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Synthesis, Structure, and Properties of Sodium or Potassium-Doped Lanthanum Orthomanganites from NaCl or KCl Flux[1]

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Lanthanum and oxygen-deficient $La_{1-x-y}A_xMnO_{3-\delta}$ (A = Na or K) ferromagnetic oxide phases have been synthesized from NaCl or KCl flux, starting from La_2O_3 and $MnCO_3$ at 900°C. Composition of the final product could be varied by varying initial composition La_yMnO_3 ($0.7 < y < 1$). Final composition of these oxides was obtained from chemical analysis of elements present. As the lanthanum content increased, Na or K content decreased and the structure changed from rhombohedral to orthorhombic symmetry. Mn^{4+} concentration was 27% in the sodium doped manganite, $La_{0.82}Na_{0.13}MnO_{2.93}$ with Curie temperature 325 K, and Mn^{4+} was 25% in the potassium doped $La_{0.82}K_{0.08}MnO_{2.89}$ with T_c of 310 K. Structure of these two phases have been refined from neutron diffraction studies. Stoichiometric $La_{1-x}A_xMnO_3$ (A = Na or K) have been obtained for the initial composition La_yMnO_3 ($y = 0.85$). Orthorhombic phases obtained were found to be Mn-deficient $La_{1-x}Na_xMn_{1-x}Mn_{1-y}O_3$ ($x \simeq 0.02$; $y \simeq 0.05$), which were ferromagnetic insulators, even though total Mn^{4+} contents were as high as 29%.

1. INTRODUCTION

Lanthanum orthomanganites of general formula $La_{1-x}A_xMnO_3$ (A = Ca, Sr, Ba, and Pb) have been known for a long time (1, 2). Recent observation of colossal magnetoresistance ($CMR = (R_H - R_o)/R_o$) in $La_{1-x}A_xMnO_3$ has generated new interest in these materials (3–6). Exact reason for CMR is a subject of current interest (7, 8). It is desirable to have CMR at 300 K for commercial application. Highest CMR is observed near the ferromagnetic transition temperature T_c, and hence the search for new materials having T_c near 300 K. Goodenough (9) has indicated that La_yMnO_3 ($y < 1$) showed T_c 165–220 K. Recently we had shown that a T_c of 220 K is obtained in the bulk solid as well as thin films of lanthanum-deficient oxide having nominal composition $La_{0.76}MnO_{2.86}$ (10). Further, films of such material showed over 80% CMR at 220 K at 6.5 T. Oxygen ion deficiency in $La_{0.67}Ba_{0.33}MnO_{3-\delta}$ and $La_{0.6}Pb_{0.4}MnO_{3-\delta}$ showed a decrease in T_c, but there is an increase in CMR(11, 12). Cation as well as anion deficiency is likely to be one of the reasons for such a large CMR in $La_yMnO_{3-\delta}$ ($y < 1$). Solid state preparation of La_yMnO_3 invariably gave multiphasic mixtures with Mn_3O_4 as an impurity. In an attempt to eliminate the Mn_3O_4 impurity via water soluble manganese salts, synthesis of lanthanum-deficient phases were attempted using neutral NaCl and KCl fluxes. Since Na or K can substitute for La (13), we obtained ferromagnetic Na or K doped lanthanum manganites. Among the large number of Na or K doped lanthanum manganites synthesized by this method, epitaxial thin film of $La_{0.82}Na_{0.13}MnO_{2.93}$ was made by pulsed laser deposition, and the thin film showed over 70% CMR at 290 K in 6T magnetic field (14). Composition of these phases has been derived by chemical analysis of La, Na/K, Mn, and oxygen independently. Here we report a new method to synthesize Na or K doped lanthanum orthomanganites by neutral NaCl or KCl flux. Structure, electrical, and magnetic properties of these oxides have been presented.

2. EXPERIMENTAL

La_2O_3 and $MnCO_3$ for a starting composition La_yMnO_3 ($0.6 < y < 1$) were mixed with dry NaCl in the weight ratio 1:16. The mixture was heated to 900°C for 24 h in an alumina crucible. The melt was furnace cooled and washed in hot, distilled water until no Na^+ or Cl^- was detected in the filtrate. The black solid was filtered and dried at 110°C. Similarly, a series of oxides were prepared in KCl melt. Powder X-ray diffraction (JEOL JDX-8P) patterns were recorded at a scan rate of 2°/min with Cu$K\alpha$ (1.5418 Å). Final composition of these oxides was obtained from chemical analysis of the elements present. Neutron diffraction patterns for the two samples with starting

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compositions $La_{0.7}MnO_3$ in NaCl and KCl melt preparation were recorded at room temperature using the T-1011 diffractometer at the 100 MW Dhruva Reactor at Trombay. The samples were in the form of cylindrical pellets (10 mm in diameter and 10 mm in height), and the wavelength was 1.216 Å. The instrument collimations (FWHM) were 0.7°–0.5°–0.7° from the in-pile to the detector end. The patterns were analyzed by Rietveld profile refinement method using a modified version of the program DBW 3.2 (15).

In order to see the stability of these oxides and for resistivity measurements, all these oxides were sintered at 850°C in flowing oxygen for 24 h. Magnetic susceptibility was measured on the powder as well as the sintered samples employing a Lewis coil magnetometer with magnetic field at 1 K gauss. Four probe electrical resistivity measurements were done on the sintered pellet. Composition of the sintered samples was again determined and no significant variation in the composition was observed.

2.1. Lanthanum Estimation

About 0.1 g of the oxide was dissolved in 10 ml of 1:1 HCl and evaporated to dryness. The salt was dissolved in 20 ml of H_2O. To this, 20 ml of 0.1 M NaF solution was added. The solution was maintained at 5.5 pH and titrated against standard $La(NO_3)_3$ solution using Fluoride ion sensitive electrode (ORION: expandable ion analyzer EA 940) (16). $La(NO_3)_3$ was independently standardized by EDTA titration employing the standard Zn^{2+} ion. Accuracy of lanthanum estimation is confirmed to be better than 0.5%. There was no interference due to Mn presence at 5.5 pH.

2.2. Manganese Estimation

After the lanthanum estimation, the same solution was used for total manganese estimation. A quantity 150 ml of sodium pyrophosphate (10 g in 150 ml) was taken and pH was brought to 6.7 ± 0.2 using a standard glass electrode. This was added to the solution containing Mn^{2+} ions. This solution was titrated against standard $KMnO_4$ solution potentiometrically using Pt and calomel electrodes holding pH at 6.7 (17). Accuracy of Mn content is better than 0.5%. Identical experiments were carried out with pure Mn_3O_4 and MnO_2 samples in the presence and absence of La^{3+} ions and there is no interference of La in the estimation of Mn at pH 6.7.

2.3. Sodium and Potassium Estimation

Na and K contents were estimated by ICP spectroscopic technique employing a Jobin YVON analyzer. A quantity 0.5 g of the oxide was dissolved in 5 ml of 6N HCl, evaporated to dryness, and redissolved in H_2O to 50 ml. Standard solutions were prepared from analytical grade NaCl and KCl salts dried at 200°C. Accuracy of estimation is better than 1%.

2.4. Oxygen Estimation

From the absolute weights of elements present in 1 g of an oxide, molar ratio of La:Na:Mn was determined. For example, $La_{0.82}Na_{0.13}Mn_1O_y$ was the composition for an oxide obtained from the starting composition $La_{0.7}MnO_3$. The formula of this oxide can be written as $La_{0.82}Na_{0.13}Mn^{3+}_{1-x}Mn^{4+}_xO_{2.795+x/2}$. The value of x was estimated by iodometric titration. Typically, about 0.1 g of oxide was dropped in 10 ml of 1:1 HCl containing 2–3 g of KI. Liberated iodine was titrated against standard sodium thiosulphate solution using starch as an indicator. Compositions of each oxide was thus determined by chemical analysis of all the elements present in the compound.

3. RESULTS

Powder X-ray diffraction patterns of typical sodium doped lanthanum manganites are shown in Fig. 1. These melt-grown solids crystallized in perovskite related structures. For the starting composition of La_yMnO_3 ($0.7 < y < 0.9$), compounds crystallized in rhombohedral structure, as can be seen from Figs. 1a and 1b. All the diffraction lines could be indexed and no impurity lines due to either La_2O_3 or any of the known oxides of Mn, such as Mn_2O_3, Mn_3O_4, and MnO_2, were seen. With the starting composition La_yMnO_3 ($0.9 < y < 1$), the product crystallized in orthorhombic structure similar to $LaFeO_3$. Indexed patterns are shown in Figs. 1c and 1d.

Powder X-ray diffraction patterns of oxides grown in KCl melt are shown in Fig. 2 for various starting compositions La_yMnO_3 ($0.7 < y < 1$). Here also, for $y < 0.9$, the oxides crystallized in rhombohedral structure and for $0.9 < y < 1$, the oxides crystallized in orthorhombic structure. For the starting composition La_yMnO_3 ($y = 0.6$ and 0.65) with NaCl flux at 900°C, γ-Mn_2O_3 impurity peaks were seen in the powder X-ray pattern. Thus, the lower limit of the starting composition for obtaining pure Na or K doped samples was $y = 0.7$. In Table 1, chemical composition, lattice parameters, cell volume per formula unit, electrical, and magnetic properties of the sodium doped lanthanum manganites are summarized. Similarly, the data on oxides grown in KCl melt for various starting compositions are given in Table 2.

The oxides synthesized from NaCl melt were doped with Na and the oxides grown in KCl melt contained K. As the La content increased, Na or K content decreased, demonstrating the substitution of Na or K in the La sites. For example, with the starting composition of $La_{0.7}MnO_3$, chemical composition of the oxide was $La_{0.82}Na_{0.13}MnO_{2.93}$, indicating both La (A site) and oxygen vacancies. Total

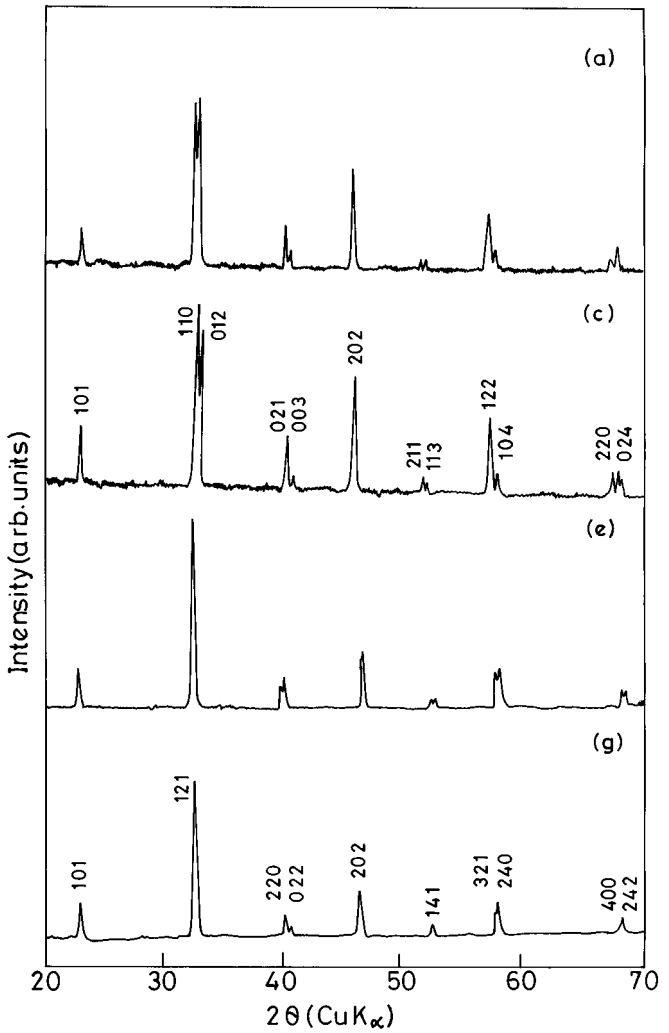

FIG. 1. Powder X-ray diffraction pattern of sodium-doped lanthanum manganites; curves (a), (c), (e), and (g) correspond to composition as in Table 1.

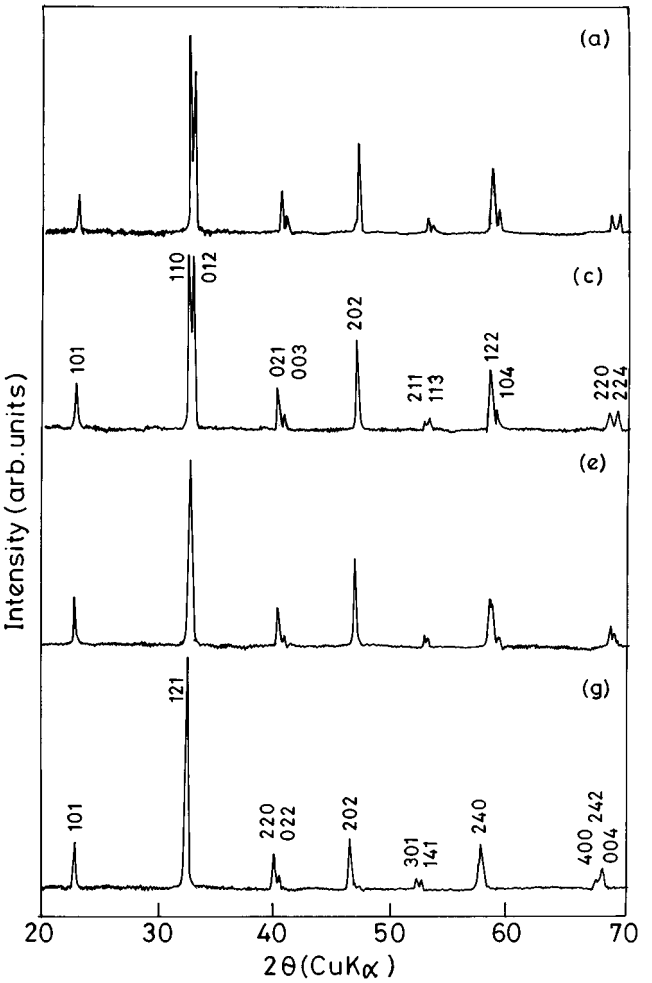

FIG. 2. Powder X-ray diffraction pattern of potassium-doped lanthanum manganites; curves (a), (c), (e), and (g) correspond to composition as in Table 2.

Mn^{4+} content in this compound is 27%. For the initial La content $y = 0.85$, final composition was $La_{0.91}Na_{0.09}MnO_3$. Thus, stoichiometric $La_{1-x}Na_xMnO_3$ could be prepared by NaCl flux method.

On increasing the starting lanthanum content, the compound crystallized in orthorhombic structure and no impurities peaks were detected in the X-ray diffraction. From the chemical analysis, we find that these oxides have Mn deficiency to the extent of 5–8%. The Mn^{4+} content was calculated from the composition, and it is in the range of 22–29%.

Typical scanning electron micrographs of the oxides crystallizing in rhombohedral and orthorhombic structure are shown in Figs. 3a and 3b. Energy dispersive X-ray analysis (EDAX) in the spot mode method confirms the presence of Na and K. A typical micrograph of sintered pellet in Fig. 3c shows over 25% porosity. A comparison of composition from spot mode on large numbers of crystals and over a large area of the pellet showed that the samples are homogeneous.

Chemical analysis was carried out on the sintered materials also. Almost no variation in composition was observed on heating to 850°C in oxygen. Powder X-ray diffraction study of the oxygen-heated samples showed no variation in the case of parent oxides crystallizing in rhombohedral structure. However, oxides which crystallized in the orthorhombic structure transformed to rhombohedral structure on heating in oxygen. This is shown in Figs. 4a and 4b. Potassium doped samples also showed a similar transformation (Figs. 4c and 4d). No detectable impurity lines were seen in the powder pattern on heating the orthorhombic phases of Na and K doped samples.

3.1. Neutron Diffraction Studies

Neutron diffraction studies were done on two compositions among the series of oxides prepared here, $La_{0.82}Na_{0.13}MnO_{2.93}$ and $La_{0.82}K_{0.08}MnO_{2.89}$. The diffraction patterns could be refined in $R\bar{3}C$ space group. The occupancy parameters of La, Mn, and O were observed to exhibit strong correlations and hence were refined in alternate cycles to minimize the effect of correlations. The proportion of La to Na (or K) at La sites was constrained to conform to the nominal composition. The Mn site indicated full occupancy and was fixed in the final cycle. The cell parameters, half width parameters, zero angle, and the scale factor were varied at all the cycles. A gaussion peak shape function was assumed. The refined parameters and bond distances are given in Table 3. Both La-site and O-site

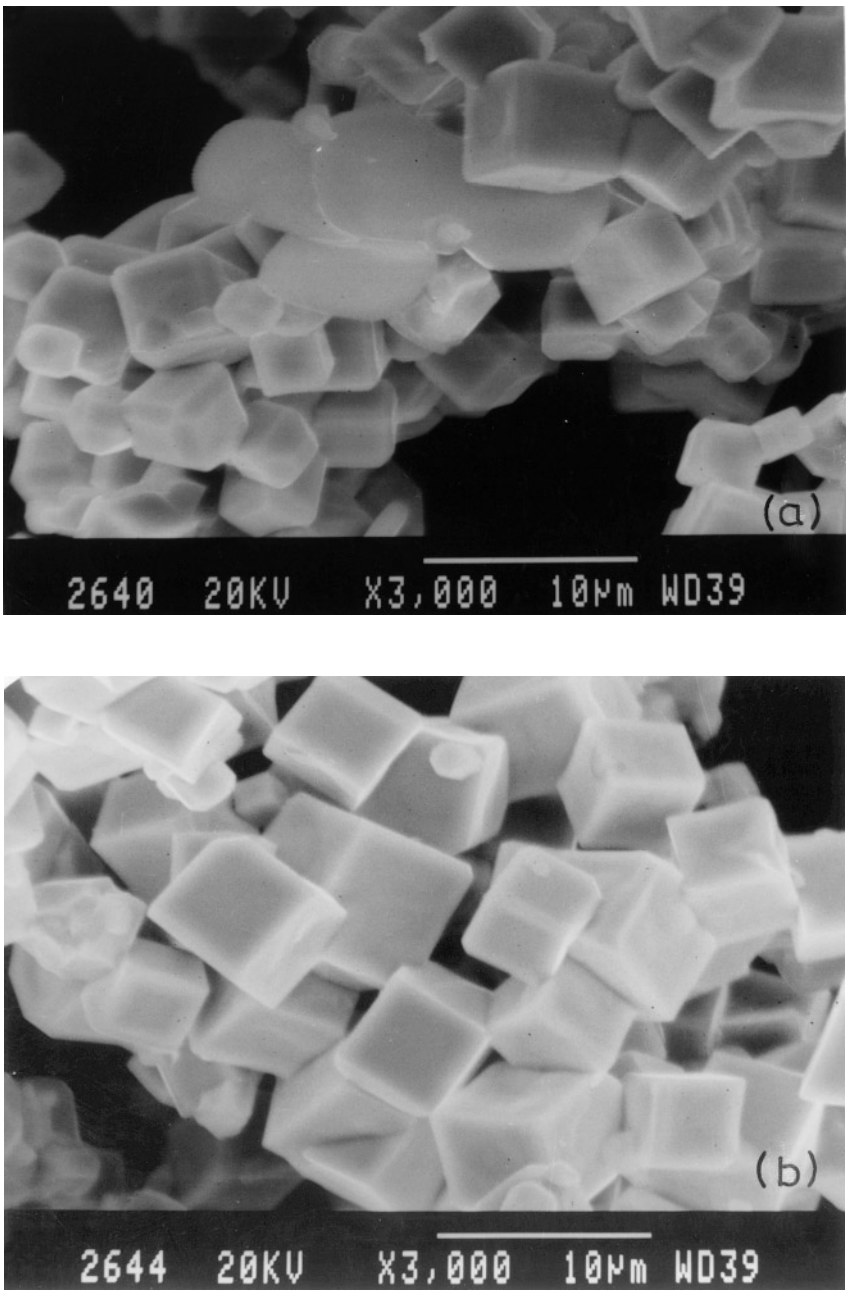

FIG. 3. Typical scanning electron micrographs (SEM) of (a) $La_{0.85}K_{0.08}MnO_{2.93}$ (b) $La_{0.99}K_{0.01}Mn_{0.92}O_{3.00}$, and (c) sintered pellet of $La_{0.82}Na_{0.13}MnO_{2.93}$ for porosity.

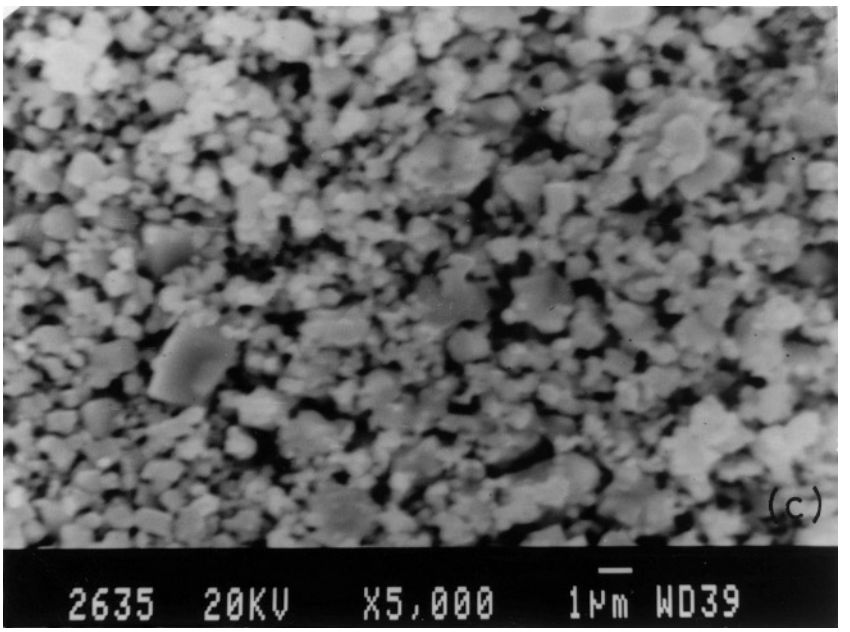

FIG. 3—*Continued*

vacancies are present. Refined cell parameters indicate larger lattice parameters for the K-substituted sample compared to the Na-substituted sample. The observed and calculated neutron diffraction patterns are shown in Figs. 5a and 5b. The refined composition of both the samples is in reasonable agreement with the chemical composition obtained earlier. The cell parameters agree well with the X-ray results.

3.2. Magnetic Properties

Magnetic susceptibility of Na doped oxides is shown in Fig. 6. The highest Curie temperature, 325 K, is seen for the oxide having composition $La_{0.82}Na_{0.13}MnO_{2.93}$, and T_c decreases with an increase in La content or decrease in Na content. The inset shows the $1/\chi$ vs T plot for the $La_{0.98}Na_{0.02}Mn_{0.92}O_3$ phase. The $1/\chi$ vs T in general showed Curie–Weiss behavior. In Fig. 7, susceptibility vs T plots of K doped samples are given. The highest T_c observed in this case is 310 K. The magnetic susceptibility measurements of oxygen-heated samples showed almost no variation in T_c in the case of oxides crystallized in rhombohedral structure. The oxides undergoing orthorhombic to rhombohedral structural transition showed a slight decrease in T_c, about 10 K. Tables 1 and 2 summarize θ and T_c of these phases.

TABLE 1
Composition, Lattice Parameters, and T_c of $La_{1-x-y}Na_xMnO_{3-\delta}$ and $La_{1-x}Na_xMn_{1-z}O_3$ Phases Obtained from NaCl Melt

Starting La content y	Final composition[a]	Crystal structure	Lattice parameters (Å)[b] a	b	c	Cell volume/ formula unit (Å^3)	Mn^{4+} content (%)	T_{I-M} ρ vs T	Transition temperature θ (K)	T_c (K)
(a) 0.70	$La_{0.82}Na_{0.13}MnO_{2.93}$	R	5.499	—	13.326	58.00	27	290	325	300
(b) 0.75	$La_{0.85}Na_{0.14}MnO_{2.97}$	R	5.488	—	13.316	58.00	25	280	310	280
(c) 0.80	$La_{0.90}Na_{0.09}MnO_{3.00}$	R	5.511	—	13.336	58.33	21	240	280	265
(d) 0.85	$La_{0.91}Na_{0.09}MnO_{3.00}$	R	5.511	—	13.318	58.33	18	225	—	—
(e) 0.90	$La_{0.97}Na_{0.03}Mn_{0.95}O_{3.00}$	O	5.511	7.767	5.477	58.50	22	Insulator	155	130
(f) 0.95	$La_{0.98}Na_{0.02}Mn_{0.93}O_{3.00}$	O	5.505	7.767	5.467	58.50	25	Insulator	150	125
(g) 1.00	$La_{0.98}Na_{0.02}Mn_{0.92}O_{3.00}$	O	5.506	7.767	5.474	58.25	29	Insulator	135	105

Note. R = Rhombohedral; O = Orthorhombic.
[a] The error in the analysis is ± 0.01.
[b] Accurate within ± 0.005.

TABLE 2
Composition, Lattice Parameters, and T_c of $La_{1-x-y}K_xMnO_{3-\delta}$ and $La_{1-x}K_xMn_{1-z}O_3$ Phases Obtained from KCl Melt

Starting La content y	Final composition[a]	Crystal structure	Lattice parameters (Å)[b] a	b	c	Cell volume/ formula unit (Å^3)	Mn^{4+} content (%)	T_{I-M} ρ vs T	Transition temperature θ (K)	T_c (K)
(a) 0.70	$La_{0.82}K_{0.08}MnO_{2.89}$	R	5.516	—	13.324	58.33	24	250	310	300
(b) 0.75	$La_{0.85}K_{0.08}MnO_{2.93}$	R	5.519	—	13.336	58.66	23	240	300	290
(c) 0.80	$La_{0.91}K_{0.06}MnO_{3.00}$	R	5.526	—	13.362	59.00	21	210	280	260
(d) 0.85	$La_{0.93}K_{0.05}MnO_{3.00}$	R	5.529	—	13.354	59.00	16	140	—	—
(e) 0.90	$La_{0.97}K_{0.03}Mn_{0.95}O_{3.00}$	O	5.514	7.763	5.471	58.50	22	Insulator	195	180
(f) 0.95	$La_{0.98}K_{0.02}Mn_{0.93}O_{3.00}$	O	5.523	7.771	5.499	59.00	25	Insulator	145	125
(g) 1.00	$La_{0.99}K_{0.01}Mn_{0.92}O_{3.00}$	O	5.521	7.759	5.495	58.75	28	Insulator	130	105

Note. R = Rhombohedral; O = Orthorhombic
[a]The error in the analysis is less than ± 0.01.
[b]Accurate within ± 0.005.

3.3. Electrical Properties

Four probe electrical resistivity measurements as a function of temperature were done on the sintered pellets. In Fig. 8, $\ln \rho$ vs T plots of sodium doped lanthanum manganites are given. In the inset, a ρ vs T plot is given for the $La_{0.85}Na_{0.14}MnO_{2.97}$ sample. In Fig. 9, $\ln \rho$ vs T plots for the potassium doped oxides are given. The oxides crystallizing in the rhombhohedral structures exhibit insulator-to-metal (I–M) transition as the temperature is decreased. This

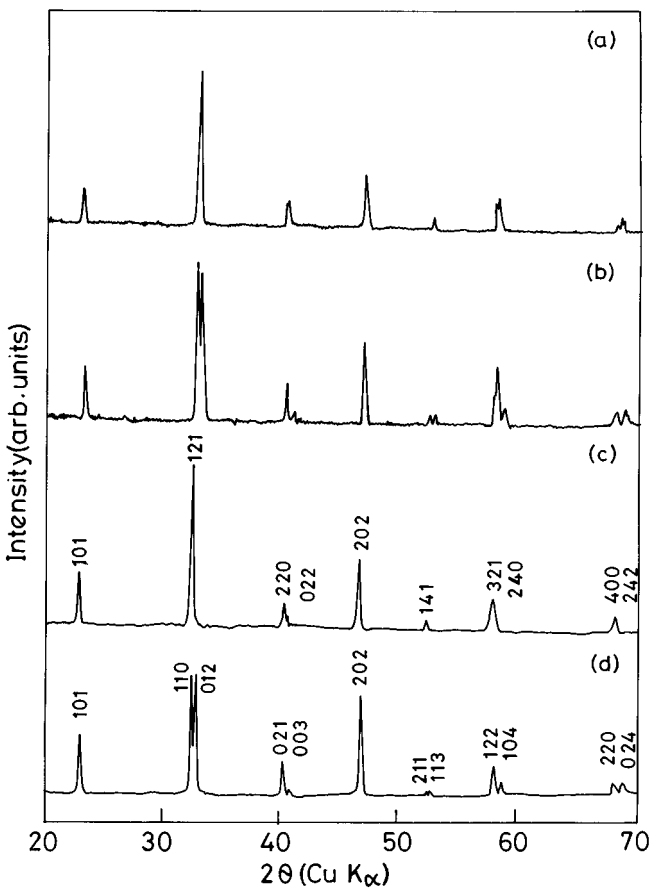

FIG. 4. Powder X-ray diffraction pattern of as-prepared sodium or potassium-doped oxide; curves (a) $La_{0.98}Na_{0.02}Mn_{0.93}O_3$, (b) after heating (a) at 850°C, (c) $La_{0.98}K_{0.02}Mn_{0.93}O_3$, and (d) after heating (c) at 850°C.

TABLE 3
Positional and Thermal Parameters (B) Obtained by Rietveld Refinement

Atom	$La_{0.82}Na_{0.13}MnO_{2.93}$	$La_{0.82}K_{0.08}MnO_{2.89}$
La (0, 0, 0.25)		
B	0.5(1)	0.6(1)
N	0.79(1) /0.12(1)	0.83(1) /0.08(1)
Mn (0, 0, 0.5)		
B	0.5	0.5
N	1.00	1.00
O (x, 0, 0.25)		
X	0.4517(4)	0.4546(4)
B	1.06(7)	1.09(6)
N	2.81(2)	2.86(2)
Cell parameters (Å)		
a	5.494(4)	5.515(5)
c	13.290(7)	13.396(9)
R factors		
R_p	3.76%	2.10%
R_{wp}	4.96	2.63
R_{exp}	3.16	2.23
Interatomic distances (Å)		
La–O	2.482(2) × 3	2.507(2) × 3
La–O′	2.737(1) × 6	2.754(1) × 6
La–O″	3.012(3) × 3	3.008(1) × 3
Mn–O	1.953(1) × 6	1.960(1) × 6
Mn–O Bond valence	3.430	3.331

Note. The numbers in parentheses represent standard deviations referred to the last digit, and 100N denotes percentage occupancy.

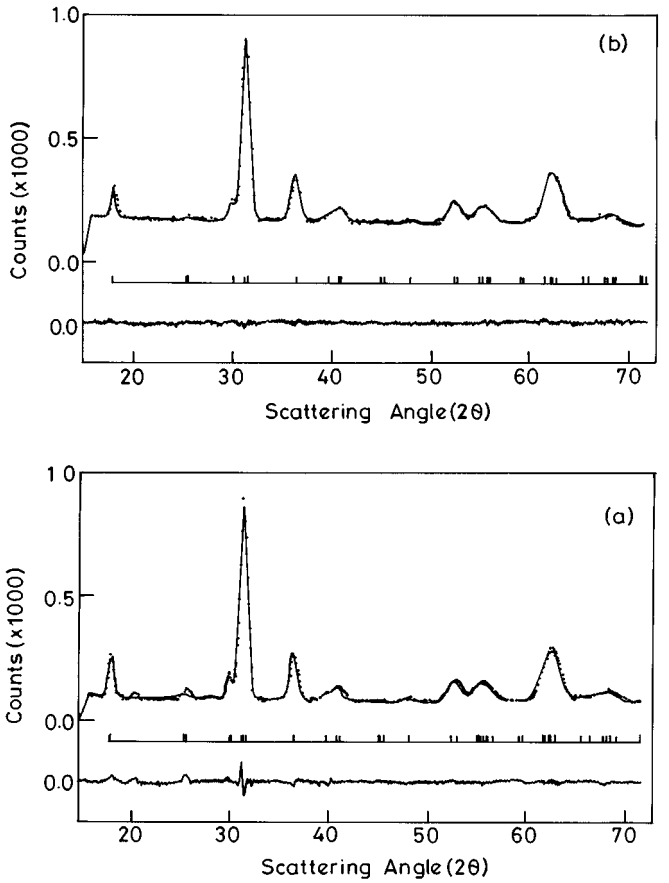

FIG. 5. Observed and calculated neutron diffraction patterns of (a) $La_{0.82}Na_{0.13}MnO_{2.93}$ and (b) $La_{0.82}K_{0.08}MnO_{2.89}$.

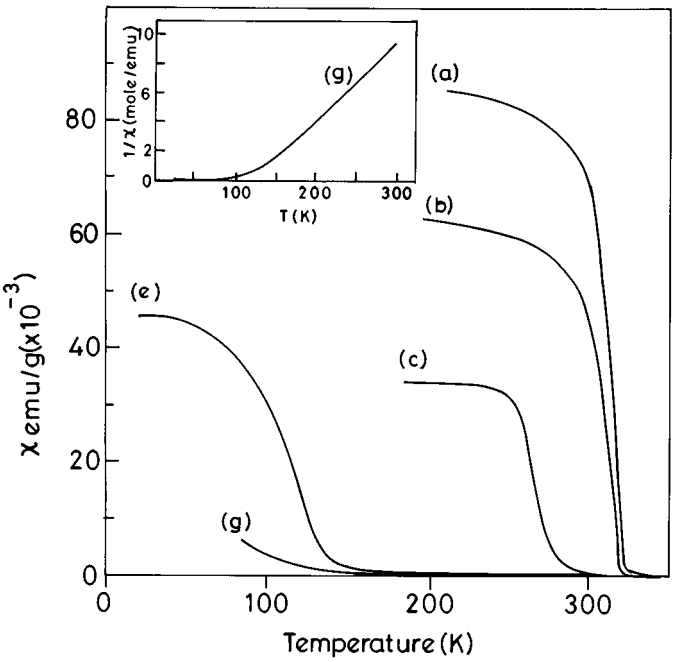

FIG. 6. Magnetic susceptibility as a function of temperature of sodium-doped lanthanum manganites measured at 1 K gauss field and 9 G gradient; curves (a), (b), (c), (e), and (g) correspond to composition as in Table 1. Inset shows $1/\chi$ vs T for oxide (g) in Table 1.

behavior is similar to the divalent ion doped lanthanum managanites. I–M transition temperature is 30–60 K lower than the T_c observed from magnetic measurements. All the oxides with the starting composition La_yMnO_3 ($0.7 < y < 0.85$) showed I–M transition as well as para- to ferromagnetic transition. Oxides having Mn deficiency showed semi conducting behavior, even though Mn^{4+} content was in the range of 22–29%. Plots of ln ρ vs $1/T$ gave band gap in the range of 0.12 to 0.13 eV for these semiconducting phases.

4. DISCUSSION

Na and K doped lanthanum manganites have been reported by Shimura *et al.* (13). They have prepared the sample by solid state method, and maximum substitution of Na for La in $LaMnO_3$ is reported to be 0.2 with Mn^{4+} concentration as high as 40%. However, the highest T_c reported by them is 325 K, which agrees with the highest T_c observed here for an oxide having 27% Mn^{4+}. For Mn^{4+} concentration of 27%, T_c of 325 K is expected when we compare our results with the divalent ion doped lanthanum manganites (5).

Na and K doped lanthanum manganites made here can be classified into three categories:

(a) Those having both La- and oxygen-site vacancies showing ferromagnetic as well as insulator-to-metal transitions, (b) those having near-stoichiometric composition and still showing ferromagnetic and I–M transition, and (c) those which are Mn-deficient oxides showing ferromagnetic and semiconducting behavior.

A recent study of $La_{1-y}MnO_3$ and $LaMn_{1-z}O_3$ by Topfer and Goodenough (18) supports the formation of the three types of phases formed in NaCl or KCl fluxes. Partial occupancy of La by Na or K is observed here in this method of preparation. The compounds crystallizing in rhombohedral structure with the formula $La_{1-x-y}Na_xMnO_{3-\delta}$ have both La and oxygen vacancies, and they showed ferromagnetic as well as metallic behavior. It may be mentioned here that oxygen deficiency does not alter the structure seen in $La_{0.67}Ba_{0.33}MnO_{3-\delta}$ (11) and $La_{0.6}Pb_{0.4}MnO_{3-\delta}$ (12). Thus, both A-site and oxygen vacancy can be accommodated in this structure. For a narrow range of initial composition La_yMnO_3 ($y = 0.85 \pm 0.05$) near-stoichiometric $La_{1-x}A_xMnO_3$ (A = Na, K) phases are indeed formed in NaCl or KCl fluxes. They do show ferromagnetic transition as well as I–M transition. In the case of oxides precipitated in the orthorhombic structure with starting composition La_yMnO_3 ($0.9 < y < 1$), the oxides

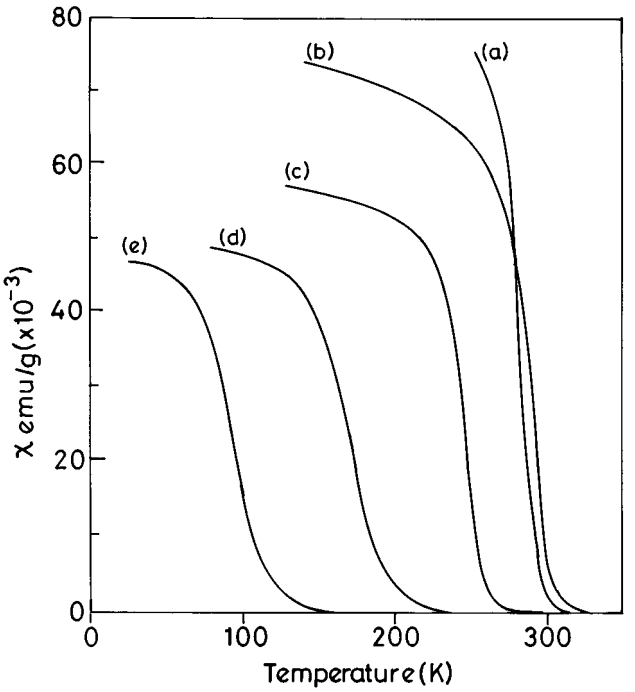

FIG. 7. Magnetic susceptibility as a function of temperature of potassium-doped lanthanum manganites measured at 1 K gauss field and 9 G gradient; curves (a), (b), (c), (e), and (g) correspond to composition as in Table 2.

gave 5–8% Mn deficiency. Mn^{4+} content was as high as 29% (see Tables 1 and 2). Ferromagnetic and insulating properties of such Mn-deficient oxide has been discussed in

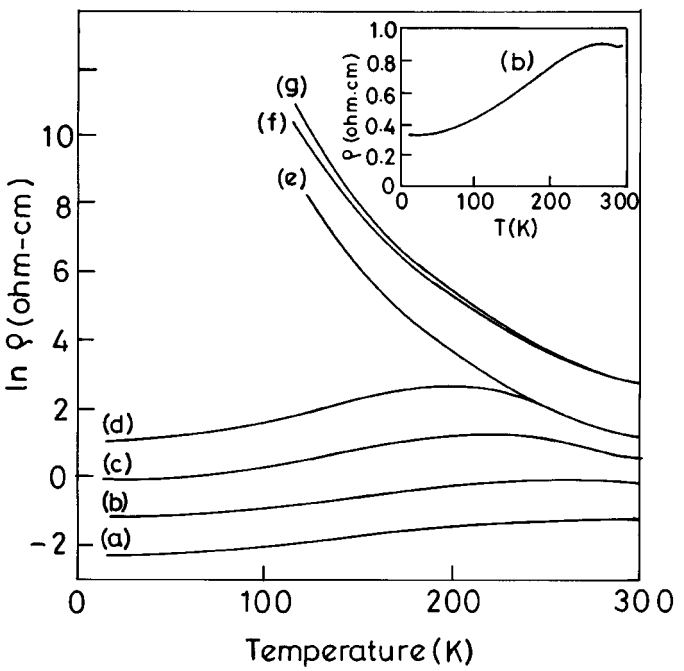

FIG. 8. Plots of $\ln\rho$ vs T of sodium-doped lanthanum manganites; curves (a), (b), (c), (d), (e), (f), and (g) correspond to composition as in Table 1. In the inset, ρ vs T plot of curve (b) in Table 1.

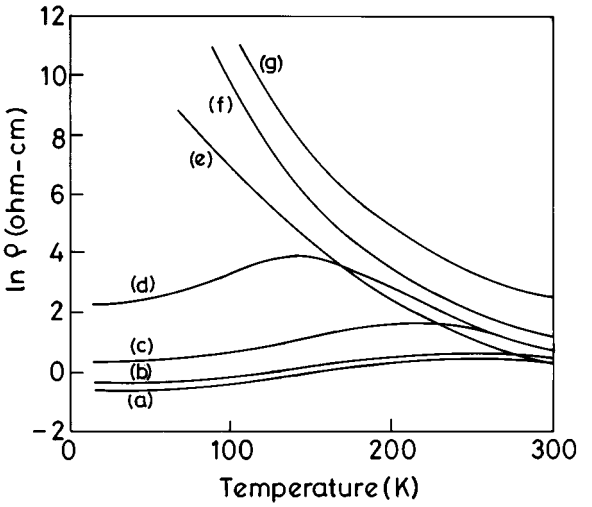

FIG. 9. Plots of $\ln\rho$ vs T of potassium-doped lanthanum manganite; curves (a), (b), (c), (d), (e), (f), and (g) correspond to composition as in Table 2.

detail by Topfer and Goodenough. They have suggested that the trapping of holes in Mn sites is the reason for the insulating behavior. It is interesting to find that these Mn-deficient oxides have T_c close to the values reported by them. Therefore, the flux method can be employed to make La site- as well as Mn site-deficient oxides by varying the La : Mn starting ratio.

The origin of orthorhombic to rhombohedral structural transition when the ferromagnetic insulating oxides are heated in oxygen or air at 850°C is not clear to us. One possibility is that further oxidation of Mn^{3+} to Mn^{4+} on heating may take place. This could create vacancy in the La site. Careful analysis and structural studies are needed to confirm this.

5. CONCLUSION

Sodium or potassium doped lanthanum orthomanganites have been grown in NaCl or KCl melts at relatively low temperatures for the first time. Maximum Na content substituted for La was 0.13, and K was 0.08. The compounds have typical composition $La_{1-x-y}Na_xMnO_{3-\delta}$, with both La and oxygen deficiencies. The highest T_c of Na-doped oxide was 325 K, and K-doped oxide was 310 K. Neutron diffraction studies supported the formation of such phases crystallizing in $R\bar{3}C$ space group. The oxides crystallizing in rhombohedral structure with A-site vacancy and Mn^{4+} content greater than 18% show insulator-to-metal transition coupled with para- to ferromagnetic transition. Oxides crystallizing in orthorhombic structure with Mn-site vacancy and 24–29% Mn^{4+} content are ferromagnetic insulators only.

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