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PREPARATION AND CRYSTALLOGRAPHIC PROPERTIES OF THE SYSTEMS $LaMn_{1-x}Mn_xO_{3+\lambda}$ AND $LaMn_{1-x}Ni_xO_{3+\lambda}$ JA-1106*

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Abstract—Lanthanum manganese oxides containing varying percentages of Mn^{+4} were prepared and their cell dimensions determined. Lanthanum manganese oxide, prepared under pure nitrogen, contained 0·02 per cent Mn^{+4}. At room temperature it possessed orthorhombic symmetry and was the most distorted member of the series. The orthorhombic-to-rhombohedral transition points for members of this series have been determined, and the shape of the resulting curve interpreted on the basis of an ordering of four, coplanar empty orbitals of the Mn^{+3} ions and steric effects. The system $LaNi_xMn_{1-x}O_{3+\lambda}$ has been prepared and its crystallographic properties studied. La_2NiO_4, $LaNiO_3$ and an intermediate lanthanum nickel oxide were prepared and their X-ray data are given.

1. INTRODUCTION

RECENTLY,(1–4) it has been reported that several rare-earth perovskite-type oxides containing Mn^{+3} ions and another transition metal ($LaMn_xM_{1-x}O_3$) have displayed interesting magnetic and crystallographic properties. JONKER and VANSANTEN(1) first investigated compounds with $M = Mn^{+4}$ and discovered ferromagnetism in the range of compositions 10–50 per cent of the total manganese as Mn^{+4}. JONKER(2) reported ferromagnetism in compounds containing $M = Ti^{+4}$ and Cr^{+3} in a range of compositions about 13 per cent $BaTiO_3$ and 25 per cent $LaCrO_3$. GILLEO(3) has reported ferromagnetism in the systems $LaCo_xMn_{1-x}O_3$ and $LaCr_xMn_{1-x}O_3$; he found no ferromagnetic region in compounds containing $LaFeO_3$. WOLD *et al.*(4) have reported ferromagnetism in the system $LaNi_xMn_{1-x}O_{3+\lambda}$ over the compositional range $0{\cdot}2 \leqslant x \leqslant 0{\cdot}5$.

GELLER(5) has indicated that the rare earth–transition metal perovskites fall into one of two groups. Most of them are orthorhombic and belong to space-group $D_{2h}(16)$—*Pbnm* with four distorted perovskite units in the true crystallographic cell, or they are rhombohedral and belong to space-group $D_{3d}(5)$—$R\bar{3}m$ with two formula units per unit cell. YAKEL(6) and WOLLAN and KOEHLER(7) have shown that $LaMnO_3$ containing 8·9 per cent Mn^{+4} is orthorhombic, and for concentrations of tetravalent manganese up to about 25 per cent, X-ray diffraction patterns indicated that an orthorhombic or monoclinic symmetry is still present. Samples of $LaMnO_{3+\lambda}$ which contained 35·3 per cent Mn^{+4} possessed rhombohedral symmetry. GELLER(5) has indicated that perovskite oxides containing V^{+3}, Cr^{+3}, Mn^{+3} and Fe^{+3} are orthorhombic, whereas Co^{+3} and Al^{+3} perovskite oxides are rhombohedral. He has deduced a set of ionic radii for these ions in perovskite lattices. The radii of the former set of ions range from 0·61 to 0·63 Å, whereas Co^{+3} and Al^{+3} have radii of approximately 0·56 Å. Thus it is implied that the difference in distortion is the result of a difference in size of the transition-element cation.

The orthorhombic distortion from cubic symmetry observed for pure $LaMnO_3$ is larger than that for the other orthorhombic perovskites. GOODENOUGH(4,8) has indicated that this large orthorhombic distortion is due to a particular

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ordering of the four coplanar, empty orbitals of the Mn^{+3} ions shown in Fig. 1; smaller distortions from cubic symmetry result when this ordering is destroyed. The introduction of ions such as Mn^{+4}, Cr^{+3}, Co^{+3} and Fe^{+3} which do not have an unequal occupation of d_{z^2} and $d_{x^2-y^2}$ orbitals when located in an octahedral oxygen-ion interstice, reduces the number of ions which are available to participate in the distortion mechanism. Consequently, the magnitude of this distortion and the temperature of the transition from orthorhombic to rhombohedral are expected to decrease with increasing concentration of foreign ions. At a greater concentration than 10–20 atomic per cent, the bond ordering which is responsible for these distortions is completely destroyed. It is a purpose of this paper to investigate the relative magnitude of these effects.

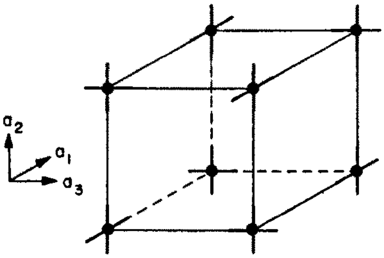

FIG. 1. Simple-cubic array of transition-element ions in perovskite-type lattice, showing the orientations of empty $d_{x^2-y^2}$ orbitals responsible for orthorhombic symmetry.

WOLD *et al.*(9) have reported the preparation and structure of $LaNiO_3$. $LaNiO_3$ belongs to space-group $D_{3d}(5)—R\bar{3}m$ with two formula weights per unit cell. The dimensions of the rhombohedral pseudocell are $a = 7{\cdot}676 \pm 0{\cdot}002$ Å, $\alpha = 90°41'$. RABENAU and ECKERLIN(10) have prepared La_2NiO_4, which possesses the K_2NiF_4 structure with $a = 3{\cdot}855$ Å and $c = 12{\cdot}65$ Å.

2. EXPERIMENTAL

Preparation of pure $LaMnO_3$. The samples were prepared by reacting lanthanum oxide with manganese (III) oxide under a pure nitrogen atmosphere at 1300°C for 18 hr. Traces of oxygen were removed by first passing the nitrogen through heated copper gauze and covering the samples with a nickel boat.

Preparation of $LaMn_x{}^{+3}Mn_{1-x}{}^{+4}O_{3+\lambda}$. Lanthanum oxide and manganese (III) oxide were heated for 72 hr under an oxygen atmosphere at 1100°C. These samples possessed the maximum amount of Mn^{+4} (30 per cent) obtained in this study. The intermediate lanthanum manganese oxides were prepared by heating portions of these samples under oxygen at various temperatures between 1100 and 1514°C, until equilibrium conditions were obtained. The samples were transferred to sealed Vycor capsules and annealed at 800°C for 72 hr in order to obtain well-crystallized products.

Preparation of $LaMn_{1-x}Ni_xO_{3+\lambda}$. These samples were prepared by reacting lanthanum oxide with varying molar mixtures of nickel (II) oxide and manganese (III) oxide in air at 1100°C and annealing the products at 800°C to improve their crystallinity.

Preparation of $LaNiO_3$ and La_2NiO_4. Lanthanum oxide and nickel (II) oxide, in the molar ratios 1 : 1 and 2 : 1, were heated at 900 and 1350°C respectively to produce $LaNiO_3$ and La_2NiO_4.

Standard analytic techniques were used to determine the total oxidation of the product; excess oxidizing power of the transition-metal cations was attributed to the presence of Mn^{+4} and a deficiency to the presence of Ni^{+2}.

The lattice symmetry and lattice parameters were calculated from spectrometer traces taken with a Philips Norelco diffractometer, using Fe$K\alpha$ and Cu$K\alpha$ radiation. The transition temperatures above room temperature were determined by using a furnace mounted on a Norelco X-ray diffractometer. The instrument is a modified version of that described by PERRI *et al*,(11) and another in the Geology Department, Columbia University. It was adapted for atmospheric control, and during measurements of samples with low Mn^{-4} content, a nitrogen atmosphere was used. Transition temperatures below room temperature were obtained by passing nitrogen, cooled with liquid nitrogen, over the samples. The instrumentation is a modified version of that described by SCHWARTZ *et al.*(12)

3. DISCUSSION

Lanthanum manganese oxides. Results of chemical and crystallographic analysis are summarized in

Table 1. Chemical and crystallographic analysis of lanthanum manganese oxides

Conditions	Mn^{+4} (per cent)	Symmetry*	Pseudocubic cell dimensions
1300°C PURE N_2	0·02	O	$a_1 = a_3 = 7{\cdot}961$ Å $a_2 = 7{\cdot}699$ Å $\beta = 91° 56'$
1514°C O_2	8·7	O	$a_1 = a_3 = 7{\cdot}895$ Å $a_2 = 7{\cdot}744$ Å $\beta = 90° 57'$
1465°C O_2	9·6	O	$a_1 = a_3 = 7{\cdot}888$ Å $a_2 = 7{\cdot}746$ Å $\beta = 90° 54'$
1281°C O_2	12·4	O	$a_1 = a_3 = 7{\cdot}865$ Å $a_2 = 7{\cdot}768$ Å $\beta = 90° 28'$
1350°C AIR	19·8	O	$a_1 = a_3 = 7{\cdot}804$ Å $a_2 = 7{\cdot}790$ Å $\beta = 90° 20'$
1100°C O_2	24·0	R	$a = 7{\cdot}784$ Å $\alpha = 90° 36'$
1100°C O_2	26·6	R	$a = 7{\cdot}777$ Å $\alpha = 90° 35'$
1100°C O_2	30·0	R	$a = 7{\cdot}777$ Å $\alpha = 90° 35'$

* O = Orthorhombic.
R = Rhombohedral.

Table 1. Pure lanthanum manganese oxide, prepared under pure nitrogen, contained 0·02 per cent Mn^{+4} and at room temperature was the most distorted member of the series. The maximum percentage of Mn^{+4} (30 per cent) was obtained by heating the samples at 1100°C in oxygen for six days. In order to illustrate the various distortions of the perovskite structure, reported in Table 1, the pseudocubic cell dimensions have been given for all cases. For the orthorhombic distortion, the pseudocubic lattice is monoclinic, and for the rhombohedral distortion it is a non-primitive rhombohedron. Fig. 2 was plotted using the monoclinic cell dimensions listed in Table 1. It is assumed that when the two cell edges become equal, the transformation to the rhombohedral structure occurs. As Fig. 2 shows, at room temperature, this transformation takes place when 21 per cent Mn^{+4} is present in the sample.

The variation of transition temperature with Mn^{+3} content for the various lanthanum manganese oxide samples is plotted in Fig. 3, the room-temperature transition point being obtained from Fig. 2.

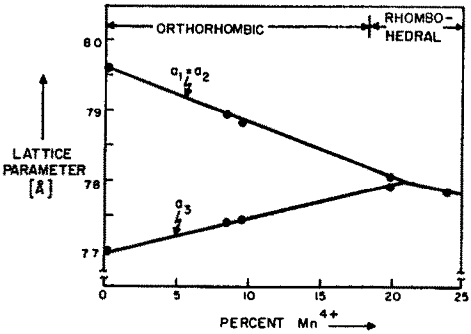

FIG. 2. Room-temperature lattice parameters for pseudo-cubic cell of $LaMnO_{3+\lambda}$ as a function of Mn^{+4} concentration. The rhombohedral phase for sample with 24 per cent Mn^{+4} undergoes a martensitic transformation through the temperature range 175°C $\leqslant T \leqslant$ −45°C, the low-temperature phase being orthorhombic. At −160°C, $a_2/a_3 = 0{\cdot}963$ for pure $LaMnO_3$. By analogy with MnF_3, this should correspond to an average axial ratio in distorted octahedra of ~ 1·15.

It should be noted that the curve plotted in Fig. 3 has an inflection point at about room-temperature. The higher-temperature portion of the curve can be explained by the bond-ordering concepts of GOODENOUGH. Perovskite oxides containing percentages of Mn^{+3} greater than approximately 75 will show an orthorhombic distortion because of the ordering of four coplanar empty orbitals of the Mn^{+3} ions (Fig. 1). This distortion is largest ($a_2/a_1 = 0{\cdot}97$) for pure $LaMnO_3$. The introduction of other ions, e.g. Mn^{+4}, which do not have an unequal occupation of d_{z^2} and $d_{x^2-y^2}$ orbitals when located in an octahedral oxygen-ion interstice, reduces the magnitude of the distortions due to bond ordering of the Mn^{+3} ions and in concentrations greater than 10–20 atomic per cent, destroys the bond ordering to eliminate lattice distortions from this effect. Smaller distortions would, therefore, result. At 21 per cent Mn^{+4}, there are sufficient foreign ions present to destroy this ordering, and the residual distortion is due to some other effect. As shown by WICKHAM and CROFT,(13) a similar effect is present in spinel oxides containing Mn^{+3}, where the critical concentration is about 60 per cent Mn^{+3}. Below that percentage, the tetragonal distortion is not present down to −180°C. The magnetic data indicate its probable absence down to liquid-helium temperature. The abrupt change in transformation temperature with composition at a critical composition is characteristic of long-range bond ordering.

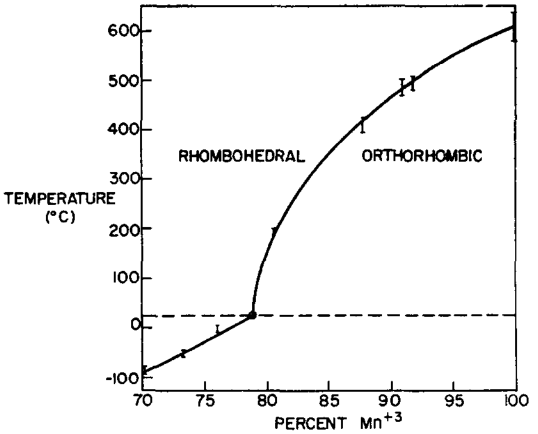

FIG. 3. Transition temperature of $LaMnO_3$ versus Mn^{+3} content.

Fig. 3 also shows that perovskite oxides, containing less than the critical amount of Mn^{+3} (79 per cent), still transform to the orthorhombic structure below room temperature. However, there is a marked change in the slope of the curve. As mentioned previously, it would be expected that $LaMnO_3$ would be orthorhombic on the basis of its ionic size alone. The presence of considerable amounts of the smaller Mn^{+4} ion should favor the formation of the rhombohedral perovskite. The change of the slope of the curve in Fig. 3 is due to the disappearance of the bond-orienting effect leaving the size effect as the predominant one.

Lanthanum nickel oxides. Lanthanum nickel oxide ($LaNiO_3$) was reported previously by WOLD *et al.*(8) Samples of $LaNiO_3$ are stable up to 900°C. Above this temperature, appreciable amounts of Ni^{+2} form. At 1300°C, pure La_2NiO_4 can be prepared and has been reported to possess the K_2NiF_4 structure. When $LaNiO_3$ is heated to 1100°C, some Ni^{+2} is formed and appears as NiO. The remaining phase cannot be indexed as either $LaNiO_3$ or La_2NiO_4, but is apparently a much distorted perovskite (Table 2). Attempts to prepare this phase pure, by heating lanthanum oxide and nickel (II) oxide were unsuccessful because of the greater stability of the La_2NiO_4 compound which formed. Evidently, the perovskite lattice will

Table 2. Comparison of unidentified lanthanum nickel oxide phase at 1100°C *with $LaNiO_3$ and La_2NiO_4*

$LaNiO_3$ (Perovskite)		Unidentified Phase		La_2NiO_4 (K_2NiF_4)	
d	*I*	*d*	*I*	*d*	*I*
				6·30	5
3·82	40	3·79	20		
				3·69	35
		3·49	10		
				3·16	15
				2·85	100
		2·77	100		
2·73	100	2·73	40	2·73	60
2·69	90	2·70	40		
2·22	30				
2·19	10	2·15	15	2·12	25
		1·996	6	2·06	35
1·917	60	1·921	40	1·932	40
1·722	10				
1·706	10			1·712	10
		1·676	10	1·673	15

Table 3. *X-ray lattice constants for the system* $LaMn_{1-x}Ni_xO_3$

Sample	Mn^{+4} (per cent)	a_0(Å)	b_0(Å)	c_0(Å)	Vol. (Å^3)
$LaMnO_{3+\lambda}$	19·8	5·501	5·536	7·786	237·0
$LaMn_{0\cdot8}Ni_{0\cdot2}O_{3+\lambda}$	13·0	5·495	5·530	7·782	236·5
$LaMn_{0\cdot7}Ni_{0\cdot3}O_{3+\lambda}$	6·2	5·487	5·523	7·773	235·6
$LaMn_{0\cdot6}Ni_{0\cdot4}O_{3+\lambda}$	6·8	5·474	5·515	7·754	234·1
$LaMn_{0\cdot5}Ni_{0\cdot5}O_{3+\lambda}$	2·1	5·463	5·512	7·740	233·1

accommodate a considerable deficiency of nickel and persist as a metastable phase.

The system $LaNi_xMn_{1-x}O_{3+\lambda}$. The system $LaNi_xMn_{1-x}O_{3+\lambda}$ consists of a single orthorhombic phase from $0 \leqslant x \leqslant 0{\cdot}5$ (Table 3). Where $x > 0{\cdot}5$, two phases appear: an orthorhombic phase which resembles $LaMn_{0\cdot5}Ni_{0\cdot5}O_3$ and the metastable lanthanum nickel oxide phase previously mentioned. Nickel oxide lines appear in increasing intensity as x increases.

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