlating the observations of the dielectric properties (dielectric loss, dielectric constant, and electrical conductivity) of the samples. The results are interesting for understanding the mechanism of ferroelectric properties in non-traditional ferroelectrics. This work opens a wide scope for reviewing the ferroelectric and multi-ferroic properties in metal doped hematite system, which is structurally different from orthorhombic phase of GaFeO₃ that showed ferroelectric properties.

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1. Introduction

The interest for multiferroics [1], where ferromagnetization and ferroelectric polarization coexist, is rapidly growing up for the basic understanding of the mechanism and potential applications of the magnetic materials. Magnetic semiconductors with multi-ferroic properties have been considered as the building blocks for spintronic devices [2,3]. The multiferroic systems are highly desirable for the applications in electro-magnetic devices such as multistate nonvolatile memories, high frequency filters, and magnetic switching [4–6]. The general belief is that ferroelectric materials are structurally non-centrosymmetric and must have non-magnetic transition metal ions with d⁰ outer shell electronic configuration. One example is BaTiO₃ where non-centrosymmetric displacement of Ti⁴⁺ (3d⁰) ions generates ferroelectric polarization. In contrast, ferromagnetic materials contain transition metal magnetic ions with partially filled d electrons (dⁿ: 1 ≤ n ≤ 9) in outer shell and ordering of electronic spins controls ferromagnetic properties. A strong interaction between the coexisting d⁰ and dⁿ metal ions is expected in multiferroics for magnetic field controlled electric polarization or electric field controlled

magnetization. Recently, multiferroic properties have been observed in systems, which do not belong to the family of traditional ferroelectrics. The electric field induced spin-flopping in BiFeO₃ [7,8] and magnetic field induced ferroelectric polarization in TbMnO₃ [9] revealed a strong effect of magnetic ordering of electronic spins on the generation of ferroelectric polarization [10]. There are no existence of d⁰ cations in BiFeO₃ and TbMnO₃. In these non-traditional ferroelectrics, Dzyaloshinskii–Moriya (DM) interaction driven spins canting and minor structural disorder generate ferroelectric polarization and multi-ferroelectric properties [11,12].

Alloying of M₂O₃ (M=Fe, Ga, Cr, Al, Ti, etc.) type oxides, e.g., Ga₂O₃ and α -Fe₂O₃ [13,14], Cr₂O₃ and α -Fe₂O₃ [15,16], TiO₂ and α -Fe₂O₃ [17,18], have received a great interest for the development of non-conventional ferromagnetic semiconductors. Hematite is a weak ferromagnet at room temperature due to DM interaction that causes spins canting among two neighboring planes. In rhombohedral structure of α -Fe₂O₃, in-plane ferromagnetic (FM) ordering of Fe³⁺ ions are separated by the layers of O²⁻ ions from adjacent ferromagnetic planes, and Fe³⁺ ions in neighboring planes are coupled via antiferromagnetic superexchange (Fe³⁺–O–Fe³⁺) interactions. The fact is that α -Fe₂O₃ is not a good multiferroic, but its weak ferromagnetic state with canted spin structure above Morin transition (~270 K) can be modified in metal doped hematite to develop multiferroelectric properties

* Corresponding author. Fax: +91 413 2655734.

E-mail address: rnbhowmik.phy@pondiuni.edu.in (R.N. Bhowmik).

[1,19–21]. For example, FeGaO₃ in distorted orthorhombic structure showed ferroelectric properties [20]. However, paramagnetic state of the FeGaO₃ compound at 300 K is not suitable for achieving room temperature multiferroic properties. On the other hand, Ga doped α -Fe₂O₃ in rhombohedral phase exhibited the properties of room temperature ferromagnetism, tuning of semiconductor band gap \sim 2.2 to 2.4 eV, and low dielectric loss [13]. Unfortunately, the number of reports on Ga doped hematite in rhombohedral structure is limited [14,22,23]. This is due to the fact that Fe₂O₃ is stable in rhombohedral phase and Ga₂O₃ is in monoclinic phase, and alloying the compound α -Fe_{1-x}Ga_xO₃ in rhombohedral phase is a challenging problem. In previous report [13], we have shown that mechanical alloying of Fe and Ga oxides and subsequent vacuum annealing could be a suitable route to stabilize rhombohedral phase. In this paper, our aim is to report the stabilization and preparation of the α -Fe_{1.6}Ga_{0.4}O₃ compound in rhombohedral phase. In the next step, the prepared samples will be characterized using X-ray diffraction and Raman spectroscopy. The characterized samples will be used to explore ferro-magnetic and ferroelectric properties, which could be treated as the first step in realizing the room temperature multiferroic properties in metal doped hematite system.

2. Experimental

2.1. Sample preparation

Stoichiometric amounts of high purity α -Fe₂O₃ and β -Ga₂O₃ were mixed to prepare the composition α -Fe_{1.6}Ga_{0.4}O₃. The mixed powder was ground for nearly 3 h to make it homogeneous. The ground powder was taken into an 80 ml stainless steel bowl and balls (combination of 10 mm stainless steel and 5 mm Tungsten Carbide) were added to material. The material to ball mass ratio was maintained at 1:8. The bowl was fixed inside the FRITTSCH (Pulverisette 6, Germany) planetary mono miller and mechanical alloying was carried out up to 100 h alloying time in air. The milling process was stopped after every 3–4 h intervals for proper mixing and to minimize agglomeration of particles due to local heating on continuous milling. Samples were taken after every 25 h of milling to check the structural phase evolution. The alloyed samples of 25, 50, 75 and 100 h were made into pellets of 13 mm diameter under pressure of 3 t. The structural phase stability of the mechanical alloyed sample with 100 h alloying time (in pellet form) was tested by annealing under non-ambient conditions ($\sim 10^{-6}$ mbar vacuum) and formation of single phased α -Fe_{1.6}Ga_{0.4}O₃ compound was checked. The 100 h as milled sample indicated an extra phase, which was gradually diminished on increasing the annealing temperature and there is no trace of extra phase for the sample annealed above 600 °C. Finally, mechanical alloyed samples with different alloying time were annealed at 800 °C for 2 h. The rate of heating and cooling was maintained at 30 °C/min during the annealing process. The 100 h mechanical alloyed (without annealing) sample was denoted as MA100AS. The mechanical alloyed samples after annealing under vacuum at 800 °C were denoted as MA25V8, MA50V8, MA75V8 and MA100V8 for alloying times 25 h, 50 h, 75 h, 100 h, respectively.

2.2. Sample characterization and measurements

Characterization and measurements of the samples were performed at room temperature in identical condition. An X-pert PANalytical X-ray diffractometer with CuK α radiation ($\lambda = 1.54056$ Å) was used to record X-ray diffraction (XRD) pattern of the alloyed samples in the 2θ range 20–80 with step size 0.01 and time per step 1 s. Raman spectra were recorded in the wave

number range 100–1600 cm⁻¹ using a micro-Raman microscope (Renishaw, UK). The spectra were excited with 514 nm radiation (2.41 eV) using an Argon-Ion laser source at power of 5 mW. Magnetization was measured using a physical properties measurement system (PPMS-EC2, Quantum Design, USA) within field range ± 70 kOe. Ferroelectric (P - E) loops were studied using a Precision Premier II ferroelectric tester (Radiant Technologies). Surface area of the samples used for ferroelectric measurements was 1.32 cm² and thickness was 1.1 mm, 1.02 mm, 1.1 mm, and 0.98 mm for MA25V8, MA50V8, MA75V8, and MA75V8, respectively. Dielectric properties of the pellet shaped samples were measured using a broad band dielectric spectrometer (Novocontrol Tech., Germany).

3. Results and discussion

3.1. Structural properties

Fig. 1 shows that XRD pattern of the α -Fe_{1.6}Ga_{0.4}O₃ samples is identical to the pattern of α -Fe₂O₃. MA100AS sample showed a minor amount of extra peak at about $2\theta \sim 21.56^\circ$, which is resembled to orthorhombic phase of Gallium oxide hydroxide (GaOOH·xH₂O) [24]. The extra phase is not visible in the XRD pattern of mechanically alloyed samples after vacuum annealing at 800 °C and pattern of these samples were matched to single phased rhombohedral structure with space group R3C or R3c. Cell parameters (lattice constants: a , c , and cell volume (V)) of the vacuum annealed samples have been calculated from profile fitting of XRD pattern using FULLPROF program and the values are shown in Table 1. These prepared samples showed decreasing trend of cell parameters (a , c , V) with the increase of alloying time as a result of better alloying and homogenization. Cell parameters of the samples are smaller than the cell parameters ($a=b=5.0386$ Å, $c=13.7598$ Å, $V=302.49$ Å³) of α -Fe₂O₃ sample. This is due to incorporation of Ga³⁺ with smaller ionic radius (0.62 Å) into the lattice sites of Fe³⁺ ions with larger radius (0.645 Å) [25]. The samples prepared by high pressure technique showed similar modifications [26]. Grain size ($\langle d \rangle$) and lattice strain (ϵ) of the samples were determined using Williamson–Hall equation, as described in Ref. [15]. Table 1 shows that grain size of the samples is in the range 25–45 nm. The increase of mechanical alloying time has decreased grain size and increase of lattice strain in the final alloyed compound. The elemental composition of Fe, Ga and O obtained from EDX is close to the expected value in α -Fe_{1.6}Ga_{0.4}O₃.

3.2. Raman spectroscopy

Raman spectra were used to get more insight of the structural phase formation in the prepared samples. Fig. 2 compares the Raman spectra of different samples. First observation is that the spectra of Ga doped α -Fe₂O₃ samples are different from those of β -Ga₂O₃. The samples mechanically alloyed and annealed at 800 °C under vacuum have exhibited spectrum that is identical to the spectrum of α -Fe₂O₃, and suggest a successful incorporation of Ga atoms in the rhombohedral structure of α -Fe₂O₃ [27]. Factor group analysis predicted seven Raman active phonon modes ($A_{1g}(1)$, $E_g(1)$, $E_g(2)$, $E_g(3)$, $E_g(4)$, $A_{1g}(2)$, $E_g(5)$) for hematite (α -Fe₂O₃) system [28–31]. As indicated in Fig. 2, the Raman active phonon modes for α -Fe₂O₃ were found at ~ 212 cm⁻¹ ($A_{1g}(1)$), ~ 223 cm⁻¹ ($E_g(1)$), ~ 270 cm⁻¹ ($E_g(2)$), ~ 282 cm⁻¹ ($E_g(3)$), ~ 386 cm⁻¹ ($E_g(4)$), ~ 478 cm⁻¹ ($A_{1g}(2)$), and ~ 590 cm⁻¹ ($E_g(5)$), respectively. The $A_{1g}(1)$, $E_g(1)$, and $E_g(2)$ bands are associated with movement of cations in rhombohedral structure [24]. For example, $A_{1g}(1)$ band is related to the movement of cations along

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