

Structural Study of $[\text{Nd}_{0.5}(\text{Ca}_{0.25}\text{Ba}_{0.25})\text{MnO}_3]$ and $[\text{Nd}_{0.5}(\text{Ca}_{0.25}\text{Sr}_{0.25})\text{MnO}_3]$ Perovskites at Room Temperature

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Two perovskite manganite compounds, namely, $\text{Nd}_{0.5}(\text{Ca}_{0.25}\text{Ba}_{0.25})\text{MnO}_3$ and $\text{Nd}_{0.5}(\text{Ca}_{0.25}\text{Sr}_{0.25})\text{MnO}_3$ have been studied by X-ray diffraction (XRD) at room temperature. The perovskite manganite $\text{Nd}_{0.5}(\text{Ca}_{0.25}\text{Ba}_{0.25})\text{MnO}_3$, was found to be orthorhombic with space group $Pbnm$ and the lattice parameters are $a = 5.4377 \text{ \AA}$, $b = 5.4387 \text{ \AA}$, and $c = 7.7084 \text{ \AA}$. The second perovskite $\text{Nd}_{0.5}(\text{Ca}_{0.25}\text{Sr}_{0.25})\text{MnO}_3$ was found to be also orthorhombic with space group $Pbnm$ and the lattice parameters are $a = 5.4078 \text{ \AA}$, $b = 5.4106 \text{ \AA}$, and $c = 7.6704 \text{ \AA}$. The differences in the lattice parameters and unit cell volumes of the two systems are likely lead to influence the transport, structure, and magnetic properties of this type of materials. The difference in the unit cell volumes for the two samples is attributed to the differences in the ionic radii of the substituted divalent alkaline earth ions present in the A-site of the two compounds.

Introduction

Since the discovery of high- T_C superconductivity in copper oxides, transition-metal oxides of perovskite structure are receiving much attention. Manganese oxide perovskite with coexisting Mn^{3+} , Mn^{4+} ions have received much attention both in fundamental and applied solid state chemistry. The most studied systems are the lanthanum-based manganites

$La_{1-x}A_x^{2+}(Mn_{1-x}^{3+}Mn_x^{4+})O_3$ ($A = Ca^{2+}, Sr^{2+}, Ba^{2+}, \text{or } Pb^{2+}$), which for $0.2 \leq x \leq 0.5$ are ferromagnets with metallic conductivity and Curie temperature as high as 370 K. Stability of these oxides even above 1000°C, considerable electronic conductivity, resistance against reactivity with yttria-stabilized zirconia electrolytes, and electrocatalytic properties for the reduction of oxygen make them suitable cathodic materials for the high-temperature solid oxide fuel cells [1]. Similar properties are expected for the other related rare-earth manganites.

The substitution of trivalent lanthanide ions by divalent alkaline earth ions in the perovskites (ABO_3) leads to the simultaneous occurrence of Mn^{3+} and Mn^{4+} ions in the B-site of the crystal lattice that significantly modifies the structural and magnetic properties. The Colossal magnetoresistance, the transitions from paramagnetic insulator to ferromagnetic metal and from ferromagnetic metal to antiferromagnetic insulator at low temperatures in the distorted perovskites $A_{1-x}A_xMnO_3$ (where A is a trivalent lanthanides and A^{\backslash} is a divalent alkaline earth) are controlled by;

- (i) the amount of ion doping, x ,
- (ii) the average radius, $\langle r_A \rangle$, of A-site contents which controls the width (W) of the one electron e_g band. The overlapping between the Mn ions d orbitals and oxygen p orbitals in the B-sites forms electronically active band e_g . This overlap can be strongly influenced by an internal pressure generated by A-site substitution with ions of different radii,
- (iii) the ionic size mismatch at the A-site [2-5].

Two structural transitions accompanying with the two magnetic transitions with respect to the temperature scale have been reported for many of these manganites [see for example refs. 6, 7 for $Pr_{0.5}Sr_{0.41}Ca_{0.09}MnO_3$ perovskite]. The transitions from paramagnetic insulating at room temperature to ferromagnetic metallic and from ferromagnetic metallic to antiferromagnetic insulating states for this system are at $T_C=250$ K and $T_N = 180$ K respectively. The accompanied structural transitions to the magnetic transitions are from $Imma$ to $I4/mcm$ and from $I4/mcm$ to $Pmmn$ for the above-mentioned system. These results suggest that there is a considerable coupling between magnetism and the lattice in the perovskite manganite systems.

With these assumptions in mind, two samples have been examined in which the average ionic radius of the A-site $\langle r_A \rangle$ is varied while keeping the

Mn^{3+} / Mn^{4+} ratio fixed at 1:1. In the present investigated systems $Nd_{0.5}(Ca_{0.25}Ba_{0.25})MnO_3$ and $Nd_{0.5}(Ca_{0.25}Sr_{0.25})MnO_3$, the ionic size mismatches at the A-site size is in the first system mixture of Ca^{2+} and Ba^{2+} of equal ratio with similar ratio of Nd^{3+} ion. While in the second system the ionic size at the A-site is a mixture of doping cations Ca^{2+} and Sr^{2+} also in equal ratio to Nd^{3+} , makes the expected ratio of Mn^{3+} and Mn^{4+} is 1:1.

Experimental

The polycrystalline samples of $Nd_{0.5}(Ca_{0.25}Ba_{0.25})MnO_3$ and $Nd_{0.5}(Ca_{0.25}Sr_{0.25})MnO_3$ were prepared by a standard ceramic method starting from mixing appropriate amounts of Nd_2O_3 , $CaCO_3$, $BaCO_3$, $SrCO_3$, and $MnCO_3$. The mixture was first heated at $900^\circ C$, two times with an intermediate grinding, to achieve decarbonation. The powder was pressed in the form of pellets under 10^5 Pa and sintered at $1300^\circ C$ for 24 hours in air. The samples were then cooled at $5^\circ C/min.$ to room temperature.

The pellets were used for phase analysis and determination of the lattice parameters at room temperature. This were carried out on an X-ray diffractometer Siemens D5000 using Ni-filtered CuK_α with radiation, $\lambda = 1.54056 \text{ \AA}$ (installed in Faculty of Petroleum and Mining Engineering, Suez, Egypt). The diffractometer was used during the measurements in a step scan mode with step angle equal to 0.04 degree and the time allowed for detection is 3.0 s.. The diffraction patterns have been analyzed by using the standard Rietveld profile method using the FULLPROF program (version 3.5d Oct 98-LLB-JRC).

Results

Rietveld analysis of the diffraction data collected at room temperature was carried out using FULLPROF program for the two perovskite manganite systems $Nd_{0.5}(Ca_{0.25}Ba_{0.25})MnO_3$ and $Nd_{0.5}(Ca_{0.25}Sr_{0.25})MnO_3$. In the analysis, background, peak width, peak shape, lattice parameters, atomic positions were refined. The crystal data for both systems are given in Table (1).

Observed reflections were best indexed, by using refs.(1 and 11) as starting models, as orthorhombic cell with Pbnm space group for both systems. It is clearly seen from Figs. (1 and 2), that the two systems are single phase perovskites and the model produced an acceptable good fit to the observed data. This is in contradiction with other previous results [7,8], which was reported as tetragonal structure with space group I4/mcm for $Pr_{0.5-x}Ce_xSr_{0.5}MnO_3$ and tetragonal structure with space group F4/mmc for $Pr_{0.5}Sr_{0.5}MnO_3$.

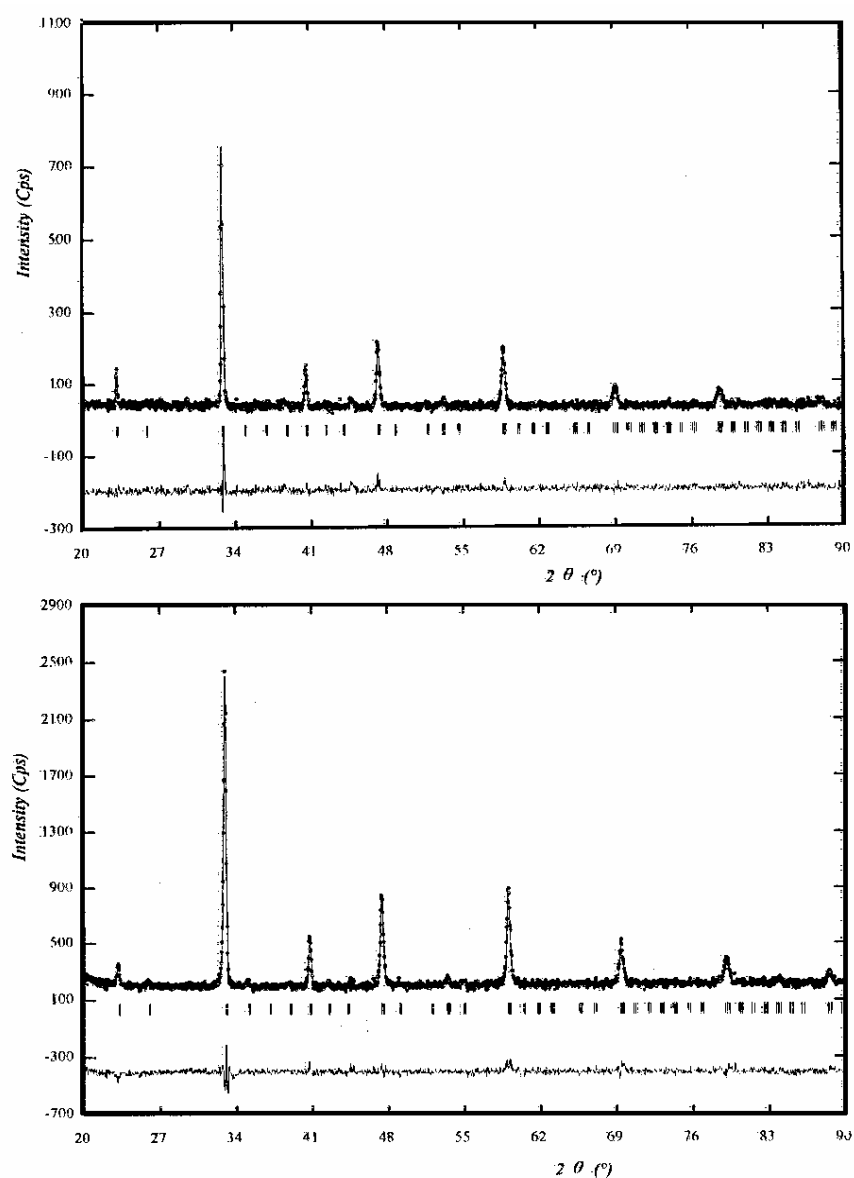


Fig. (1,2) : Observed (closed circles) and calculated (solid line) diffraction patterns of both $\text{Nd}_{0.5}(\text{Ca}_{0.25}\text{Ba}_{0.25})\text{MnO}_3$ and $\text{Nd}_{0.5}(\text{Ca}_{0.25}\text{Sr}_{0.25})\text{MnO}_3$ in respective manner measured at room temperature. The location of expected reflections and the difference between observed and calculated patterns are shown beneath in the two Figures.

Table (1): Crystal data for the two systems.

Chemical formula	$\text{Nd}_{0.5}(\text{Ca}_{0.25}\text{Ba}_{0.25})\text{MnO}_3$	$\text{Nd}_{0.5}(\text{Ca}_{0.25}\text{Sr}_{0.25})\text{MnO}_3$
Crystal system	Orthorhombic	Orthorhombic
Space group	Pbnm	Pbnm
a (Å)	5.4357	5.4122
b (Å)	5.4619	5.4073
c (Å)	7.6789	7.6699
c/√2 (Å)	5.4298	5.4234
V (Å)³	227.9804	224.4595
R_p	13.9	5.83
R_{wp} (%)	17.5	7.41
R_{exp}	16.22	6.58
Goodness of fit	1.16	1.27

The refined data as, the position of the atoms, temperature factors, and the occupancies for the two perovskite systems are given in Tables (2 and 3). The lattice parameters for $\text{Nd}_{0.5}(\text{Ca}_{0.25}\text{Ba}_{0.25})\text{MnO}_3$ manganite sample are [a=5.4377 Å, b = 5.4387 Å, and c = 7.7084 Å] whereas for $\text{Nd}_{0.5}(\text{Ca}_{0.25}\text{Sr}_{0.25})\text{MnO}_3$ system are [a = 5.4079 Å, b = 5.4106 Å, and c = 7.6704 Å].

Table (2): Atomic Positions, Temperature Factors and Occupation Ratios for $\text{Nd}_{0.5}(\text{Ca}_{0.25}\text{Ba}_{0.25})\text{MnO}_3$

Name	x	Y	Z	B	Occup.
Mn³⁺	0.50000	0.00000	0.00000	0.500	0.250
Mn⁴⁺	0.50000	0.00000	0.00000	0.500	0.250
Nd³⁺	-0.00300	0.00000	0.25000	0.500	0.250
Ca²⁺	-0.00300	0.00000	0.25000	0.500	0.125
Ba²⁺	-0.00300	0.00000	0.25000	0.500	0.125
O_I	0.07286	0.49498	0.24725	1.000	0.500
O_{II}	-0.25763	0.26661	0.02537	1.000	1.000

Although, the two samples have the same ratio of $\text{Mn}^{3+}/\text{Mn}^{4+}$ as 1:1, there are clearly differences in the lattice volumes of them as indicated from Table (1). The unit cell volumes for the $\text{Nd}_{0.5}(\text{Ca}_{0.25}\text{Ba}_{0.25})\text{MnO}_3$ and $\text{Nd}_{0.5}(\text{Ca}_{0.25}\text{Sr}_{0.25})\text{MnO}_3$ perovskites are 227.9804 Å³ and 224.4595 Å³, respectively.

Table (3): Atomic Positions, Temperature Factors, and the Occupation Ratios for $\text{Nd}_{0.5}(\text{Ca}_{0.25}\text{Sr}_{0.25})\text{MnO}_3$

Name	x	y	Z	B	Occup.
Mn^{3+}	0.50000	0.00000	0.00000	0.500	0.250
Mn^{4+}	0.50000	0.00000	0.00000	0.500	0.250
Nd^{3+}	-0.00940	0.02720	0.25000	0.500	0.250
Ca^{2+}	-0.00940	0.02720	0.25000	0.500	0.125
Sr^{2+}	-0.00940	0.02720	0.25000	0.500	0.125
O_I	0.04727	0.49772	0.24448	1.000	0.500
O_{II}	-0.28433	0.27372	0.02268	1.000	1.000

Discussion

In the perovskite NdMnO_3 , the Mn ions are known to occupy the B-sites which are surrounded by oxygen octahedra and A-sites occupied by Nd-ions between these octahedra. The overlap between B-ions, Mn d orbits and oxygen p orbits form the electron active band, and ions with different radii in A-sites $\langle r_A \rangle$ can exert internal pressure which strongly influence the overlap as mentioned in the introduction. In the present manganite compounds $\text{Nd}_{1-x}\text{Ca}_x\text{MnO}_3$, the A sites Ca ions are substituted by either Ba^{2+} or Sr^{2+} ions (by 50%); both increase the average $\langle r_A \rangle$ radii, but it is more in case of (Ba+Ca) as compared with (Sr+Ca) ions. It has been indicated [9] that charge-ordering associated with $\text{Mn}^{3+}/\text{Mn}^{4+}$, consists of stacked antiferromagnetic octant, and the absence or presence of the charge ordering and its nature depends on the size $\langle r_A \rangle$ cation. Also, T_N (FM \rightarrow AFM) transition temperature is expected to decrease significantly, whereas T_C (PM \rightarrow FM) to increase slightly with increasing the average size of $\langle r_A \rangle$ cation, where similar anticipation could be made for the present compounds, since both Ba and Sr increase the average radii. Thus, it is possible to increase the transition temperature T_N of this type of manganites and also decrease slightly T_C , with different cations size in A-site, to reach single magnetic transition PM \rightarrow AFM. It had also been demonstrated that the $R_0 / R_{H=7T}$ ratio of $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ (where R_0 is the resistance at zero magnetic field while $R_{H=7T}$ is the resistance at 7T magnetic field) can be multiplied by 100 with calcium doping [6, 10]. These results strongly suggested that it should be possible to optimize the magnetoresistance properties of these materials by various substitutions on the A-sites of the perovskite

The main effect of increasing or decreasing $\langle r_A \rangle$ has been reported [3] to influence the Mn-O-Mn bond angle and consequently change the matrix element to which describes the electron hopping between Mn-ions i.e., Mn ions get farther apart or close, the bond lengths and angles between Mn and O ions have been reported in Table (4).

Table (4): Selected Bond Distances (\AA) and Angles ($^\circ$) for the Two Compounds

	$\text{Nd}_{0.5}(\text{Ca}_{0.25}\text{Ba}_{0.25})\text{MnO}_3$	$\text{Nd}_{0.5}(\text{Ca}_{0.25}\text{Sr}_{0.25})\text{MnO}_3$
Mn₃-O_I	1.9397	1.8925
Mn₄-O_{II}	1.9734	1.8930
O_I-Mn₃-O_{II}	87.127	90.149
O_I-Mn₄-O_{II}	87.127	90.149
O_{II}-Mn₄-O_{II}	90.409	90.238
Mn₃-O_I-Mn₃	156.630	164.776
Mn₄-O_{II}-Mn₄	167.198	163.213

According to the fact that Ba^{2+} ion is much larger than Ca^{2+} , Sr^{2+} and Nd^{3+} ions and Gold Shmidt tolerance factor (t) for both $\text{Nd}_{1-x}(\text{CaBa})_x\text{MnO}_3$ and $\text{Nd}_{1-x}(\text{CaSr})_x\text{MnO}_3$ less than 1, the perovskite structure tends to be unstable [11] and a more complex structure can be anticipated. Moreover, the octahedra MnO_6 can be regular only if the overall distortion due to tilting is vanishes, i.e., $c/\sqrt{2} \approx a \approx b$. The analysis of the two investigated lattice parameter indicates that the lattice distortion is in the form $c/\sqrt{2} > a \approx b$ for both structures. Such relation could be envisage the structure as an orthorhombic phase with Pbnm space group with a quasitetragonal distortion, characterize by an elongation in the c-direction, i.e., I bnm which implying a tilting only around [010] axis [11]. Such crossover from the expected orthorhombic to quasitetragonal structure could well be size mismatch between A and A' sites ions i.e., between Nd and both (Ca+Sr) in one compound and Nd and (Ca+Ba) in the other. The refinement results in Table (1) indicates that both structures are orthorhombic with Pbnm Space group, however, they can be very close to the proposed quasitetragonal structure base on the type of lattice distortion. This could be a step end in X-ray detection that makes it difficult to distinguish between the close symmetry. In that respect, the Mn-O-Mn bond angle (θ) will not be 180° and due the expansion in the c-axis bond distance, the octahedra tilt and relate to increase the available space around the A-site. Furthermore, the difference between the two Mn-O distance, see table (4), is only 0.04 and 0.001 Å for the two compounds in respective manner indicate that the distortion in MnO_6 octahedra is small which is consistence with the high concentration of Mn^{4+} (nominal 50 %).

Conclusions

The room temperature structure for both $\text{Nd}_{0.5}(\text{Ca}_{0.25}\text{Ba}_{0.25})\text{MnO}_3$ and $\text{Nd}_{0.5}(\text{Ca}_{0.25}\text{Sr}_{0.25})\text{MnO}_3$ polycrystalline perovskites is orthorhombic of (Pbnm) space group, with unit cell parameters of [$a = 5.4377$ Å, $b = 5.4387$ Å, and $c = 7.7084$ Å] and [$a = 5.4079$ Å, $b = 5.4106$ Å, and $c = 7.6704$ Å] in respective manner. The analysis of the lattice parameters indicates that the lattice distortion is in the form $c/\sqrt{2} > a \approx b$ for both structures. Such relation can suggest that the structure, with a quasitetragonal distortion, characterizes by an elongation in the

c-direction, i.e., Ibm which implying a tilting only around [010] axis. The difference in the unit cell volume between the two samples is attributed to greater radius of Ba ion than Sr, ($\text{Ba}^{2+} \approx 1.43 \text{ \AA}$) and ($\text{Sr}^{2+} \approx 1.27 \text{ \AA}$) [12]. The temperature dependence of the crystal structure for these samples and their transport and magnetic properties are under taken.

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