Study on the Properties of Fe-substituted NdMn$_2$O$_5$

K. Saravana Kumar and C. Venkateswaran

Department of Nuclear Physics, University of Madras, Guindy Campus, Chennai 600 025, India

E-mail: cvunom@hotmail.com

Abstract. The oxide, NdFeMnO$_5$, has been synthesized using a two-step synthesis process. First the precursor oxides are high-energy ball milled and the as-milled powders are then sintered to obtain the NdFeMnO$_5$ phase. X-ray diffraction confirms phase formation and the calculated pattern is obtained by the substitution of Mn$^{3+}$ sites by Fe$^{3+}$ sites. Agglomeration of small sized grains is observed from the scanning electron microscopy images. Room temperature magnetization measurement shows a paramagnetic behaviour. A ferrimagnetic ordering is observed to be established below $\sim$110 K from the thermo-magnetization measurements.

1. Introduction

Materials of the RMn$_2$O$_5$ (R=Rare earths, Bi) family has Mn at two different crystallographic sites [1]. Mn$^{4+}$ ions occupy the octahedral pyramidal ($4f$) sites where it is coordinated with six oxygen atoms and Mn$^{3+}$ ions at tetragonal pyramidal ($4h$) sites having coordination with five oxygen atoms [1]. They have complex magnetic structures which give rise to magnetodielectric effect around the magnetic transition temperatures [2]. Generally, RMn$_2$O$_5$ systems have the orthorhombic structure with Pbam spacegroup and paramagnetic behaviour at room temperature. They have Neel transition temperature around 40 K below which antiferromagnetic ordering exists.

The magnetic ordering in these systems can be investigated by the substitution of Mn$^{3+}$ ions with Fe$^{3+}$ ions [3, 4]. The magnetic properties of Fe-substituted RMn$_2$O$_5$ in few cases are reported to be ferrimagnetic in nature at low temperatures [5–7]. The Fe substitution has its effect on the structural and magnetic properties due to its high spin only effective magnetic moment. We report the synthesis and properties of Fe-substituted NdMn$_2$O$_5$. It is considered that Fe$^{3+}$ occupies the Mn$^{3+}$ ($4h$) sites, and the corresponding change in properties observed is compared with the already reported properties of the parent system.

2. Experimental

Powders of neodymium oxide, manganese mono-oxide and iron oxide were taken in stoichiometric proportions and milled for a total of 5 h at 400 RPM with a ball to powder ratio of 28:2. The obtained reddish brown powders were then pressed into dense pellets of 12 mm diameter, sintered at 1073 K for 24 h and furnace cooled. Sintered samples were then ground in a mortar to obtain the black powders of NdFeMnO$_5$. The X-Ray Diffraction (XRD) data was obtained with Cu-Kα radiation at room temperature. High resolution-scanning electron microscopy (HR-SEM) was done in FEI Quanta FEG 200 HR Microscope. Isothermal magnetization and Zero field cooled (ZFC)-Field Cooled (FC) measurements were carried out in the range 20 K-300 K in a
Lakeshore VSM 7410 instrument. A field of 1000 Oe was applied for the ZFC-FC experiment and for iso-thermal magnetization curves a maximum field of 20 KOe was applied.

3. Results and discussion
X-ray diffraction (XRD) pattern is given in fig 1, indicating the formation of stoichiometric NdFeMnO$_5$ which is iso-structural with NdMn$_2$O$_5$ along with the few secondary phases. The calculated pattern, matching with the experimental pattern, is obtained by using the FULLPROF [8] program by the substitution of Fe$^{3+}$ in Mn$^{3+}$ $(4f)$ sites. From the structural point of view, NdFeMnO$_5$ has the same orthorhombic (Pbam) structure as that of its parent NdMn$_2$O$_5$. Parent system has the Mn$^{4+}$ octahedra network connected through oxygen atoms, extending along c−axis [9], and has Mn$^{3+}$ and Nd$^{3+}$ layers between these Mn$^{4+}$ layers. In the case of NdFeMnO$_5$, these Mn$^{3+}$ layers are completely replaced by Fe$^{3+}$ layers connecting Mn$^{3+}$ ions through oxygen atoms. The arrangement of Nd, Mn and Fe atoms in a unit cell of NdFeMnO$_5$ is illustrated in fig 2, along the c−axis (a) and a−axis (b). HR-SEM image is shown in fig 3, illustrating the random distribution of particles with agglomeration and the EDAX

![XRD plot with the experimental and generated patterns. * indicates the secondary peaks.](image1)

**Figure 1.** XRD plot with the experimental and generated patterns. * indicates the secondary peaks.

![View of Nd, Mn & Fe layers (a) along c−axis (left) (b) along a−axis(right)](image2)

**Figure 2.** View of Nd, Mn & Fe layers (a) along c−axis (left) (b) along a−axis(right)
Room temperature magnetization measurements confirm the near stoichiometric presence of all elements in NdFeMnO$_5$.

Room temperature magnetization study, given in fig 4, indicates a paramagnetic behaviour and a weak ferromagnetic property is also observed at initial low fields. The low temperature Zero field cooled-field cooled (ZFC-FC) curves are shown in fig 5, which exhibits a split below $\sim$110 K and an increase in magnetization values till 20 K. This behaviour is indicative of the ferrimagnetic property below $\sim$110 K and is supported by the linear dependence of magnetization on the applied magnetic field obtained at 20 K (inset of fig 5). The parent NdMn$_2$O$_5$, has a Neel transition ($T_N$) temperature of $\sim$75K, below which it is reported to have
antiferromagnetic ordering [10]. The magnetic transition is due to the ordering of magnetic moments in Nd$^{3+}$, Mn$^{4+}$ and Mn$^{3+}$ layers. Global magnetic behaviour in RMn$_2$O$_5$ is based on the type of magnetic ordering in Mn$^{4+}$-O-Mn$^{4+}$ and Mn$^{4+}$-O-Mn$^{3+}$-O-Mn$^{4+}$ chains determined through superexchange interaction. The spin only effective magnetic moments of Mn$^{4+}$, Mn$^{3+}$ and Fe$^{3+}$ are 3.87 $\mu_B$, 4.89 $\mu_B$ and 5.92 $\mu_B$, respectively [11]. The magnetic ordering arises due to the alignment of magnetic Nd$^{3+}$, Fe$^{3+}$ and Mn$^{4+}$ moments in the unit cell. Due to Fe$^{3+}$ substitution at Mn$^{3+}$ sites, the magnetic ordering of the chain Mn$^{4+}$-O-Fe$^{3+}$-O-Mn$^{4+}$ through the superexchange interaction is affected as the magnetic moment of Fe$^{3+}$ is higher than Mn$^{3+}$. The interaction in Mn$^{4+}$-O-Mn$^{4+}$ chains through Nd$^{3+}$ may induce a weak ferromagnetic interaction below the ordering temperature, contributing to the ferrimagnetic ordering observed at low temperatures.

4. Conclusion

The compound, NdFeMnO$_5$, has been synthesized by initial high-energy ball milling of oxides and then sintering of milled powders. Fe$^{3+}$ substitution in the NdMn$_2$O$_5$ at Mn$^{3+}$ affects the magnetic ordering at low temperatures due to which a ferrimagnetic ordering occurs below $\sim$110 K. This is the result of change in interaction in Mn$^{4+}$-O-Mn$^{4+}$ chains due to Fe substitution.

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References

[1] Munoz A, Alonso J A, Casais M T, Martinez-Lope M J, Martinez J L and Fernandez-Diaz M T 2002 Phys. Rev. B 65(14) 144423
[2] Retuerto M, Martinez-Lope M, Muoz A, Ruskov T, Spirov I, Krezhov K, Fernandez-Daz M, Garcia-Hernandez M and Alonso J 2010 Solid State Communications 150 1831 – 1836
[3] Retuerto M, Martinez-lope M, Munoz A, Ruskov T, Spirov I, Krezhov K, Fernandez-Daz M, Garcia-Hernandez M and Alonso J 2010 Solid State Communications 150 1831–1836
[4] Kumar K S and Venkateswaran C 2011 Journal of Physics D: Applied Physics 44 325001
[5] Muoz A, Alonso J A, Martinez-Lope M J and Martinez J L 2004 Chemistry of Materials 16 4087–4094
[6] Muoz A, Alonso J A, Martinez-Lope M J and Martinez J L 2005 Phys. Rev. B 72(18) 184402
[7] Martinez-Lope M, Retuerto M, Alonso J and Pomjakushin V 2008 Journal of Solid State Chemistry 181 2155 – 2160
[8] Rodriguez-Carvajal J 2001 Commission on Powder Diffraction (IUCr) Newsletter 26 12–19
[9] Alonso J, Casais M, Martinez-Lope M and Rasines I 1997 Journal of Solid State Chemistry 129 105 – 112
[10] Chen Y, Yuan H, Tian G, Zhang G and Feng S 2007 Journal of Solid State Chemistry 180 1340 – 1346
[11] Martinez-Lope M, Retuerto M, Alonso J, Garcia-Hernandez M, Krezhov K, Spirov I, Ruskov T and Fernandez-Daz M 2009 Solid State Communications 149 540 – 545