Structural and magnetic properties of RFe$_{0.5}$Mn$_{0.5}$O$_3$ (R = Ho, Eu)

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Polycrystalline samples of HoFe$_{0.5}$Mn$_{0.5}$O$_3$ (HFMO) and EuFe$_{0.5}$Mn$_{0.5}$O$_3$ (EFMO) were synthesized and crystal structures were analyzed by using X-ray powder diffraction followed by rietveld refinement using FULLPROF software. The magnetization measurements were carried out in a SQUID based vibrating sample magneto meter by varying temperature and magnetic field. Both the samples crystallize in orthorhombic structure with Pbnm space group. In both the materials Rare earth atoms occupy 4c (x, y, 1/4) positions, Fe/Mn atoms occupy the octahedral sites 4b (0, 0.5, 0) and the oxygen atoms occupy 4c (x, y, 1/4) and 8d (x, y, z) positions. The lattice parameters of EFMO were calculated by rietveld refinement as follows; a = 5.3498(1) Å, b = 5.6676(1) Å, and c = 7.5890(2) Å. HFMO has lattice parameters of a = 5.2688(1) Å, b = 5.6762(2) Å, and c = 7.5066(2) Å. The volume of the unit cell is found to be 224.50(1) Å$^3$ for HFMO and 230.11(1) Å$^3$ for EFMO. Difference in the volume of unit cell between both the compounds arises due to the different ionic sizes of Eu$^{3+}$ (1.12 Å) and Ho$^{3+}$ (1.072 Å). Since Eu$^{3+}$ ion is bigger than Ho$^{3+}$ ion, the octahedral distortion in HFMO is higher compared to EFMO which results in smaller B-O-B bond angles for HFMO. In rare earth orthoferrites, the complex magnetic interactions between R$^{3+}$-R$^{3+}$, R$^{3+}$-Fe$^{3+}$ and Fe$^{3+}$-Fe$^{3+}$ play a vital role and they give rise to many interesting magnetic phenomenon like spin reorientation, magnetization reversal and exchange bias. The temperature dependent magnetization curve of HFMO shows a transition at 293 K, which can be assigned to the weak ferromagnetic ordering of Fe/Mn moments. At low temperatures, there is a transition observed from dM/dT curve below 10 K, which may be due to the Ho$^{3+}$-Ho$^{3+}$ interaction. The M vs T curve of EFMO shows two magnetic transitions, one near to room temperature and other at 223 K. The transition near room temperature can be assigned to the Fe/Mn ordering and the one at 223K may be attributed to the spin reorientation of Fe/Mn sublattice moments. The inverse susceptibility Curie Weiss fit gives Curie constant $\theta = -12.48$ K for HFMO, and $\theta = -225.6$ K for EFMO. The negative values indicate the presence of dominant antiferromagnetic interactions. The effective magnetic moment was calculated from the fit as $\mu_{eff} = 11.31$ $\mu_B$ for HFMO and $\mu_{eff} = 6.3$ $\mu_B$ EFMO. Compared to RFeO$_3$ (R = Ho, Eu), substituting Mn for Fe has brought down the Néel temperature near to room temperature in both the materials. Since EFMO and HFMO have near room temperature transitions, they stand as good candidates for practical applications.


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