Magnetic, electrical transport and structural investigations of orthorhombic perovskite Pr 2 MnFeO 6

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Magnetic, electrical transport and structural investigations of orthorhombic perovskite Pr_2MnFeO_6

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Substituting Mn ions in $PrMnO_3$ by 3d-transition metal Fe ions, the structural, magnetic and magnetotransport properties are modified due to change in tolerance factor. The compound has an orthorhombic structure with the space group *Pbnm*. The field cooled magnetization data with temperature indicates that the compound is ferromagnetic below ~200 K. The variation in magnetization with applied magnetic field show a hysteresis behavior, which confirms the ferromagnetic nature. The remanent magnetization and coercive field of the compound, at 2 K, were found to be $0.6169\mu_B$/f.u. and 0.4291 T respectively. Mössbauer spectrum indicates that the Fe^{3+} ions are in high spin state. The temperature variation in electrical resistivity measurement shows the sample to be insulating in nature. © *2010 American Institute of Physics*. [doi:10.1063/1.3359441]

I. INTRODUCTION

In recent years, manganites with perovskite structure has got considerable interest due to its magnetic and transport properties, mangnetocaloric[1] and magnetoelectric effects.[2] Manganese perovskite $RMnO_3$ with trivalent rare earth ions R^{3+} are antiferromagnetic (AFM) insulator. Doping trivalent transition metal ions on Mn site can result in ferromagnetic (FM) insulators.[3] By doping, there is a change in tolerance factor which leads to deviation from the ideal perovskite structure. Moreover, double perovskites of the form $A_2BB'O_6$ has got particular interest because of their basic physics and materials aspect. It is well known that the magnetic and electronic properties of double perovskites depend on the degree of ordering between the B and B′ ions. This ordering mainly depends on the size and charge difference between cations.[4] In order to understand the electronic structure and magnetic exchange mechanism in double perovskites, intensive research has been devoted to both the variation in magnetic ions on the B and B′ sites and also the presence of different rare earth ions on the A sites. The aim of this paper is to investigate the magnetic and transport properties of Pr_2MnFeO_6 (PMFO) double perovskite.

II. EXPERIMENTAL DETAILS

Polycrystalline sample Pr_2MnFeO_6 (PMFO) was prepared from stoichiometric mixture of Pr_6O_{11}, MnO_2, and Fe_3O_4, with purity ranging from 99.99% to 99.999%, from Sigma-Aldrich. The mixture was well mixed, placed in Al_2O_3 crucible, and then repeatedly heated with intermediate grinding. The final sintering temperature was 1100 °C. The sample was characterized by powder x-ray diffraction (XRD) data using PANalytical X'Pert Pro x-ray diffractometer with Cu $K\alpha$ radiation. The structural refinements of the sample were carried out using general structure analysis system.[5] The magnetization measurements were performed using a physical property measurement system magnetometer from Quantum Design operating up to 9 T and from 2 to 300 K. The Mössbauer spectrum was recorded at room temperature using a standard spectrometer and an Rh(^{57}Co) source. The spectrometer was calibrated using a standard α-Fe foil and the spectrum is presented relative to the center of the α-Fe spectrum. The temperature dependent electrical resistivity measurement for the sample, with temperature range of 15–300 K, was carried out by a two probe method using JANIS cryostat and with the help of a Keithley 617 programmable electrometer and Lakeshore 331 temperature controller.

III. RESULTS AND DISCUSSION

A. Crystal structure analysis

The Rietveld refinement was carried out and it was found that the compound crystallizes in *Pbnm* space group. A good fit was obtained with R_{wp}=6.05% R_p=4.81% and

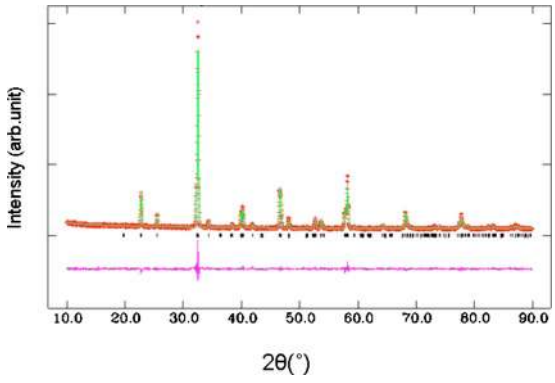

FIG. 1. (Color online) Rietveld refinement profiles of x-ray powder diffraction data for PMFO. The solid line is the calculated profile and a difference curve is plotted at the bottom.

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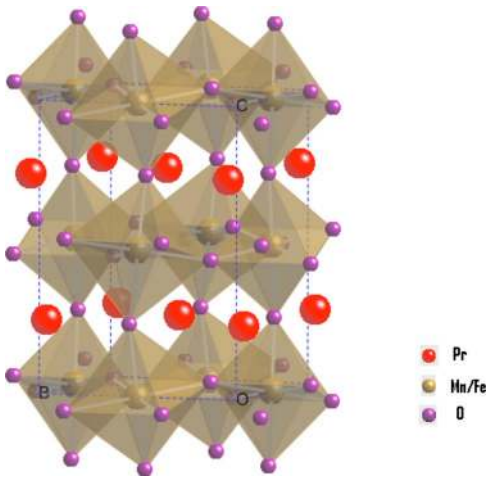

FIG. 2. (Color online) A perspective view of the orthorhombic crystal structure of PMFO. Mn/Fe are at the center of each octahedra.

$\chi^2 = 1.605$. The Rietveld analysis of the XRD data confirms the phase purity of the sample synthesized and has an orthorhombic structure (Fig. 1). Structure model of PMFO using the refined coordinates is shown in Fig. 2. The refined lattice parameters are given in Table I, whereas structural details are given in Table II. The Mn and Fe ions are distributed randomly in the B and B′-sites of $A_2BB'O_6$.

B. Magnetic properties

The temperature dependent magnetization of PMFO at an applied field of 100 Oe is shown in Fig. 3. Below 200 K, the field cooled (FC) curve shows spontaneous ordering indicating a FM-like transition. The magnetic interaction of Fe^{3+} and Mn^{3+} is determined by superexchange interaction, Dzyaloshinsky–Moriya interaction, and magnetic anisotropy of Fe^{3+} and Mn^{3+} ions.[6] The magnetic interactions in this system can be quite complex as the B-site ions are disordered and we have to consider the Fe^{3+}–O–Mn^{3+}, Fe^{3+}–O–Fe^{3+}, and Mn^{3+}–O–Mn^{3+} superexchange interactions. The FC curve gradually increases with decreasing temperature, due to the presence of FM interactions in the sample. Around 50 K, the Pr moments starts ordering and the ordering of Pr^{3+} ions with the nearest neighbor transition metal ions cannot be understood from the magnetic measurements alone.[7] The ordering of Pr^{3+} ions below 50 K indeed affects the conductivity as can be seen from the increase in resistivity, as shown in Fig. 6. This can even be a FM ordering of Pr moments arising due to the exchange coupling between 4f spins of Pr ions and neighboring spins of Fe/Mn ions, as reported earlier.[7] Figure 4 shows the field dependent magnetization of PMFO at different temperatures. It exhibits a hysteresis loop at temperatures from 2 K to 300 K, reflecting the FM interaction between Fe^{3+} and Mn^{3+} ions. However, the magnetization does not saturate even at fields as high as 7T, which indicates the presence of AFM interactions along with FM interactions or the absence of a true long range FM order, with the AFM interaction bringing in the disorder factor. It can also be considered as a coexistence of FM and AFM clusters, which explains the absence of a saturation magnetization. The remanent magnetization and coercive field of PMFO, at 2 K, is found to be $0.6169\mu_B$/f.u. and 0.4291 T. At 100 K, the observed magnetic moment for an applied field of 7 T is $1.32\mu_B$.The calculated net magnetic moment of the AFM alignment of Fe^{3+} ($5\mu_B$) and Mn^{3+} ($4\mu_B$) is equal to $1\mu_B$ and it will be $4.5\mu_B$ if the arrangement is FM.[8] At 2 K, the observed magnetic moment for the applied field of 7 T is $2.83\mu_B$. The difference in calculated and observed magnetic moment is due to the complex magnetic interactions involved in this system brought about by the random distribution of Fe and Mn ions.

TABLE I. Lattice parameters of PMFO.

PMFO	
a (Å)	5.4728(2)
b (Å)	5.5284(2)
c (Å)	7.7496(3)
V (Å^3)	234.47(3)
Fe/Mn–O (Å)	1.982(2)
Pr-O (Å)	2.553(1)
Mn/Fe–O1–Mn/Fe (°)	154.7(8)
Mn/Fe–O2–Mn/Fe (°)	158.7(5)

TABLE II. Structural parameters of PMFO as obtained from the Rietveld refinement of the XRD data.

Atom	Site	x	y	z	U_{iso}	Occupancy
Pr	4c	0.0083(5)	−0.0375(16)	0.25	1.66(5)	1.0
Mn/Fe	4b	0.5	0	0	0.65(7)	0.5/0.5
O1	4c	−0.0766(27)	0.5131(7)	0.25	1.90(5)	1.0
O2	8d	0.2403(28)	0.2150(20)	0.0423(14)	1.60(4)	1.0

C. Mössbauer spectroscopy

Mössbauer spectroscopy was used to confirm the phase purity and ionic state of the Fe in PMFO. The Mössbauer spectrum of the compound, at room temperature, is shown in Fig. 5. The spectrum can be described in terms of two quadrupole doublets with quadrupole splitting values of 0.51767 and 0.45159 mm/s. The isomer shifts for the doublets are 0.33692 and 0.23989 mm/s, indicating that the Fe^{3+} (high spin)[9] ions are all in octahedral site.

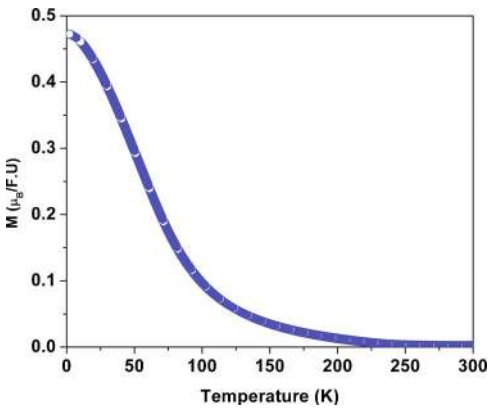

FIG. 3. (Color online) Temperature dependence of FC (100 Oe) magnetization of PMFO.

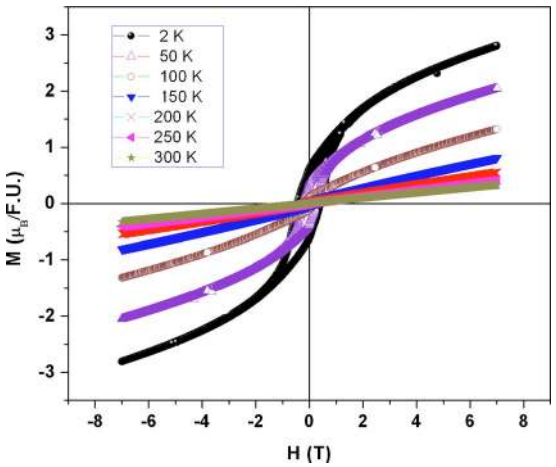

FIG. 4. (Color online) Field dependent magnetization of PMFO at various temperatures.

D. Electrical resistivity

The temperature dependent electrical resistivity is important to understand the effect of Fe substitution in $PrMnO_3$. The temperature variation in electrical resistivity of PMFO, as shown in Fig. 6, shows an insulating behavior. The resistivity at room temperature is found to agree with the report with similar composition of Nagata *et al.*[6] Around 100 K, the resistivity increases sharply, associated with the FM-AFM interaction between Fe^{3+}/Mn^{3+} ions. Below 50 K, resistivity shows a change in slope and an increase in magnitude and this will be due to the ordering of Pr^{3+} moments in the lattice

The double perovskite, Pr_2MnFeO_6 is a disordered system and hence the magnetic interactions are quite complex. The Fe^{3+} ionic state, confirmed by the Mössbauer spectroscopy confirms that the manganese ions are also in the trivalent state. As in the La_2MnFeO_6, the $Fe^{3+}-O-Mn^{3+}$ superexchange interaction is FM.[10] However, the other two superexchange interactions, $Fe^{3+}-O-Fe^{3+}$ and $Mn^{3+}-O-Mn^{3+}$, are AFM in nature. This strong competition between the FM and AFM regions can lead to a cluster glass state, which doesn't allow saturation of the magnetization even at fields as high as 7 T. The ordering of Pr^{3+} ions indeed

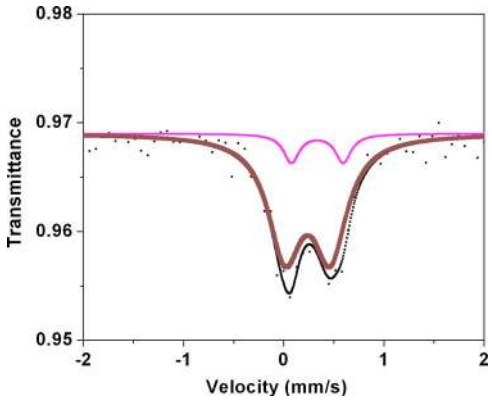

FIG. 5. (Color online) Mössbauer spectrum of PMFO at room temperature. The fit of the two site model for PMFO is represented by thick and thin line for Fe^{3+}.

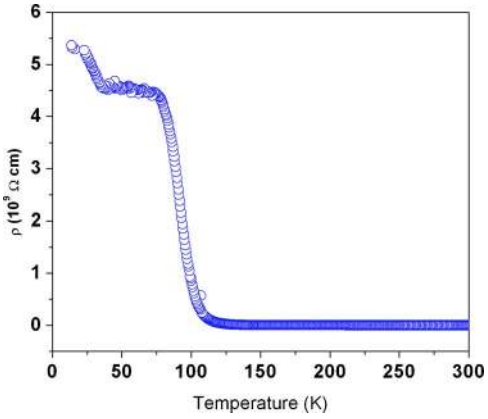

FIG. 6. (Color online) Temperature dependence of resistivity of PMFO.

have some effect on the increase in magnetic moments at low temperatures and this seems to affect the conductivity, shown as an increase in resistivity at low temperatures. We need to carry out neutron diffraction studies to figure out the ordering nature of Pr^{3+} ions with other magnetic ions in the system. The increase in resistivity at low temperatures is in tune with the magnetic glassy nature of the sample.

IV. CONCLUSION

The polycrystalline double perovskite Pr_2FeMnO_6 is found to have an orthorhombic structure with *Pbnm* space group. The FC curve shows a weak FM behavior that can be explained by the competitions between the FM-AFM interactions. Mössbauer spectrum indicates that the Fe^{3+} ions are occupying octahedral sites with high spin state. Magnetic ordering of Pr^{3+} ions has a direct influence on the increase in resistivity below 50 K. A detailed study on the magnetic properties by looking at the ac susceptibility and specific heat along with neutron diffraction data has to be done to understand this system perfectly.

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