Structure and Magnetism of $FeMnO_3$

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Abstract. The compound $FeMnO_3$ crystallizing in the mineral bixbyite structure has been prepared by mechanochemical synthesis achieved by high energy ball milling of starting compounds. The structure and magnetism have been studied using powder neutron diffraction and magnetization measurements. Magnetization measurements exhibits ferrimagnetism at 300 K and antiferromagnetic (T_N) ordering around 36 K. Magnetic structure has been determined from the Rietveld analysis of the neutron diffraction pattern recorded at 300 K. Fe and Mn occupy both 8*b* and 24*d* sites in 1:1 ratio. Interaction between Fe and Mn atoms is antiferromagnetic. The ferrimagnetism arises due to anti-parallel alignment of unequal moments on 8*b* and 24*d* sites.

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INTRODUCTION

Iron-Manganese oxide based mixed systems have important applications such as superparamagnetic materials, oxidation catalysis, negative temperature coefficient thermistors (NTC-T) etc. [1-3]. The Fe-Mn-O systems are also interesting due to the fact that Mn is an element generally found in iron ore. The incorporation of Mn in steel greatly influences its metallurgical properties [3]. Fe-Mn based oxide systems are also well in demand for their catalytic properties [3].

The solid solutions of Fe-Mn-O yield a rich phase diagram [3]. Among the various phases possible for Fe-Mn oxides, the bixbyite $(Fe,Mn)_2O_3$ solid solution is obtained on mixing Fe_2O_3 and MnO_2 at 950°C under pure CO_2. It is also known in the literature that by mechanical alloying of α-Fe_2O_3 (hematite) and β-Mn_2O_3 (bixbyite), β-$FeMnO_3$ can be formed [4].

In the solid-state reaction method, formation of the product phase takes place at the interfaces of the reactants. For complete formation of the final product, the interfacial barrier needs to be surmounted, which is achieved by applying high temperatures. However, during mechanical alloying or mechano-chemical synthesis, mechanical energy is converted to chemical energy which induces chemical reactions [5]. Thus, mechanical alloying can be a useful method in increasing the reaction kinetics without the need for elevated temperatures. Due to repeated welding and fracturing of reactant powder particles during mechanical alloying, the particle size decreases, yielding larger contact area for the reactants. Larger the area of contact between reactant powders faster will be the reaction between them [5]. Therefore, there is clear benefit of expediting product formation rate using mechanical alloying over conventional solid-state reaction method.

It has been reported in the literature that $FeMnO_3$ prepared by mechanical alloying exhibits ferrimagnetic order at room temperature [4]. In the present work, we have carried out detailed studies on the structure and magnetism of $FeMnO_3$. We provide convincing evidence for ferrimagnetism in this compound using powder neutron diffraction.

EXPERIMENTAL DETAILS

Stoichiometric quantities of Fe_2O_3 (Alfa-Aesar, 99.9% pure) and MnO_2 (Alfa-Aesar, 99.999% pure) were taken in a tungsten-carbide (WC) jar with WC balls (10 mm balls). The charge was ball-milled at a speed of 400 rpm for a total time of about 18 hours in a high energy planetary ball mill. Small quantities of sample were taken out after every 6 hours of milling for checking the progress of the reaction. The final product was sintered at 825°C for 72 hours.

Structural properties were studied using X-ray diffraction (XRD) and neutron diffraction (ND) carried out on powder samples at room temperature. XRD was done on Philips X'pert Pro diffractometer, whereas ND was carried out on a focusing crystal based

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powder diffractometer of UGC-DAE CSR at Dhruva reactor, Trombay. Magnetic measurements were carried out at UGC-DAE CSR, Mumbai Centre on a Quantum Design physical property measurement system based vibrating sample magnetometer.

RESULTS AND DISCUSSIONS

The XRD and ND patterns recorded at 300 K are shown in Fig. 1. The structural details were obtained from the Rietveld refinement of the powder data using Fullprof program. The structure was refined on the basis of bixbyite $(Fe,Mn)_2O_3$ compound reported in Ref 6. The compound crystallizes in a cubic structure, space group *Ia*3 (SG No. 206). Refinement of both XRD and ND data converged well with reasonable refinement (R-values) parameters. The fit exhibits single-phase formation of the compound. Cell parameter (*a*) is 9.41Å. Fe and Mn occupy both 8*b* and 24*d* sites in equal proportions, i.e., Fe and Mn are distributed in 1:1 ratio at 8*b* as well as 24*d*. Oxygen resides at site 48*e*.

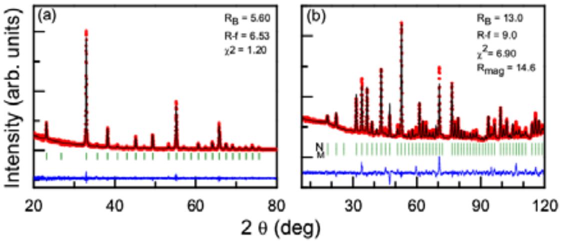

FIGURE 1. Rietveld refinement of (a) XRD and (b) ND profiles of $FeMnO_3$ taken at T = 300K. The two rows of vertical tick marks in (b) indicate nuclear and magnetic Bragg peak positions.

The magnetic structure for $FeMnO_3$ has been determined from the refinement of the ND data for the magnetic structure along with the nuclear (crystalline) part. Since Fe and Mn occupy both site 8*b* and 24*d* in equal proportions, the magnetic structure was refined assuming 16 pairs of Fe-Mn symmetry positions. The structure was refined using a propagation vector, *k* = [0 0 0]. The Fe and Mn moments (in μ_B) obtained from the refinement, are, 2.48,(-1.0) per Fe(Mn) at 8*b* and 3.97, (-3.01) per Fe(Mn) at 24*d* sites, respectively. The negative sign on Mn moments indicates that Fe and Mn moments are coupled antiferromagnetically. From these site specific values, the total moment calculated per formula unit is $0.05\mu_B$ which is close to the value obtained experimentally from the magnetization measurement.

In Fig. 2, magnetic susceptibility ($\chi = M/H$) measured in a field of 1 kOe is plotted as a function of temperature. As the sample is cooled below 100 K, there is a gradual rise in χ culminating in a peak around 36 K ($=T_N$) and then falling rapidly with decreasing T. The decrease of χ with decreasing T below 36K is an indication of the antiferromagnetically ordered state of the sample.

Fig. 2 also shows the plot of $\chi^{-1}(T)$. The values of paramagnetic Curie temperature (θ_p) and effective Bohr magneton number (μ_{eff}) calculated from the linear part of the plot are -56K and 7.9 μ_B per formula unit. The free ion magnetic moments for Fe^{3+} and Mn^{3+} are $5.9\mu_B$ and $4.9\mu_B$ respectively. Thus, the total calculated moment per formula unit is $7.6\mu_B$. This value is close to our μ_{eff} value obtained experimentally. Further, the negative sign of θ_p indicates antiferromagnetic coupling between the spins.

In Fig. 3, magnetization measured as a function of ramping field is shown. The hysteresis loop at T = 300 K exhibits that the sample is magnetic at room temperature (300K). With initial increase in H, M increases non-linearly as if there is a small antiferromagnetic moment, and beyond 1 kOe there is linear variation in M with respect to H. Around the origin, M(H) exhibits hysteresis loop with a coercive field of around 200 Oe. The highest moment value at the maximum field (10kOe) is close to $0.03\mu_B$/f. u.

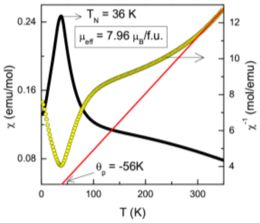

FIGURE 2. Plot of $\chi(T)$ and $\chi^{-1}(T)$ in ZFC condition of the sample, measured in a field of 1 kOe.

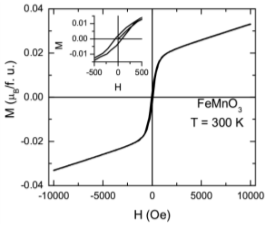

FIGURE 3. M vs. H for $FeMnO_3$ measured at T = 300 K is shown. The inset shows the hysteresis loop.

In conclusion, $FeMnO_3$ prepared using mechanochemical synthesis method has been studied for its structural and magnetic properties. Ferrimagnetism at room temperature has been established using magnetization and ND studies. The origin of ferrimagnetism is attributed to the anti-parallel arrangement of unequal moments on 8*b* and 24*d* sites.

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