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Magnetic Behaviour of Fe Doped PrCrO₃ Perovskite

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ABSTRACT: PrCr_{1-x}Fe_xO₃ (PCFO) samples were prepared by Sol-Gel method. The characterization is done by SEM & XRD. It is found from the characterization that they belong to orthorhombic structure and Pbnm space group. The Temperature dependent and field dependent magnetic measurements are measured in the range of 5K- 400K at 100 Oe field and isothermal magnetization curves were recorded in the field range +5T to -5T at 5K temperature. The substitution of Fe³⁺ in Cr³⁺ site increases the Cr-O-Fe ferromagnetic superexchange interaction and thus increase in magnetic moments, with maximum at x=0.8. The frustration of co-existence of antiferromagnetism and ferromagnetism leads to decrease of magnetic ordering transition temperature from 240K to 98K.

KEY WORDS: Multiferroic, Superexchange, Canted, magnetization

I. INTRODUCTION

Multiferroic materials are attracting great attention in the last few years because of their potential applications [1-3]. Most of the multiferroic investigated in recent years are ABO₃ oxides with a perovskite structure [2-4]. In ABO₃ structure, the zero occupancy of the transition metal B cation are chemically known to favor ferroelectricity [5, 6]. While the availability of transition metal d electrons in the perovskite oxides necessary for magnetism reduces the tendency for off-centering ferroelectric distortions [5]. Hence, ferromagnetism and ferroelectricity seem to be mutually exclusive in perovskite structure oxides and the scarcity of ferromagnetic and ferroelectric materials has stimulated many theoretical and experimental works [7-9]. The design for the materials with a large ferromagnetic ordering is still a challenge. Previous studies on Cr-doped rare earth (Re) ferrites, ReFe_{1-x}Cr_xO₃ with ABO₃ perovskite structures have predicted their possible strong ferromagnetic (FM) coupling [10, 11]. According to the Kanamori-Goodenough (KG) rule, Fe(d₅)-O-Cr(d₃) would show FM behavior through super exchange interaction when Fe and Cr were arranged orderly at B sites. Suchomel et al. [12] prepared the room temperature multiferroic solid BiFe_{0.5}Cr_{0.5}O₃ at high pressure, but it is still AFM, even though FM and ferroelectric Bi₂NiMnO₆ were synthesized by a similar process [13]. So far, FM spin order was found in LaCrO₃-LaFeO₃ superlattice, artificially created by laser molecular beam epitaxy, where layered CrO and FeO were stacked alternately along [111] direction [14]. In this paper we report the temperature dependent and field dependent magnetic properties of the PrCr_{1-x}Fe_xO₃ samples prepared by citric acid route. From these studies it is found that substitution of Fe³⁺ in Cr³⁺ site in PrCrO₃ perovskite increases the ferromagnetic moment due to Fe-O-Cr superexchange interaction and the magnetic ordering decreases with increase in Fe content.

II. EXPERIMENTAL DETAILS

Polycrystalline powders of PCFO (x=0.0, 0.2, 0.4, 0.6, 0.8, 1.0) were prepared by the citric acid route. Stoichiometric amounts of Cr(NO₂)₃·6H₂O, Fe(NO₂)₃·9H₂O and Pr₆O₁₁ were taken. Pr₆O₁₁ is converted into nitrate by adding concentrated HNO₃ and evaporated to dryness. All the nitrates were dissolved in de-ionized water. Citric acid was added in 1:2 ratio of metal Nitrate to citric acid. The solution was stirred and simultaneously heated at 80°C to evaporate water until a sol was obtained, and then ethylene glycol was added as fuel. The resulting gel was combusted. Collected powders were annealed at 650 °C for 2 h. Circular pellets were pressed at 4000 kgcm⁻² in uniaxial disc. These pellets were sintered at 1200 °C for 4h. The field dependent and temperature dependent magnetic measurements are performed using MPMS made Quantum Design Inc (USA) with the precision of 0.5K for temperature and 0.33 Oe for magnetic field between 5K to 400K in ZFC and FC modes with an applied field of 100 Oe. The isothermal magnetization curves were measured in the range of + 5T and -5T at 5K temperature. Sintered pellets were characterized by X-ray diffraction (XRD) using SHIMADZU XRD - 7000 using monochromatic Cu Ka radiation.

Microstructure and the grain size distribution of the sintered pellets were studied using a Scanning Electron Microscope (SEM) HITCHIS-3400 N. Densities of these samples were determined using the Archimedis Principle.

III. RESULTS

All the samples were characterized by room temperature XRD. Figure 1 shows the XRD patterns of the PCFO ($x=0.0, 0.2, 0.4, 0.6, 0.8, 1.0$). All the peaks were indexed to orthorhombic system associated with space group Pbnm. The lattice parameters were determined using UFIT Powder diffraction data analysis software [15]. The variation of unit cell parameters with Fe content (x) of PCFO is shown in fig 2. The lattice parameters for PrCrO_3 and PrFeO_3 are well in agreement with that reported literature [16,17]. As seen in increase with increase of Fe content, such a monotonous

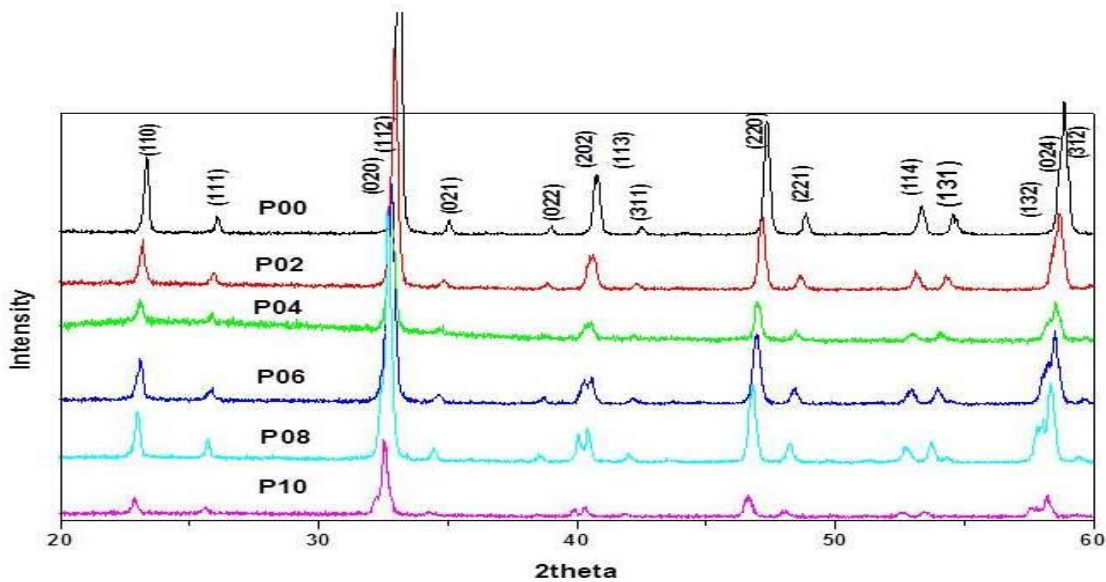


Fig.1 Patterns of PCFO samples for Fe content from $x=0.0$ to $x=1.0$

Table : Sample Codes Followed Throughout The Text

x	Formula	Code
0.0	PrCrO_3	P00
0.2	$\text{PrCr}_{0.8}\text{Fe}_{0.2}\text{O}_3$	P02
0.4	$\text{PrCr}_{0.6}\text{Fe}_{0.4}\text{O}_3$	P04
0.6	$\text{PrCr}_{0.4}\text{Fe}_{0.6}\text{O}_3$	P06
0.8	$\text{PrCr}_{0.2}\text{Fe}_{0.8}\text{O}_3$	P08
1.0	PrFeO_3	P10

increase is associated with the incorporation of bigger Fe^{3+} ion (0.645 \AA) into the site of Cr^{3+} (0.615 \AA). The fact of single phase and gradual increase in lattice parameters imply the incorporation of Fe^{3+} ion into B (Cr^{3+}) of ABO_3 perovskite. Typical SEM micrographs of PCFO pellets sintered in air at 1200°C for 4 hrs are shown in Fig. 3.

From Fig.P00,i.e.forx=0.0, it can be seen that the pellets of PrCrO₃ consists of porous and small grains with estimated average grain size of150 nm. The increase in Fe content increased the average grain size and decreased the porosity tremendously (fig 3).Theceramic density (d) of samples were estimated by Archimedesmethod and compared them to expected from the theoreticalX-ray density (dth), the ratio d/dth of all samples are increased from 40% (x=0) to 90% (x=1) are in consistent with theresults of SEM micrographs..Fig 4.shows the temperature dependence magnetization both in FC and ZFC modes at 100 Oe. The magnetization isstrongly depended on composition. It can be seen in Fig 4 that there exist two magnetic transitions marked as T_{N1} and T_{N2} in all the samples. The transition temperatures were

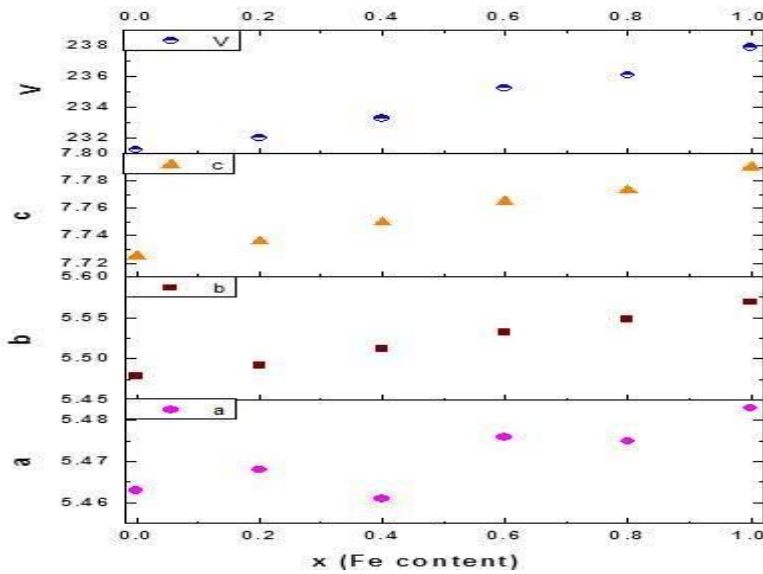


Fig. 2 The unit cell parameters (a,b,c) and volume (V) with Fe content PCFO samples

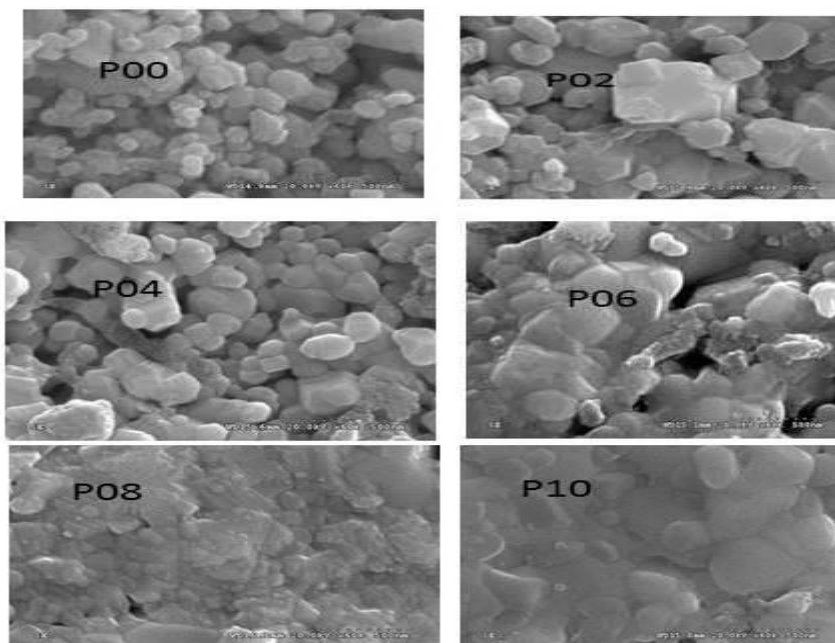


Fig 3:SEM micrographs of PCFO samples

estimated by taking dM_{FC}/dT vs T curve (seen in inset of P00 of Fig 4). The variation in transition temperature (Neel Temperature) with composition is shown in Fig.5. It can be observed from Fig. 5 that the T_{NI} value decreased from

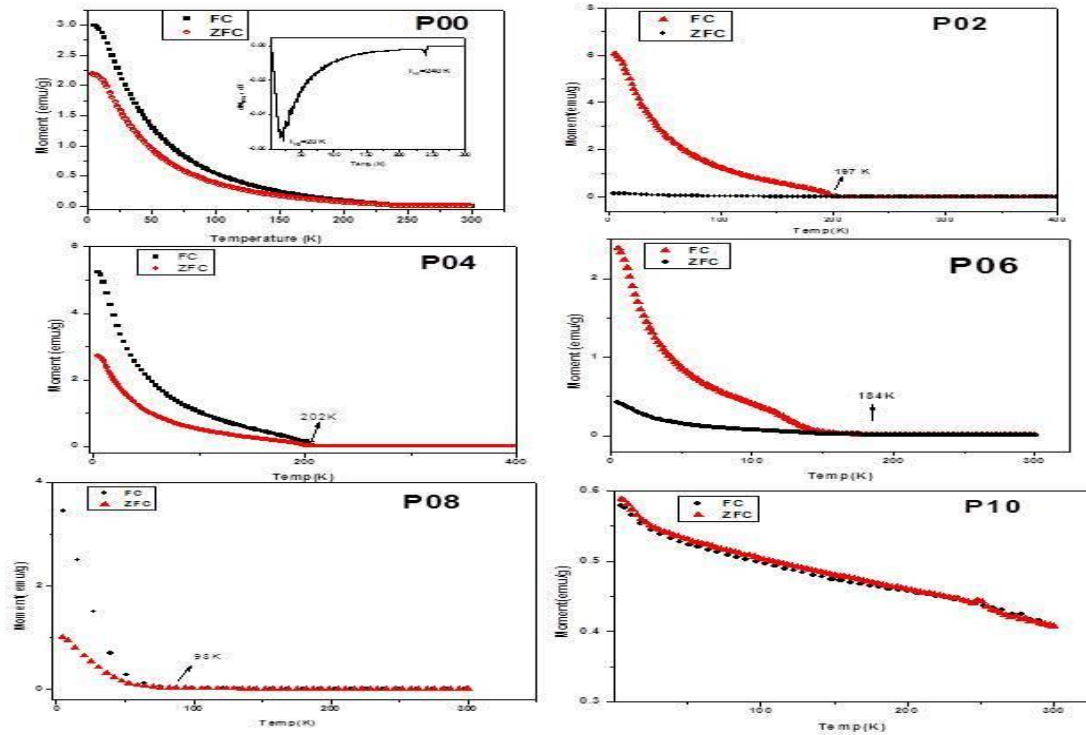


Fig 4: Temperature dependent magnetization curves of PCFO samples for Fe content from $x=0.0$ to $x=1.0$ (Inset of P00 is dM_{FC}/dT vs Temp for $x=0.0$)

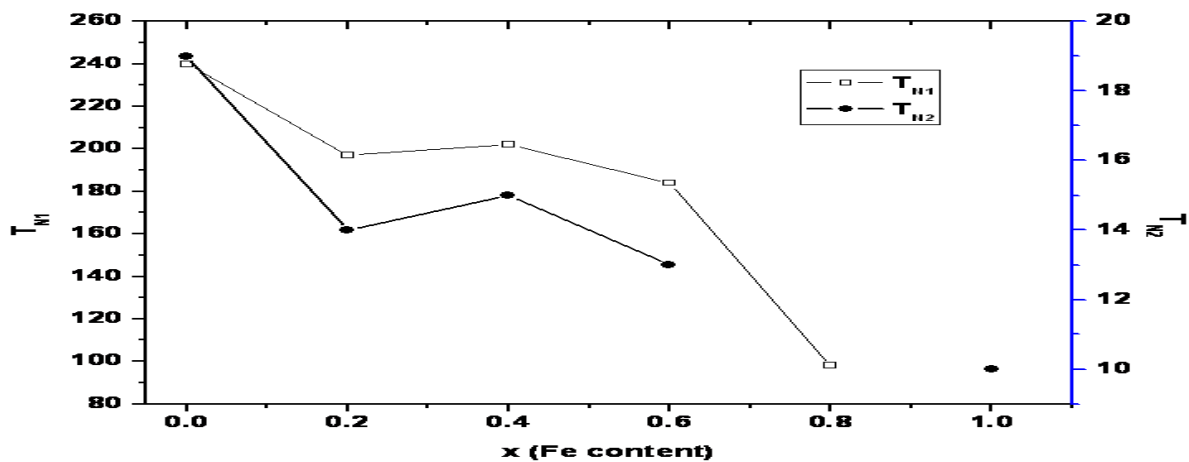


Fig. 5 Variation of Neel temperature of PCFO samples of Fe content from $x=0.0$ to $x=1.0$

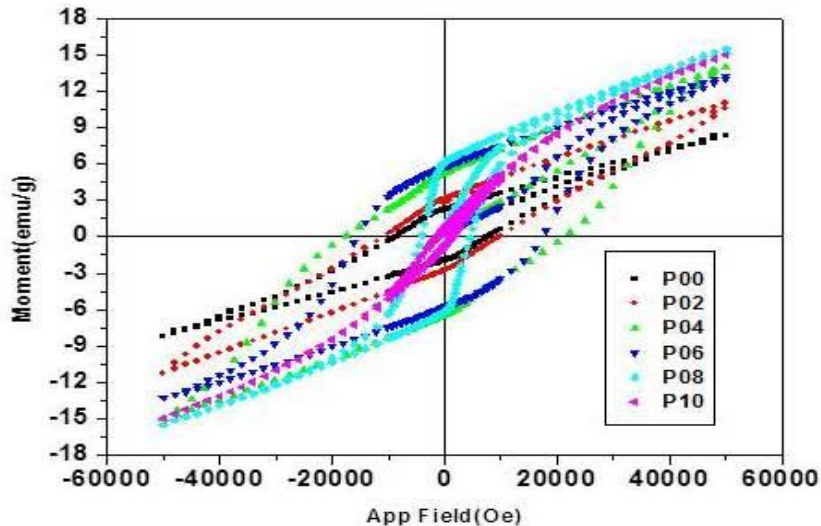


Fig. 6 Field dependent magnetization curves of PCFO samples at 5K

240 K at $x=0.0$ to 98 K with increase in Fe content upto $x=0.8$. For the sample PrFeO_3 ($x=1$), transition temperature was beyond the measuring temperature range, whereas T_{N2} value changed slightly with composition. In CrO_6 octahedron, if the temperature is low enough, the super exchange interaction between the large spins on the nearest Cr^{3+} ions sandwiching O^{2-} ion is generated resulting in anti-parallel spin configuration. Due to the orthorhombic distortion of PrCrO_3 structure, Cr-O-Cr bond angle slightly deviates from 180° , resulting in residual electronic spin originating from imperfect super exchange interaction and showing that the sample PrCrO_3 is canted antiferromagnetic (AFM) below $T_{N1}=240$ K. The ferromagnetic component is due to the AFM exchange interaction between Cr^{3+} spins [18, 19]. For change at T_{N2} , it would be caused from rare earth Pr^{3+} spin ordering in antiferromagnetic arrangement [20, 21]. A small change in T_{N2} with Fe content indicates that the dopant is not affecting the Pr^{3+} spin ordering. Fig 6 gives the isothermal M-H loops of PCFO at 5 K indicate presence of FM behavior in all samples. However, none reached the saturation up to 5T field. The remnant magnetization (M_r) and maximum magnetization (M_{MAX}) were estimated and their variation with composition is shown in Fig. 7. It can be noticed that the M_{max} and M_r showed the same tendency with magnetization versus temperature. Both of them increased from $M_{MAX}=8$ emu/g, $M_r=2.18$ emu/g respectively at $x=0.0$ and reached maximum at $x=0.8$ with $M_{MAX}=15$ emu/g and $M_r=6.0$ emu/g respectively and decreased to 14 emu/g and 0.72 emu/g respectively at $x=1.0$. This trend was formed by the substitution of Fe^{3+} ion for Cr^{3+} ion, which entered into the lattice of PrCrO_3 . Similar tendency was observed by Kuznetsov et al [22]. As discussed earlier PrCrO_3 is canted AFM due to Cr-O-Cr exchange interaction below T_{N1} . As Fe^{3+} ions are incorporated into B-site, three exchange interactions may be present due to the random distribution of the B-site cations, Fe-O-Fe, Fe-O-Cr and Cr-O-Cr. It is well known that Cr-O-Cr and Fe-O-Fe are AFM interactions, whereas Fe-O-Cr superexchange interaction shows FM interaction [23], which will enhance the magnetization with increase of Fe content. The Cr-O-Fe interaction increased leading to FM cluster in the lattice and reached maximum at $x=0.8$ as seen in Fig. 7. The PrFeO_3 ($x=1.0$) sample consists of only Fe-O-Fe, AFM interaction exists there by M_r and M_{MAX} decreased. According to KGrule [24, 25], combined Cr-O-Fe linkages would show FM behavior through superexchange interaction when Fe^{3+} and Cr^{3+} ions were arranged orderly in B-sites. However, no saturated magnetic moment was found even at $x=0.8$ in this work, due to the mixed distribution of Fe-O-Fe, Cr-O-Cr and Fe-O-Cr exchange interactions. The decrease of magnetic ordering in

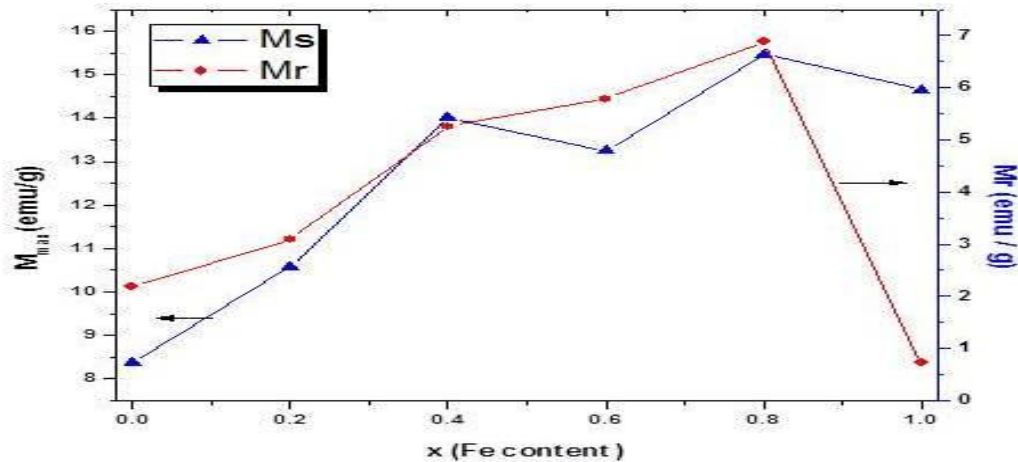


Fig. 7 Variation of Mmax and Mr of PCFO samples with Fe contents

transition temperature (T_{N1}) with increase in Fe content upto $x=0.8$ may be due to frustration of co-existence of FM and CAFM phase.

IV. CONCLUSIONS

All the samples of $\text{PrCr}_{1-x}\text{Fe}_x\text{O}_3$ compound were synthesized using citric acid route and well characterized by XRD and SEM micrographs. The substitution of Fe^{3+} in Cr^{3+} site increases the Cr-O-Fe ferromagnetic superexchange interaction and thus increase in magnetic moments, with maximum at $x=0.8$. The frustration of co-existence of antiferromagnetism and ferromagnetism leads to decrease of magnetic ordering transition temperature from 240 K ($x=0.0$) to 98 K ($x=0.8$).

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