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Synthesis of nanocrystalline $YFeO_3$ and its magnetic properties

Ramaprasad Maiti [a], Soumen Basu [b], Dipankar Chakravorty [c,*]

[a] Department of Electronics, Vidyasagar University, Midnapore, West Bengal 721102, India
[b] National Institute of Technology, Durgapur, West Bengal 713209, India
[c] DST Unit on Nano Science, Indian Association for the Cultivation of Science, Kolkata 700 032, India

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ABSTRACT

Single phase nanocrystalline $YFeO_3$ has been synthesized by a simple solution method. The average particle diameter is 42.2 nm. The particles exhibit ferromagnetic behaviour in the temperature range 10–300 K with a coercivity of 23 kOe. The magnetization versus temperature over the temperature range 2–300 K obeys Bloch equation with a Bloch constant value $9.98 \times 10^{-6}\,K^{-3/2}$. Ferromagnetic hysteresis loops have been observed up to a temperature of 300 K. At 10 K a field-cooled sample shows an exchange bias field.

1. Introduction

Rare earth orthoferrites have attracted considerable attention in recent years because of their interesting magnetic properties [1–5]. These exhibit a weak ferromagnetic behaviour. Yttrium orthoferrite which has been investigated by several groups has a distorted perovskite structure. A super-exchange magnetic interaction occurs between two iron ions separated by an oxygen ion. The alignment of iron moments is not perfectly antiparallel but there is a slight canting. This results in a small magnetization giving rise to weak ferromagnetism. Preparation of single phase yttrium orthoferrite by conventional solid state reaction of precursor oxides has been reported to be difficult because of the formation of secondary phases like Fe_3O_4 and $Y_3Fe_5O_{12}$ (yttrium–iron garnet) [1]. A novel Y–Fe alkoxide has been developed to make $YFeO_3$ by a sol–gel process [4]. We have used a simple solution method to synthesize $YFeO_3$ in the nanocrystalline state. No secondary phase has been observed. The magnetic properties have been delineated. The details are reported in this paper.

2. Experimental

The precursor solution was prepared using Y_2O_3 (Sigma-Aldrich, purity 99.99%) and $Fe(NO_3)_3$.(Alfa-Aesar, purity 99.9%). Y_2O_3 (0.4 gm) was taken in 16 ml distilled water. The mixture was continuously stirred and the temperature raised slowly to 343 K adding a few drops of concentrated HNO_3. The stirring was continued for 2 h when Y_2O_3 was completely dissolved. $Fe(NO_3)_3$ (1.43 g) was added to the solution under stirring for $\frac{1}{2}$ h. A polyvinyl alcohol (Loba-Chemie, purity 98%) (PVA) solution was prepared by taking 0.5 g PVA in a beaker containing 40 ml distilled water. The mixture was stirred continuously and the temperature raised gradually to 347 K. The stirring and heating was continued until the PVA was completely dissolved in water. The stirring time was 2 h. The two solutions prepared as above (viz, $Y(NO_3)_3$+ $Fe(NO_3)_3$ and PVA, respectively) were mixed with a volume ratio 5:2. The final solution was allowed to form a clear gel at room temperature. The gel was dried. The temperature was raised at a rate of 5 K/min till it reached 693 K. The solution was thereafter furnace cooled to room temperature. These heating and cooling cycles were repeated three times. By this process PVA was removed completely. The resultant gel was subjected to heat treatment at 1073 K for $\frac{1}{2}$ h to crystallize the $YFeO_3$ phase.

The crystalline phase in the sample was identified by taking X-ray diffractograms in a Rich Seifert diffractometer using CuK_α radiation. The microstructure was investigated by a JEM 2010 transmission electron microscope operated at 200 KV. Magnetic property measurements in the sample were carried out in a Quantum Design MPMS system having a SQUID magnetometer in the temperature range 2–300 K. The magnetization values were measured under zero field-cooled (ZFC) and field-cooled (FC) conditions at an applied magnetic field of 500 Oe

3. Results and discussion

Fig. 1 is the X-ray diffractogram obtained from the specimen synthesized. All the lines have been identified with those of pure

* Corresponding author.
E-mail address: mlsdc@iacs.res.in (D. Chakravorty).

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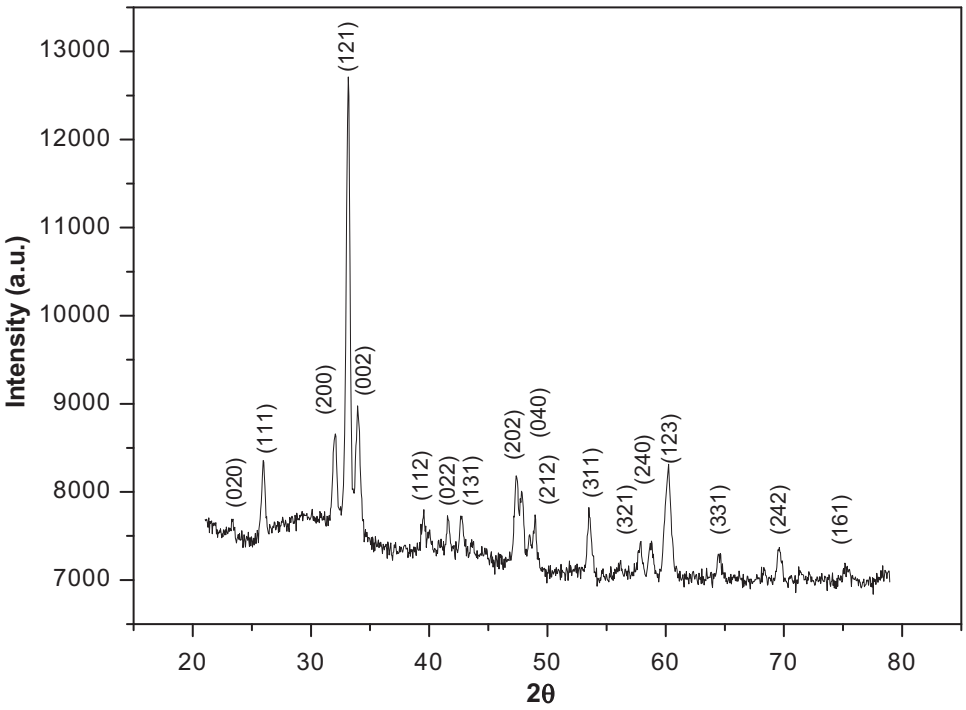

Fig. 1. X-ray diffractogram obtained from $YFeO_3$ specimen.

Table 1
Refined structural parameters of $YFeO_3$ (Rietveld analysis).

Compound	$YFeO_3$
Crystal system	Orthorhombic
Space group	Pnma
Lattice parameters (Å)	
a	5.584
b	7.597
c	5.274
Unit cell volume (Å^3)	224.05
Average grain size (nm)	42.2

R factors (%): R_w (%) = 1.08, R_{exp} (%) = 1.16, GoF = (R_w/R_{exp}) = 0.93.

$YFeO_3$ as given in JCPDS file no. 39-1489. The (*h k l*) values have been shown against the intensity peaks in the figure. Rietveld analysis of the X-ray data was carried out and the results are shown in Table 1. The average diameter of the orthoferrite grain has been estimated to be 42.2 nm.

Fig. 2(a) is the transmission electron micrograph of a specimen. There is a distribution of particle sizes and this particular area in the micrograph gives large-sized particles. Fig. 2(b) is the electron diffraction pattern obtained from Fig. 2(a). The interplanar spacings were calculated from the positions of the diffraction spots. These are summarized in Table 2. It is evident that all the diffraction spots arise due to the presence of $YFeO_3$ phase.

Fig. 3 shows the variation of magnetization as a function of temperature under both zero field-cooled and field-cooled conditions. The latter was cooled under a field of 500 Oe. The nature of the curves indicates that there is a superparamagnetic behaviour exhibited by the particles. The latter have weak ferromagnetic characteristics. Hence, this type of variation is expected. The blocking temperature is estimated from the broad maximum in the ZFC curve to be around 50 K. The data indicate a distribution of particle sizes over a wide range. We have analyzed the magnetization behaviour on the basis of Bloch equation [6,7], given by

$$M_s(T) = M_s(0)[1 - BT^{3/2}] \quad (1)$$

where $M_s(T)$ and $M_s(0)$ are the saturation magnetizations at temperatures *T* and 0 K, respectively, and *B* is the Bloch constant. It should be noted here that our samples do not show saturation even at 50 K Oe. We have therefore estimated M_s value at any temperature by extrapolating the *M* vs. $1/H$ curve to $H^{-1} \rightarrow 0$ [8]. Fig. 4 gives the plot of $[M_s(0)-M_s(T)]/M_s(0)$ as a function of $T^{3/2}$. The slope of the straight line fitted to the experimental data is found to be $B = 9.98 \times 10^{-6}\,K^{-3/2}$. This is much larger than those observed in the case of ferromagnetic metal like α-Fe [4]. It may be mentioned here that the value of *B* obtained by us is of the same order as that reported by Mathur et al. for single phase $YFeO_3$ samples [4].

Figs. 5(a)–(c) show the magnetization versus magnetic-field hysteresis loops for the $YFeO_3$ specimen at temperatures 300, 200 and 100 K, respectively. The coercivity is found to be around 23 K Oe. This is in agreement with values reported earlier [4].

Fig. 6 shows the hysteresis loop for $YFeO_3$ sample at 10 K. The data were collected after field cooling of the sample from 300 to 2 K. It can be seen that the loop is highly asymmetrical and an exchange bias field of 18 K Oe in the negative direction is obtained. Such behaviour has not been reported before. It is believed that this effect arises because of the presence of an antiferromagnetic layer at the surfaces of the nanoparticles of $YFeO_3$. These results