

Influence of dopant concentration on the structure and physical properties of $\text{Nd}_{1-x}\text{Pb}_x\text{MnO}_3$ single crystals

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Abstract

The structure of $\text{Nd}_{1-x}\text{Pb}_x\text{MnO}_3$ crystals is determined by single crystal X-ray diffraction. Substitution of Pb at the Nd site results in structural phase change from tetragonal ($x = 0.25$) to cubic ($x = 0.37$). These changes are attributed to the progressive removal of inter-octahedral tilting and minimization of the octahedral distortion leading to a higher symmetry as doping concentration increases. While the unit cell volume of tetragonal structure ($P4/mmm$) is comparable to that of parent NdMnO_3 , the volume of cubic unit cell ($Pm\bar{3}m$) is doubled. Electron diffraction patterns support these results and rule out the possibility of twinning. Changes in transport properties as a function of temperature at different doping levels are in accordance with the observed structural changes. It is noticed that T_c and T_{MI} increase with x .

Introduction

Rare-earth manganites exhibiting colossal magnetoresistance (CMR) continue to attract research attention because of diverse physical properties and possible technological applications. Subtle structural changes between multiple phases and their relationship with physical properties have led to detailed structural investigations. The RMnO_3 perovskites (R is any rare earth between Lanthanum and Dysprosium) are orthorhombically distorted ($Pnma$) and isostructural with $\text{GdFeO}_3^{1,2}$. On the other hand, the crystal structure is hexagonal with space group $P6_3cm$ for rare-earths from Holmium to Lutetium as well as Yttrium^{2,3}. Substitution of trivalent lanthanides by divalent alkaline earth ions (Ca, Sr, Ba and Pb) leads to the simultaneous occurrence of Mn^{3+} and Mn^{4+} in the crystal lattice. This modifies the structural and physical properties significantly. A number of structural modifications have been discovered in manganite systems⁴⁻⁷. In general, majority of CMR compounds fall into two types: rhombohedral ($R\bar{3}m$) and orthorhombic ($Pnma/Pbnm$). A structural

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change is noticed in manganites with increase in divalent doping. For example, the structure of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ changes from orthorhombic ($Pnma$) to rhombohedral ($R\bar{3}m$) as doping concentration increases^{6,8}. However, other symmetries are also observed as in the case of $\text{Nd}_{1-x}\text{Sr}_x\text{MnO}_3$ which changes from orthorhombic ($Imma$) to tetragonal ($I4/mcm$) system as x increases⁹. Symmetry relationships between perovskite polymorphs have been investigated from a group theoretical standpoint. This demonstrates a path of continuous phase transition through a sequence of space group-subgroup steps which is consistent with experiments¹⁰.

The parent compounds (LaMnO_3 , NdMnO_3 and PrMnO_3) are A-type antiferromagnetic insulators. Their insulating nature as well as anisotropic magnetic interaction are related to structure. There are two characteristic distortions that influence the perovskite structure of manganites. One relates to co-operative tilting of MnO_6 octahedra which is established below 1000K as a consequence of mismatch of ionic radii between the rare-earth and divalent ions¹¹. This often takes the form of rigid rotations of the MnO_6 octahedra and modifies the co-ordination sphere of the R-site cation¹². The other, Jahn-Teller (JT) distortion arises due to electronic instability of Mn^{3+} in the octahedral crystal field influenceing the MnO_6 octahedra in such a way that there are long and short Mn-O bonds and deviations in O-Mn-O bond angles from 180° . These two distortions play a key role in structural evolution of perovskite manganites. Electronic transport is often strongly influenced by structural changes. For example, in $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ the rhombohedral phase is metallic while the orthorhombic phase is insulating at low temperature^{6,8} where as in $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$, the orthorhombic symmetry is retained both in insulating and metallic phases. Local structural features have profound influence on the conduction mechanisms in manganites¹². As divalent ions are doped in these systems, the ferromagnetic (FM) double exchange (DE) Mn^{3+} -O- Mn^{4+} interaction begins to compete with antiferromagnetic (AFM) super exchange (SE) Mn^{3+} -O- Mn^{3+} interaction. The basic mechanisms of SE and DE interactions are mediated by the d-electron overlap between two transition metal ions via the intervening oxygen p-orbital. The extent of overlap depends on cation-oxygen-cation bond angle and cation-cation bond length in different perovskite systems¹³⁻¹⁵. In manganites, this overlap integral depends on Mn-O-Mn bond angle and Mn-Mn bond length which are sensitive to the tilt of neighbouring MnO_6 octahedra^{6,16}. Hence it is interesting to study the influence of divalent dopant on the local structural modifications and the relevant physical properties. This paper reports the study of Pb substitution in NdMnO_3 and its impact on the structure, transport and magnetic properties.

Crystal Growth

$\text{Nd}_{1-x}\text{Pb}_x\text{MnO}_3$ single crystals are obtained by high temperature solution growth technique using PbO/PbF_2 solvent with Nd_2O_3 , MnCO_3 and PbO in stoichiometric quantities as solute¹⁷. The homogenized mixture was contained in a platinum crucible and growth was carried out in a resistive furnace. The cationic ratio was varied to obtain a range of x values. The composition of resulting crystals was determined by Energy Dispersive X-ray (EDX) Analysis followed by Inductively Coupled Plasma Emission Spectroscopy (ICPAES) for better accuracy.

Structural Studies

A crystal of nominal lead content $x = 0.25$ and size $0.3 \times 0.2 \times 0.04 \text{ mm}^3$ was mounted on a BRUKER AXS SMART APEX CCD diffractometer¹⁸ at a distance of 6.03 cm from the detector. The diffraction intensities were measured with monochromated MoK_α radiation ($\lambda = 0.7107 \text{ \AA}$). The orientation

matrix was obtained at room temperature from reflections derived from 50 frames to give the tetragonal unit cell (Table 1). Data were collected in four batches covering a complete sphere of reciprocal space with each batch at different ϕ angles ($\phi = 0, 90, 180, 270^\circ$) and each frame covering 0.3 degree in ω at 10 seconds exposure time. The data was 98.7% complete to 56° in 2θ . An approximate empirical absorption correction was applied assuming the crystal shape to be cylindrical. Positional coordinates of Nd and Mn atoms were obtained by direct methods using the SHELX97 module and refined by SHELXL97¹⁹. The Nd atoms occupy three crystallographically distinct sites (2e, 1d and 1b). In order to account for the presence of Pb in any of Nd sites, occupancy refinements were carried out (constraining the overall site occupancy to 1.0) indicating that the Pb atom fully occupies the 1d site and amounts to the presence of 25% of Pb at Nd sites. Hence, refinement confirms that Pb and Nd occupy different crystallographic sites (1d and 2e,1b respectively) suggesting ordering at R-site in RMnO_3 perovskite structure²⁰. Difference Fourier synthesis revealed the positions of the remaining oxygen atoms, which were included in the refinement. The occupancy refinements on the oxygen atoms suggest an occupancy of 96% for O(1) and 80% for O(3) leading to an acceptable R index of 8.3% (Table 2). The structure of crystals with higher lead content ($x = 0.4$) was determined in a similar way. A crystal of size $0.18 \times 0.057 \times 0.2 \text{ mm}^3$ was used for data collection. The orientation matrix was obtained from reflections derived from 400 frames at 12 seconds exposure time giving a cubic unit cell. The data was 97.9% complete to 55° in 2θ . An empirical absorption correction was applied assuming the crystal shape to be nearly spherical. The positional coordinates of Pb/Nd and Mn atoms were obtained as before. Occupancy refinements carried out to ascertain the amount of Pb and Nd resulted in a ratio of 57:37 (Nd:Pb) with 96% Nd(2) at 3c site and 72% Nd(3) at 1b site. According to results of refinements it is observed again that Nd and Pb occupy different crystallographic sites (1a, 3c and 1b for Nd and 3d for Pb)²⁰. The occupancy refinements of oxygen atoms indicated full occupancy in their respective sites (Table 2). The results of measurement and structural refinement are summarized in Table 1. The atomic coordinates along with the equivalent thermal parameters are listed in Tables 2 and 3. The packing diagrams of tetragonal and cubic structures are shown in Fig.1(a) and (b). The structural refinement data obtained from single crystal x-ray diffraction experiments are used to simulate the powder x-ray diffraction pattern for both the crystals. Fig.2(a) and (b) show that they are matching well with the experimental powder diffratograms. In order to rule out the possibility of twinning, electron diffraction experiments are carried out. Fig.3(a) and (b) show no evidence of twinning for both the tetragonal and cubic phases. Superlattice spots are seen along a direction for tetragonal and along a and c directions for cubic crystal. Hence, the significance of cell doubling is quite evident for the cubic phase as shown in Fig.3(b).

Physical Properties

Transport and magnetization measurements were carried out on crystals of various doping levels. Resistivity was measured by four probe method in the temperature range 300 to 80 K and shown in Fig.4. Magnetic properties were determined by A.C susceptibility measurements in the same temperature range. All the doped crystals exhibited a paramagnetic to ferromagnetic transition as the temperature is lowered. Transition temperature T_c progressively shifted upwards with increase in x values as seen in Fig. 5.

Results and Discussions

The parent NdMnO_3 has an inherent perovskite distortion due to the presence of Nd in the R-site. As Nd is partially replaced by the larger cation Pb, the distortion is progressively reduced and the symmetry becomes tetragonal at 25% substitution. The distortion is almost removed in the case of 37% lead substitution which results in cubic symmetry as well as cell doubling. It is also evident

from the electron diffraction pattern (Fig.3(b)). The unit cell parameters can be related as $a_t = b_t \approx 2a_p$; $c_t \approx a_p$ for tetragonal structure and $a_c \approx 2a_p$ for cubic structure where a_p is cell parameter of ideal primitive ($Pm\bar{3}m$) perovskite structure. The unit cell consists of corner sharing regular MnO_6 octahedra in which Mn-O bonds become more symmetric as the structure changes from tetragonal to cubic (Tables 4 and 5). However the Pb-O bonds are significantly shorter than the Nd-O bonds in both structures. All Mn-O-Mn bond angles are nearly equal ($178^0(3)$) in cubic structure while they are dissimilar in the tetragonal phase. Consequently the co-operative tilting of MnO_6 octahedra observed in $NdMnO_3$ is reduced considerably in $Nd_{0.75}Pb_{0.25}MnO_{2.72}$ and the least in $Nd_{0.57}Pb_{0.37}MnO_3$. R-site cationic deficiency is noticed in cubic crystals as seen in the formula (after refinement) while tetragonal crystals are oxygen deficient. The oxygen deficiency is known to occur in manganites²¹ while cationic deficiency observed in the cubic structure is rare. The apparent R-site deficiency may be attributed to the refinement result which is strongly affected by excessive X-ray absorption due to higher lead content in the cubic crystal.

Aleksandrov²² and Barnighausen²³ investigated the existence of symmetry relationship between perovskite polymorphs from the view point of group theory. Aleksandrov reports transition routes from $Pm\bar{3}m$ to $Pnma$ symmetry via five intermediate space groups¹⁰. On the other hand, Barnighausen demonstrated path of continuous phase transitions from $Pm\bar{3}m$ to $Pnma$ symmetry via a sequence of space group-subgroup steps $Pm\bar{3}m - P4/mmm - Cmmm - Icmm - Pbnm(Pnma)$ ¹⁰. The structural transformation route observed in the present investigation is in accordance with Barnighausen's prediction, although intermediate stages like $Cmmm$ and $Icmm$ were not observed. These intermediate structures might be discernible at other doping concentrations.

Fig.6 shows the variation of different Mn-O bond lengths with divalent dopant concentration. The static distortion of MnO_6 octahedra is maximum for parent orthorhombic $NdMnO_3$ ($x = 0$)²⁴. The mismatch between different Mn-O bond lengths of $Nd_{1-x}Pb_xMnO_3$ is much less at $x = 0.25$ and 0.37 for the tetragonal and cubic structures respectively. In manganites, $\langle r_A \rangle$ gives the measure of one electron (e_g) band width¹² which is very sensitive to the concentration and ionic radii of divalent dopant. It is noted that when $\langle r_A \rangle \gg 1.31 \text{ \AA}$ ($x = 0.2$) the Mn-O bond lengths are almost equal (inset of Fig. 6). The distortion in perovskite unit cell consequent to its octahedral tilting is estimated by the tolerance factor (t_G). The structural change of $Nd_{1-x}Pb_xMnO_3$ from orthorhombic to cubic (via tetragonal) with increase in x is consistent with the t_G approaching unity. The dependence of t_G on dopant concentration (x) is shown in Fig.7.

It is seen from the temperature dependence of resistivity (Fig.4) that the metal-insulator transition temperature (T_{MI}) (vertical arrows in the figure) increases with x . The magnitude of resistivity at room temperature decreases with increase of x . This is attributed to the increment of Mn-O-Mn bond angle with x (or $\langle r_A \rangle$) which results in increase of Mn-Mn electron hopping rate²⁵. The plot for sample with $x = 0.2$ has a plateau-like region around 127 K suggesting the onset of metallic phase. However the sample exhibits an insulating behaviour as temperature is further lowered. But, the resistivity profile for sample with $x = 0.3$ flattens after 146 K as temperature decreases indicating metal like behaviour. Thus, one can see that the MI transition starts to occur when lead concentration is 20% ($x = 0.2$) in $Nd_{1-x}Pb_xMnO_3$ and becomes more prominent as x increases. From Fig. 4 and 6 it can be inferred that metal insulator transition occurs when $\langle r_A \rangle$ exceeds a critical value $r_{MI} \sim 1.314$ at $x = 0.2$. The Mn-O bond lengths are almost equal at $\langle r_A \rangle \gg 1.314$ where metallicity is observed. This can be due to the removal of static coherent distortion of MnO_6 octahedra which causes charge localization in the metallic phase²⁶.

The direct exchange interaction between Mn ions is not possible in manganites because of the intervening oxygen. According to Goodenough²⁷, the nature of interaction depends on the extent of

overlap between Mn d-orbitals and O p-orbitals which is very sensitive to Mn-Mn distance. In the Mn-O-Mn bonding patterns, if both Mn-O bonds are covalent the Mn-Mn distance will be shortest and interaction will be antiferromagnetic (AFM). If one Mn-O bond is covalent and the other ionic, the Mn-Mn separation is larger and results in ferromagnetic (FM) interaction. Magnetic properties of NdMnO_3 where in-plane FM and out-of-plane AFM interactions have been noticed^{12,27} are consistent with this theoretical prediction. However, the predominant mechanism involved in doped NdMnO_3 is Double Exchange (DE) ferromagnetic interaction. A.C susceptibility data shown in Fig.5 clearly exhibits the presence of FM phase at low temperature in the range of x of the present investigation. In doped systems, Mn^{4+} -O- Mn^{3+} bonding arrangement is degenerate with Mn^{3+} -O- Mn^{4+} . This implies charge hopping between Mn ions leading to metallicity which is observed in the present case at $x \gg 0.2$ (Fig.4). In DE, Mn-Mn distance is shorter than that of the other ferromagnetic case (described before) and hopping integral between Mn d-orbitals is proportional to $\cos(\theta_{ij}/2)$ where θ_{ij} is the angle between two Mn moments at i and j sites²⁸. Since, the direction of the Mn moment relative to the axes of the MnO_6 octahedron is determined in large part by crystal field, it is expected that θ_{ij} will depend on the Mn-O-Mn tilt angle⁶. So, the hopping rate will depend on Mn-O-Mn bond angle^{6,16,25} which in turn will depend on the magnitude of tilt between two neighbouring octahedra. The deviation of Mn-O-Mn bond angle from 180^0 is maximum in NdMnO_3 and decreases with increase of x (Fig.7).The Mn-Mn bond distances and corresponding magnetic interactions for various dopant concentration are shown in Table.6. Thus, it is evident that structural changes due to doping plays an important role to control the physical properties of the system.

Conclusions

The structure of $\text{Nd}_{1-x}\text{Pb}_x\text{MnO}_3$ single crystals are determined for $x = 0.25$ and 0.37 . Structural changes from orthorhombic \rightarrow tetragonal \rightarrow cubic are discernible with increasing dopant concentration (x). No evidence for twinning is observed in electron diffraction experiments. The MnO_6 octahedral distortion and inter octahedral tilt are removed progressively with higher doping. A correlation between the modulation in structure and physical properties has been presented. It is observed that, insulator to metal as well as paramagnetic to ferromagnetic transition temperatures are sensitive to divalent doping concentration.

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Table 1: Crystal data, Measurements and Refinement parameters for $\text{Nd}_{0.75}\text{Pb}_{0.25}\text{MnO}_{2.72}$ and $\text{Nd}_{0.57}\text{Pb}_{0.37}\text{MnO}_3$

Crystal Data

Empirical-Formula	$\text{Nd}_{0.75}\text{Pb}_{0.25}\text{MnO}_{2.72}$	$\text{Nd}_{0.57}\text{Pb}_{0.37}\text{MnO}_3$
Crystal Symmetry	Tetragonal	Cubic
Crystal habit, colour	Blocks, black	Blocks, Black
Crystal Size(mm)	$0.3 \times 0.2 \times 0.04 \text{ mm}^3$	$0.18 \times 0.057 \times 0.2 \text{ mm}^3$
Crystal System	Tetragonal	Cubic
Space group	$\text{P}4/\text{mmm}$	$\text{Pm}\bar{3}\text{m}$
Cell dimensions(\AA)	$a = b = 7.725(1)$, $c = 3.884(1)$	$a = b = c = 7.737(2)$
Volume(\AA^3)	234.19(7)	463.22(2)
Formula Weight	263.09	697.8
Density(calculated)	7.457 g/cm^3	6.73 g/cm^3
Z	4	8
F(000)	457.8	817.7

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Figure Captions

Fig.1 Packing diagram of (a) $\text{Nd}_{0.75}\text{Pb}_{0.25}\text{MnO}_{2.72}$ and (b) $\text{Nd}_{0.57}\text{Pb}_{0.37}\text{MnO}_3$ along the b-direction.
 Fig.2(a) The simulated and experimental powder x-ray diffraction patterns for $x = 0.25$.
 Fig.2(b) The simulated and experimental powder x-ray diffraction patterns for $x = 0.37$.
 Fig.3 Electron diffraction pattern of $\text{Nd}_{1-x}\text{Pb}_x\text{MnO}_3$ for (a) $x = 0.25$ and (b) $x = 0.37$ respectively.
 Fig.4 Resistivity vs temperature plots of $\text{Nd}_{1-x}\text{Pb}_x\text{MnO}_3$ for $x = 0.2, 0.3$ and 0.5 in the range of 70-300 K.
 Fig.5 The A.C susceptibility plots for $x = 0.2, 0.3$ and 0.5 at 100Hz and magnetic field $\sim 5 \text{ Oe}$.
 Fig.6 Mn-O bond lengths as a function of lead concentration. Inset:- Mn-O bond lengths as a function of $\langle r_A \rangle$. The points indicate experimental data and the lines are guide to the eye. The data for $x = 0$ has been taken from Ref 24.
 Fig.7 Tolerance factor (t_G) and $\delta\theta$ plotted as a function of Pb concentrations(x), where $\delta\theta = 180 - \theta_{ij}$. The points indicate experimental values and line guide to the eye. The data for $x = 0$ has been taken from Ref 24.

Data Collection

Equipment	Bruker APEX SMART CCD	Bruker APEX SMART CCD
λ (Mo K α (graphite monochromator))(\AA)	0.7107	0.7107
Scan mode	ω scan	ω scan
Temperature(K)	298	298
θ range(deg)	2.8-28	2.6-27.5
Recording reciprocal space	$-10 \leq h \leq 9$, $-10 \leq k \leq 9$ $-5 \leq l \leq 5$	$-10 \leq h \leq 9$, $-9 \leq k \leq 9$ $-9 \leq l \leq 9$
Number of measured reflections	1336	3621
Number of independent reflections	202[R(int)= 0.0443]	143[R(int)= 0.0489]
μ (mm-1)	39.485	33.096

Refinement

Number of refined parameters	18	18
Refinement method	Full matrix least squares	Full matrix least squares
R[I > 4 σ I]/R[all data]	0.083/0.087	0.103/0.101
WR[I > 4 σ I]/R[all data]	0.233/0.226	0.394/0.39
GoF	1.323	2.021
Max/min $\Delta \rho$ \AA^{-3}	3.987/-3.448	5.318/-8.343

Table 2: Fractional atomic coordinates and anisotropic thermal parameters (U_{ij}) at 298K for $\text{Nd}_{0.75}\text{Pb}_{0.25}\text{MnO}_{2.72}$

Atom	X	Y	Z	site	Occupancy	U_{equvi}
Nd1	0.5	0	0.5	2e	1.0	0.0322(12)
Pb1	0.5	-0.5	0.5	1d	1.0	0.02444(10)
Nd2	0	0	-0.5	1b	1.0	0.0730(26)
Mn1	0.2504(4)	-0.2504(4)	0	4j	1.0	0.0261(16)
O1	0.2562(6)	-0.2562(6)	-0.5	4k	0.96	0.0926(241)
O2	0	-0.2508(7)	0	4l	1.0	0.1002(215)
O3	0.2655(9)	-0.5	0.0	4n	0.80	0.1009(268)

Table 3: Fractional atomic coordinates and anisotropic thermal parameters (U_{ij}) at 298K
 $\text{Nd}_{0.57}\text{Pb}_{0.37}\text{MnO}_3$

Atom	X	Y	Z	site	Occupancy	U_{equvi}
Nd1	0	0	0	1a	1.0	0.015(3)
Nd2	0	0.5	0.5	3c	0.96	0.041(3)
Nd3	0.5	0.5	0.5	1b	0.72	0.060(6)
Pb1	0	0.5	0	3d	1.0	0.034(2)
Mn1	0.2499(4)	0.2499(4)	0.2499(4)	8g	1.0	0.030(7)
O1	0.2460(40)	0.2460(40)	0.5	8g	1.0	0.120(5)
O2	0.2520(30)	0.2520(30)	0	12i	1.0	0.110(40)

Table 4: Selected bond lengths(Å) and bond angles (°) for $\text{Nd}_{0.75}\text{Pb}_{0.25}\text{MnO}_{2.72}$

4x(Nd1-O1) = 2.74(3)
4x(Nd1-O2) = 2.749(1)
4x(Nd1-O3)= 2.832(1)
4x(Nd2-O1)= 2.81(3)
4x(Nd2-O2)=2.75(3)
4x(Pb1-O1) = 2.67(3)
4x(Pb1-O3) = 2.66(4)

Mn1-O1 = 1.943(2)	O1-Mn1-O1 = 176(3)
Mn1-O1 = 1.943(2)	O3-Mn1-O2 = 176(3)
Mn1-O2 = 1.944(4)	...
Mn1-O3 = 1.942(7)	Mn1-O1-Mn1 = 176(2)
Mn1-O3 = 1.942(7)	Mn1-O2-Mn1 = 179(3)
Mn1-O2 = 1.944(4)	Mn1-O3-Mn1 = 173(4)

Table 5: Selected bond lengths(Å) and bond angles(°) for $\text{Nd}_{0.57}\text{Pb}_{0.37}\text{MnO}_3$

12x(Nd1-O2) = 2.76(5)
8x(Nd2-O1) = 2.736(1)
4x(Nd2-O2) = 2.71(5)
4x(Pb1-O1) = 2.69(4)
8x(Pb1-O2) = 2.736(1)
3x(Mn1-O1) = 1.933(3)
1x(Mn1-O2) = 1.933(3)
2x(Mn1-O2) = 1.934(3)

O1-Mn1-O1 = 91.7(1)
O1-Mn1-O2 = 179.6(1)
O1-Mn1-O2 = 88.6(1)
Mn1-O1-Mn1 = 178(3)
Mn1-O2-Mn1 = 178(3)

Table 6: Mn-Mn distances and corresponding interactions in pure and doped $\text{NdMnO}_3(x = 0)^{24}$ structures.

Formula	Mn-Mn distance(\AA)	Interaction
NdMnO_3	3.7945(6)	AFM(out of plane)
	3.9342(4)	F M (in plane)
$\text{Nd}_{0.75}\text{Pb}_{0.25}\text{MnO}_{2.72}$	3.8836, 3.8878, 3.876	F M (DE)
$\text{Nd}_{0.57}\text{Pb}_{0.37}\text{MnO}_3$	3.8654, 3.8674	F M (DE)