Effect of Gd/Nd doping on the magnetic properties of PrMnO₃

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Abstract
A study on temperature dependent magnetic properties of single-phase orthorhombic perovskites system associated with space group \textit{Pbnm} compounds Pr$_{1-x}$(Gd/Nd)$_x$MnO$_3$ ($x = 0.3, 0.5, 0.7$) was carried out. A magnetization reversal is observed below the Néel temperature ($T_N$), in dc magnetization measurements (at 50 Oe) in the doped compounds. This may be due to the antiparallel coupling between the two magnetic sublattices (Pr + Gd/Nd and Mn). With lowering of temperature, the Pr + Gd/Nd ions begin to polarize under the negative internal field due to canted moment of Mn moments. The hysteresis plot taken at 50 K shows a ferrimagnetic characteristic and the presence of spin canting of ions in the magnetic sublattices. Arrott plot indicates field induced second-order paramagnetic to ferrimagnetic (PM–FiM) phase transition in this system.

Keywords: manganite, magnetic properties, exchange interaction, magnetization reversal

1. Introduction
Rare-earth transition metal oxides (RTmO$_3$) are still a centre of attention due to their potential application as multifunctional materials \cite{1-6}. A large number of studies have been performed since the last decade to elucidate the nature of spin, charge, orbital ordering or the exchange interaction of the transition metals. The magnetic moments of rare-earth ions have been polarized due to the coupling with the Mn subsystem and affect the low-temperature magnetic and thermodynamic properties of the manganites as observed in PrMnO$_3$ and NdMnO$_3$ \cite{6, 7}. Yoshii \textit{et al} \cite{8} studied GdCrO$_3$ and showed that rare-earth ions (Gd) and transition metal ions (Cr) canted or aligned in opposite directions. In Nd$_{1-x}$Ce$_x$MnO$_3$ manganite the low temperature magnetization reversal phenomenon has been described by the ferrimagnetic coupling between Mn$^{3+}$/Mn$^{4+}$ and Mn$^{3+}$/Mn$^{4+}$ sublattices \cite{9}. It has been shown earlier \cite{5} that in Gd$_{0.5}$Ce$_{0.5}$Mn$_{1.5}$O$_4$, magnetic moment of Gd ions aligned against the Cr and Mn ions. Sharma \textit{et al} \cite{10} showed that for La$_3^{3+}$ non-magnetic, reversal of magnetization in La$_{0.5}$Gd$_{0.5}$CrO$_3$ is due to canted opposite direction of the magnetic moment of Gd and Cr. Again in Sr$_{2}$YbRuO$_6$ \cite{11} Ru and Yb are canted in opposite directions. This type of reversal of magnetization has also been discovered in La$_{1-x}$Pr$_x$CrO$_3$ \cite{12}, Bi$_{0.3}$Ca$_{0.7}$Mn$_{0.75}$Cr$_{0.25}$O$_3$ \cite{3}, La$_{1-x}$Gd$_x$MnO$_3$ \cite{13}, La$_{1-x}$Ce$_x$CrO$_3$ \cite{14} and explained considering two sublattices system which are aligned antiparallel to each other. Again in YFe$_{1-x}$Mn$_x$O$_3$ \cite{15} manganites, the magnetization reversal has originated from the random occupation of magnetic ions and different magnetic interactions such as Fe–O–Fe, Fe–O–Mn and Mn–O–Mn. In LaVO$_3$ \cite{16}, orthovanadate which undergoes a transition from orthorhombic (space group \textit{Pbnm}) to monoclinic (space group P2$_1$/b11) unit cell symmetry below the Néel temperature ($T_N$) which causes the reversal of magnetization.

So the magnetization properties drastically changes with the replacement of one rare earth ion with another. In this paper, we have investigated the magnetic properties of the solid solutions of Pr$_{1-x}$Gd$_x$MnO$_3$ and Pr$_{1-x}$Nd$_x$MnO$_3$ ($x = 0.3, 0.5, 0.7$) and it is interesting to observe how the magnetic properties change with doping of Gd or Nd ions in place of Pr.

2. Experimental
The polycrystalline samples Pr$_{1-x}$(Gd/Nd)$_x$MnO$_3$ ($x = 0.3, 0.5, 0.7$) were prepared following standard solid state ceramic
method using high purity oxides Pr$_2$O$_3$, Gd$_2$O$_3$, Nd$_2$O$_3$ and MnO$_2$. Starting materials were mixed in proper stoichiometric ratio, ground and then heated at 900 °C for 24 h. The mixed powders thus obtained were reground, pelletized and sintered at 1500 °C for 24 h and cooled down to room temperature at a rate of 100 °C h$^{-1}$. Structural characterization was done by powder x-ray diffraction (XRD) measurements using CuK$_α$ radiation (Philips diffractometer). The Rietveld analysis of the XRD data using FULLPROF program [17] gives the lattice parameters.

A Quantum Design magnetometer (SQUID) was used for the magnetic measurement. Temperature dependent magnetization ($M$–$T$) data were recorded in the temperature range 5–200 K in both zero field cooled (ZFC) and field cooled (FC) modes under externally applied magnetic field 50 Oe. The samples were first cooled down to 5 K in zero field for ZFC measurements, an external magnetic field (50 Oe) was applied and magnetization was recorded in the presence of this field in the warming cycle. Again, the samples were cooled under the presence of an external field of the same strength then the samples were heated up to 200 K and magnetization was recorded in the cooling cycle for FC measurements. Magnetization ($M$) isotherms were recorded at 50 K on Pr$_{0.5}$Gd$_{0.5}$MnO$_3$ and Pr$_{0.5}$Nd$_{0.5}$MnO$_3$ up to an applied magnetic field ($H$) of ±70 kOe.

### 3. Results and discussion

A powder x-ray diffraction (XRD) pattern of Pr$_{0.5}$Gd$_{0.5}$MnO$_3$ and Pr$_{0.5}$Nd$_{0.5}$MnO$_3$ taken at room temperature is shown in figure 1. The Rietveld refinement of XRD peaks were indexed to the single-phase orthorhombic perovskites system associated with space group Pbnm in which the following parameter relation is observed: $b > a > c / \sqrt{2}$ for all the samples. This relation indicates a static Jahn–Teller (J–T) distortion [13]. The obtained lattice parameters values are in between the end compounds GdMnO$_3$, PrMnO$_3$, NdMnO$_3$ reported earlier [1, 6]. With the increase of Gd and Nd concentration, the lattice parameters $a$ and $c$ decrease, whereas $b$ increases and the volume decreases, as shown in table 1. The parameter $\varepsilon = (b - a)/(a + b)$ describes the orthorhombic distortion [13]. The distortion and lattice parameters changes with the doping concentration (table 1).

The change of distortion and lattice parameters due to substitution of Pr$^{3+}$ ions (ionic radius = 1.09 Å) by the Gd$^{3+}$ ions (ionic radius = 0.938 Å) is greater than the Nd$^{3+}$ ions (ionic radius = 1.08 Å) [18].

The temperature dependent dc magnetization of Pr$_{1-x}$Gd$_x$MnO$_3$ and Pr$_{1-x}$Nd$_x$MnO$_3$ ($x = 0.5, 0.3, 0.5, 0.7$) under the external applied field 50 Oe in ZFC and FC processes is presented in figures 2(a), (b) and 3(a), (b), respectively. The ZFC magnetization displayed a positive maximum below the Néel temperature for all the compounds. The temperature at which magnetization becomes maximum is considered as $T_{\text{max}}$. Ferromagnetic (FM) ordering has been observed in Pr$_{0.7}$Gd$_{0.3}$MnO$_3$ and Pr$_{0.7}$Nd$_{0.3}$MnO$_3$ but is missing in other samples because larger magnetic anisotropy arises with increasing doping concentration ($x = 0.5, 0.7$). With decreasing temperature, the ZFC magnetization decreases and reaches zero at compensation temperature ($T_{\text{comp}}$) 13, 24, 34 K for Pr$_{1-x}$Gd$_x$MnO$_3$ ($x = 0.3, 0.5, 0.7$), respectively, and 18 K for Pr$_{0.7}$Nd$_{0.3}$MnO$_3$. Below the $T_{\text{comp}}$, the ZFC magnetization shows a negative value. The reason for this characteristic may be due to the small magnetic moment of Nd ions compared to the Gd ions and larger magnetic anisotropy arises in the sample due to Gd doping than the Nd doping. So, the Pr and Gd ions are more and more aligned opposite to the Mn moments due to the external field and internal field of the Mn moment. So the magnetic moment of Pr$^3+$Gd easily surpasses the magnetic moment of the Mn and shows the negative magnetization in Pr$_{1-x}$Gd$_x$MnO$_3$ ($x = 0.3, 0.5, 0.7$). But the magnetic moment of Pr$^3+$Nd for Pr$_{1-x}$Nd$_x$MnO$_3$ ($x = 0.5, 0.7$) does not exceed the magnetic moment of the Mn and is unable to show negative magnetization. The FC magnetization also increases with the decrease of temperature and shows a positive maximum magnetization ($M_{\text{max}}$) at respective $T_{\text{max}}$ below the Néel temperature ($T_N$). With decreasing temperature the FC magnetization decreases and reaches zero at the compensation temperature ($T_{\text{comp}}$) 14, 29, 36 K for Pr$_{1-x}$Gd$_x$MnO$_3$ ($x = 0.3, 0.5, 0.7$) and 18, 22 K for Pr$_{1-x}$Nd$_x$MnO$_3$ ($x = 0.3, 0.5$), respectively. Below the $T_{\text{comp}}$.
The magnetization becomes negative and reaches $M_{\text{min}}$ at temperature 5 K. The reversal of magnetization can simply be explained in these samples considering $M_{\text{Mn}}$ is parallel to the applied field but $M_{\text{|Pr+A|}}$ ($A = \text{Gd/Nd}$) are anti-parallel to the field. With dropping of temperature, the disordered $M_{\text{|Pr+A|}}$ ions begin to polarize against the canted field of $M_{\text{min}}$ moments. The net magnetization of the system becomes $M = M_{\text{Mn}} - M_{\text{|Pr+A|}}$. When the temperature drops from $T_{\text{max}}$, the value of $M_{\text{|Pr+A|}}$ rises considerably quicker than $M_{\text{Mn}}$. At the compensation temperature ($T_{\text{comp}}$), the magnetizations of the two sublattices become identical and net magnetization turns into zero. Below the $T_{\text{comp}}$ the net magnetization becomes a negative value.

The solid lines in figures 2(a), (b) and 3(a), (b) show that the magnetization ($M$) can well be approximated by\cite{5, 6, 11}

$$M = M_{\text{Mn}} + \frac{C_{\text{Gd/Nd}}(H_{\text{int}} + H_{\text{ext}})}{(T - \Theta_W)} \quad (1)$$

Where $M_{\text{Mn}}$, $H_{\text{int}}$, $H_{\text{ext}}$, $C_{\text{Gd/Nd}}$, $\Theta_W$ stand for the canted moment of Mn, internal field due to the canted Mn moment, applied field, Curie constant and Weiss constant, respectively. The constraint of this analysis has been made to assume that $M_{\text{Mn}}$ and $H_{\text{int}}$ are independent of temperature, which is usually true if $T \ll T_N = T_{\text{N exp}}$. It would be interesting to compare the parameters obtained from the fitting using the equation (1). The positive value of $M_{\text{Mn}}$ is consistent with the result that the magnetization goes through a positive maximum before

| Compounds | $a \pm 10^{-3}$ (Å) | $b \pm 10^{-3}$ (Å) | $c \pm 10^{-3}$ (Å) | $V \pm 10^{-3}$ (Å$^3$) | $\varepsilon = (b-a)/(a+b)$ |
|-----------|---------------------|---------------------|---------------------|---------------------|---------------------|
| $\text{Pr}_{0.7}\text{Gd}_{0.3}\text{MnO}_3$ | 5.4066 | 5.8294 | 7.5372 | 237.5516 | 0.0376 |
| $\text{Pr}_{0.7}\text{Gd}_{0.3}\text{MnO}_3$ | 5.3795 | 5.8408 | 7.5065 | 235.8616 | 0.0411 |
| $\text{Pr}_{0.3}\text{Gd}_{0.7}\text{MnO}_3$ | 5.3537 | 5.8492 | 7.4780 | 234.1726 | 0.0442 |
| $\text{Pr}_{0.7}\text{Nd}_{0.3}\text{MnO}_3$ | 5.4378 | 5.8163 | 7.5749 | 239.58 | 0.0336 |
| $\text{Pr}_{0.5}\text{Nd}_{0.5}\text{MnO}_3$ | 5.4316 | 5.8195 | 7.5687 | 239.24 | 0.0344 |
| $\text{Pr}_{0.3}\text{Nd}_{0.7}\text{MnO}_3$ | 5.4239 | 5.7977 | 7.5597 | 237.73 | 0.0333 |

Table 1. The values of the lattice parameters and orthorhombic distortion of $\text{Pr}_{1-x}\text{Gd}_x\text{MnO}_3$ ($x = 0.3, 0.5, 0.7$).
reaching the compensation point and the values change from 280 emu mol$^{-1}$ to 820 emu mol$^{-1}$ in FC mode and 47 emu mol$^{-1}$ to 290 emu mol$^{-1}$ in ZFC mode for different samples. $M_{\text{MB}}$ has been used as a fitting parameter and considered to be constant well below the temperature $T_{\text{max}}$. The Weiss constant $\theta_{\text{W}}$ shows a negative value (up to $-9$ K). The internal field ($H_{\text{int}}$) shows also negative value (up to $-10^4$ Oe) for all the samples. The negative value of the internal field ($H_{\text{int}}$) directs that its direction is contrary to both the applied field and the canted Mn moments. Comparable results have also been observed in Gd$_{0.5}$Ca$_{0.5}$MnO$_3$ [5], Bi$_{0.3}$Ca$_{0.7}$Mn$_{0.75}$Cr$_{0.25}$O$_3$ [3], GdCrO$_3$ [8], and La$_{0.5}$Gd$_{0.5}$CrO$_3$ [10].

The dc susceptibility ($\chi$) above the transition temperature ($T_{\text{max}}$) curve follows a Curie–Weiss behaviour $\chi = \mu_{\text{eff}}^2/8(T-\Theta)$, as shown in figures 4(a) and (b). Positive paramagnetic temperature $\Theta$ is obtained for Pr$_{1-x}$Gd$_x$MnO$_3$ but negative $\Theta$ is obtained for Pr$_{1-x}$Nd$_x$MnO$_3$ ($x=0.5$ and 0.7). However, for Pr$_{1-x}$Nd$_x$MnO$_3$ ($x=0.5$ and 0.7), all samples shows a positive $\Theta$ value. These outcomes imply that, the samples change from ferromagnetic background to ferrimagnetic background with doping of Gd but ferromagnetic background remains in the Nd doping samples. Effective magnetic moment ($\mu_{\text{eff}}$) per mole for all the samples could be obtained from the fitting using Curie–Weiss law. The value of $\mu_{\text{eff}}$ for the samples Pr$_{1-x}$Gd$_x$MnO$_3$ ($x=0.3$, 0.5, 0.7) are larger than the samples Pr$_{1-x}$Nd$_x$MnO$_3$ ($x=0.3$, 0.5, 0.7) due to the large magnetic moment of Gd ions compared to the Nd ions. The quantum mechanical spins of different magnetic ions to calculate $\mu_{\text{eff}}$ per mole are: $2^2\mu_B^2(1-x)/2\times 9/2$ form Pr$^{3+}$; $2^2\mu_B^2(x\times 3/2\times 5/2)$ from Nd$^{3+}$; $2^2\mu_B^2(4/2\times 6/2)$ from Mn$^{3+}$. Theoretically from the quantum mechanical spins we calculate $\mu_{\text{eff}}$ per mole for Pr$_{1-x}$Gd$_x$MnO$_3$ ($x=0.3$, 0.5, 0.7) are 6.96$\mu_B$, 7.71$\mu_B$, and 8.4$\mu_B$, respectively, and for Pr$_{1-x}$Nd$_x$MnO$_3$ ($x=0.3$, 0.5, 0.7) are 5.839$\mu_B$, 5.958$\mu_B$, 6.074$\mu_B$, respectively. The Curie–Weiss law gives from experimental result $\mu_{\text{eff}}$ per mole for Pr$_{1-x}$Gd$_x$MnO$_3$ ($x=0.3$, 0.5, 0.7) are 6.79$\mu_B$, 7.95$\mu_B$, 8.17$\mu_B$, respectively, and for Pr$_{1-x}$Nd$_x$MnO$_3$ ($x=0.3$, 0.5, 0.7) are 5.54$\mu_B$, 5.429$\mu_B$, 5.77$\mu_B$, respectively. The experimental and theoretical values deviate slightly. This is a very common phenomenon in these type of oxides [4, 19]. This may be due to some of the ions Pr$^3+$Al ($A=\text{Gd/Nd}$) being aligned opposite or canted from the direction of Mn ions due to the magnetic anisotropy in the compounds in the temperature range of Curie–Weiss fit. So the net effective magnetic moment differs from the theoretically and experimentally calculated result.

For better understanding of the magnetic property, field dependent magnetization measurement has been performed at 50 K on Pr$_{0.5}$Gd$_{0.5}$MnO$_3$ and Pr$_{0.5}$Nd$_{0.5}$MnO$_3$. The measurements have been performed after cooling the sample under zero field and the results are shown in figure 5. For Pr$_{0.5}$Gd$_{0.5}$MnO$_3$ the $M–H$ curve shows a small hysteresis with coercive field ($H_C$) $\approx$980 Oe and for Pr$_{0.5}$Nd$_{0.5}$MnO$_3$ the $M–H$ curve shows very small hysteresis (with coercive field ($H_C$) $\approx$350 Oe). A narrow hysteresis loop and a large slope at high fields in $M–H$ curve, suggesting the coexistence of ferromagnetic and antiferromagnetic phases. The hysteresis loops are symmetric about the origin and specify the lack of the exchange bias field for the samples. It is clear due to the spin

![Figure 4](image_url)

**Figure 4.** Temperature dependent inverse magnetic susceptibility of (a) Pr$_{1-x}$Gd$_x$MnO$_3$ ($x=0.3$, 0.5, 0.7) and (b) Pr$_{1-x}$Nd$_x$MnO$_3$ ($x=0.3$, 0.5, 0.7). Solid line is the high temperature fit using equation $\chi = \mu_{\text{eff}}^2/[8(T-\Theta)]$.

![Figure 5](image_url)

**Figure 5.** $M–H$ curves recorded for Pr$_{0.5}$Gd$_{0.5}$MnO$_3$ and Pr$_{0.5}$Nd$_{0.5}$MnO$_3$ at 50 K.
cisting of ions in the magnetic sublattices a large magnetic anisotropy arises in the samples. So the magnetization does not reach any saturation value, the magnetization increasing almost linearly up to the magnetic field \( H = \pm 40 \, 000 \, \text{Oe} \) in the \( M - H \) curve.

Figure 6 shows the Arrott plots of isotherms for \( \text{Pr}_0.5\text{Gd}_0.5\text{MnO}_3 \) at different temperatures near to \( T_{\text{max}} \). One can distinguish the order of the phase transition from the slope of the line. According to previous reports [20, 21] the magnetic transition is second order if all the Arrott plots have positive slope and negative slope essentially indicates that the phase transition is of first order. In our case we get a positive slope for all the plots, so it is clear that the compound shows field induced second-order paramagnetic to ferrimagnetic (PM–FiM) phase transition. Similar second-order phase transition has also been observed for the \( \text{Pr}_0.5\text{Nd}_0.5\text{MnO}_3 \).

4. Conclusions

The solid solution of rare-earth-based single phase orthorhombic perovskites system \( \text{Pr}_{1-x}(\text{Gd/Nd})_x\text{MnO}_3 \) \((x = 0.3, 0.5, 0.7)\) was studied. In all the samples for both the doping element Gd or Nd, an internal field generates due to the Mn sublattice which polarizes the rare-earth ions' magnetic moments in the opposite direction, resembling the situation found in ferrimagnetic systems. The experimental magnetization reverses its sign and shows a negative value in ZFC and FC process. The magnetic moments of rare-earth network vary with temperature when the magnetic moment is larger than the Mn moment leading to a negative magnetization. Due to the large magnetic moment of Gd ions compared to the Nd ions, the samples doped with Gd show larger magnetic anisotropy and magnetization reversal.

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