

# ALaMn<sub>2</sub>O<sub>6-y</sub> (A = K, Rb): Novel Ferromagnetic Manganites Exhibiting Negative Giant Magnetoresistance

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We report the synthesis of a new series of manganese oxides, ALaMn<sub>2</sub>O<sub>6-y</sub>, for A = K, Rb, and Cs, that adopt an ordered superstructure of the perovskite. The K and Rb phases are tetragonal ( $a_t \sim 7.75$ ,  $c_t \sim 7.10$  Å) and the Cs phase is orthorhombic ( $a_0 = 5.511$ ,  $b_0 = 5.468$ ,  $c = 7.311$  Å) indicating  $2a_p \times 2a_p$  and  $\sqrt{2}a_p \times \sqrt{2}a_p \times 2a_p$  ( $a_p$  = perovskite subcell) superstructures, respectively. The K and Rb phases are ferromagnetic ( $T_c \sim 327$  and 300 K) metals, exhibiting a giant magnetoresistance behavior similar to alkaline earth metal substituted lanthanide manganites. The results reveal that it is possible to induce Mn(III)/Mn(IV) mixed valency and the related electronic properties through anion deficiency in ordered perovskites of the kind ALaMn<sub>2</sub>O<sub>6</sub>.

## Introduction

The discovery of a large negative magnetoresistance in perovskite manganites of the general formula Ln<sub>1-x</sub>A<sub>x</sub>MnO<sub>3</sub> (Ln = La, Nd; A = Ca, Sr, Ba, Pb)<sup>1-3</sup> has created a renewed interest in this family of oxides which were known to be unique among perovskite oxides exhibiting ferromagnetic and metallic properties.<sup>4,5</sup> While the exact mechanism of magnetoresistance is yet to be established unambiguously, systematic investigations carried out so far have revealed the importance of mixed valency of manganese (Mn<sup>III</sup>/Mn<sup>IV</sup>) as well as the mean size of the large Ln/A atoms in determining the electronic properties of these materials.<sup>6-8</sup> Thus, La<sub>1-x</sub>A<sub>x</sub>MnO<sub>3</sub> (A = Ca, Sr, Ba) are in general ferromagnetic conductors for  $x \approx 0.25-0.33$  (mean oxidation state of Mn = +3.25–3.33) and antiferromagnetic insulators for  $x \geq 0.5$  (mean oxidation state of Mn  $\geq +3.5$ ). In the ferromagnetic region, the materials exhibit a large negative magnetoresistance (known as colossal magnetoresistance, CMR), while for  $x = 0.5$  the materials are, in general, charge-ordered insulators due to ordering of charges at distinct Mn<sup>III</sup> and Mn<sup>IV</sup> sites.

Besides substitution of alkaline earth or alkali cations at the Ln sites of LnMnO<sub>3</sub>, a mixed valency of manganese can in principle be produced in two other ways. One way is to create cation vacancies at the Ln/Mn sites (Ln<sub>1-x</sub>Mn<sub>1-x</sub>O<sub>3</sub>), and the other way is to create anion vacancies, AMnO<sub>3-x</sub>. While the former mode has already been well-characterized in nominally oxygen-excess LaMnO<sub>3+y</sub> perovskites,<sup>9,10</sup> the latter mode of creating mixed-valency, namely, anion-deficient nonstoichiometry in the perovskite manganites, has not been investigated, to our knowledge.

In an attempt to realize this possibility, we investigated the formation of manganites of the general formula ALaMn<sub>2</sub>O<sub>6-y</sub> for A = K, Rb, and Cs. While substitution of small amounts of alkali metals in LaMnO<sub>3</sub> giving La<sub>1-x</sub>A<sub>x</sub>MnO<sub>3</sub> for  $x \leq 0.2$  has been reported in the literature,<sup>11,12</sup> manganites of the composition ALaMn<sub>2</sub>O<sub>6-y</sub> (which would correspond to  $x = 0.5$  in the formula La<sub>1-x</sub>A<sub>x</sub>MnO<sub>3</sub>) have not been reported. To our knowledge, YBaMn<sub>2</sub>O<sub>5</sub> is the only other mixed-valent manganite which has an anion-deficient perovskite related structure.<sup>13</sup>

We have been able to synthesize for the first time an isotopic series of manganites of the formula ALaMn<sub>2</sub>O<sub>6-y</sub> for A = K, Rb, and Cs. The value of  $y$  in these materials varies with the identity of the A cation. All of these phases are ferromagnetic (the  $T_c$ 's are 325, 300, and ~175 K for the K, Rb, and Cs phases, respectively)

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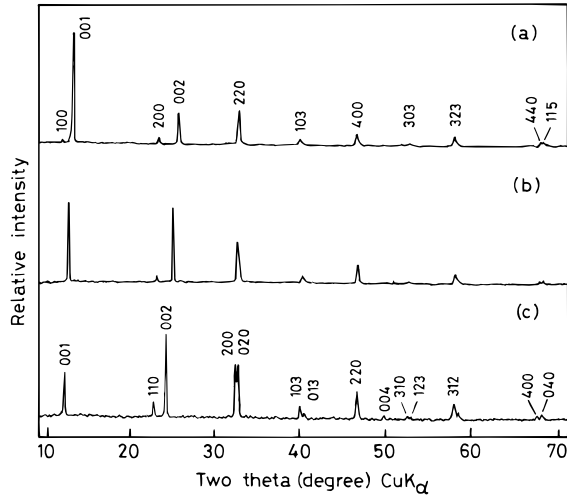
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**Table 1. Chemical Composition and Lattice Parameters of *ALaMn<sub>2</sub>O<sub>6-y</sub>* Manganites**

composition	Mn(III)%	Mn(IV)%	lattice parameters (Å)		
			<i>a</i>	<i>b</i>	<i>c</i>
<i>K</i> <sub>1.02</sub> <i>La</i> <sub>0.99</sub> <i>Mn</i> <sub>1.98</sub> <i>O</i> <sub>5.43</sub>	53	47	7.745(1)		7.020(2)
<i>Rb</i> <sub>0.997</sub> <i>La</i> <sub>1.00</sub> <i>Mn</i> <sub>2.00</sub> <i>O</i> <sub>5.53</sub>	47	53	7.773(1)		7.149(1)
<i>Cs</i> <sub>0.99</sub> <i>La</i> <sub>0.98</sub> <i>Mn</i> <sub>1.96</sub> <i>O</i> <sub>5.59</sub>	30	70	5.511(2)	5.468(3)	7.311(4)
<i>Cs</i> <sub>0.98</sub> <i>La</i> <sub>0.99</sub> <i>Mn</i> <sub>1.98</sub> <i>O</i> <sub>5.80</sub> <sup>a</sup>	14	86	5.509(2)	5.470(2)	7.389(5)

<sup>a</sup> Obtained by the citrate method



**Figure 1.** Powder X-ray diffraction patterns of *ALaMn<sub>2</sub>O<sub>6-y</sub>*. (a) A = K. (b) A = Rb. (c) A = Cs.

conductors (K, Rb) exhibiting CMR. Here we describe the synthesis and the investigation of structure and electronic properties of these manganites.

**Experimental Section**

Oxides of the composition *ALaMn<sub>2</sub>O<sub>6-y</sub>* for A = K, Rb, or Cs were synthesized by dissolving required quantities of *A<sub>2</sub>CO<sub>3</sub>*, *La<sub>2</sub>O<sub>3</sub>*, and *MnC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O* in 1:1 *HNO<sub>3</sub>*, evaporating the solution to dryness, and heating the dried mass in air at 750–900 °C for varying durations. Samples were also prepared by the citrate method<sup>10</sup> followed by prolonged annealing in oxygen at 750 °C to obtain a high oxygen content in *ALaMn<sub>2</sub>O<sub>6-y</sub>* for A = K and Cs. Formation of single-phase products was monitored by powder X-ray diffraction (JEOL-JDX 8P Powder X-ray diffractometer, Cu Kα radiation). Single-phase products for K and Rb manganites were obtained by reaction at 900 °C for 24 h with one intermittent grinding, while the Cs manganite was obtained by reaction at 800 °C for 24 h.

Chemical compositions of the manganites were determined by EDX analysis and redox titrations by the method of Bloom et al.<sup>14</sup> EDX analysis (JEOL JSM 840A scanning electron microscope) was employed to determine the A:La:Mn ratios, while redox titrations were carried out to determine the total manganese content as well as the individual Mn(III) and Mn(IV) contents of each sample. The compositions of the manganites determined by combining the results of EDX analysis and redox titrations are given in Table 1. X-ray powder patterns of the manganites (Figure 1) were indexed on tetragonal/orthorhombic systems using the PROSZKI program,<sup>15</sup> and the least-squares refined lattice parameters are listed in Table 1. Indexed powder diffraction data for *KLaMn<sub>2</sub>O<sub>6-y</sub>* and *CsLaMn<sub>2</sub>O<sub>6-y</sub>* are given in Tables 2 and 3. Magnetization was measured using a commercial SQUID magnetometer. Resistivity was measured by a standard 4-line contact technique.

**Table 2. Indexed Powder Diffraction Data for *KLaMn<sub>2</sub>O<sub>6-y</sub>* (*y* = 0.47)<sup>a</sup>**

<i>hkl</i>	<i>d</i> <sub>obs</sub> (Å)	<i>d</i> <sub>calc</sub> (Å)	<i>I</i> <sub>obs</sub>
100	7.761	7.745	2
001	7.025	7.020	100
200	3.867	3.872	8
002	3.507	3.510	30
220	2.739	2.738	32
103	2.241	2.240	7
400	1.937	1.936	11
303	1.734	1.734	2
323	1.583	1.582	9
440	1.369	1.360	4
115	1.361	1.360	2

<sup>a</sup> *a* = 7.745(1); *c* = 7.020(2) Å.

**Table 3. Indexed Powder Diffraction Data for *CsLaMn<sub>2</sub>O<sub>6-y</sub>* (*y* ≈ 0.4)<sup>a</sup>**

<i>hkl</i>	<i>d</i> <sub>obs</sub> (Å)	<i>d</i> <sub>calc</sub> (Å)	<i>I</i> <sub>obs</sub>
001	7.314	7.311	51
110	3.875	3.881	18
002	3.655	3.656	100
200	2.751	2.755	65
020	2.730	2.734	65
103	2.231	2.229	16
013	2.225	2.226	8
220	1.941	1.941	33
004	1.828	1.828	8
310	1.743	1.741	4
123	1.727	1.727	3
312	1.574	1.572	10
400	1.377	1.378	6
040	1.367	1.367	6

<sup>a</sup> *a* = 5.511(2); *b* = 5.468(3); *c* = 7.311(4) Å.

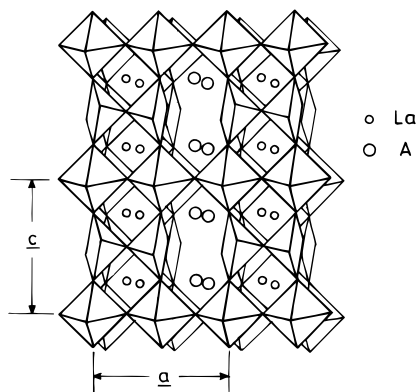
**Results and Discussion**

New manganites corresponding to the nominal composition *ALaMn<sub>2</sub>O<sub>6-y</sub>* are readily formed for A = K, Rb, and Cs by reacting the constituents in air around 800–900 °C. Determination of their chemical composition by redox titrations to give total manganese as well as individual Mn(III) and Mn(IV) contents together with EDX analysis shows that the actual compositions (Table 1) are close to the nominal composition, except that the phases are anion-deficient due to mixed valency of manganese. Significantly, the anion deficiency (*y*) of the as-prepared samples decreases (Mn(IV) content increases) as the A cation changes from K to Rb to Cs.

Powder X-ray diffraction (XRD) (Figure 1) shows that the *ALaMn<sub>2</sub>O<sub>6-y</sub>* oxides possess a unique structure different from the common perovskite structure of *La<sub>1-x</sub>A<sub>x</sub>MnO<sub>3</sub>* (A = Ca, Sr, Ba). We could index the XRD patterns of *ALaMn<sub>2</sub>O<sub>6-y</sub>* for A = K and Rb on tetragonal cells with *a<sub>t</sub>* ~ 7.75 and *c<sub>t</sub>* ~ 7.10 Å (Tables 1 and 2). The tetragonal cell is probably related to the cubic perovskite cell as *a<sub>t</sub>* ~ 2*a<sub>p</sub>* and *c<sub>t</sub>* ~ 2*a<sub>p</sub>* (*a<sub>p</sub>* = perovskite subcell). The cesium manganite, *CsLaMn<sub>2</sub>O<sub>6-y</sub>*, however, is slightly different, adopting an orthorhombic cell (Table 3) with *a<sub>o</sub>* ~ √2*a<sub>p</sub>*, *b<sub>o</sub>* ~ √2*a<sub>p</sub>*, and *c<sub>o</sub>* ~ 2*a<sub>p</sub>*.

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**Figure 2.** A possible structure for  $\text{ALaMn}_2\text{O}_{6-y}$  ( $y = 0.5$ ) manganites showing ordering of both oxygen vacancies and A and La atoms. In the real samples, the ordering of A and La atoms may not be complete.

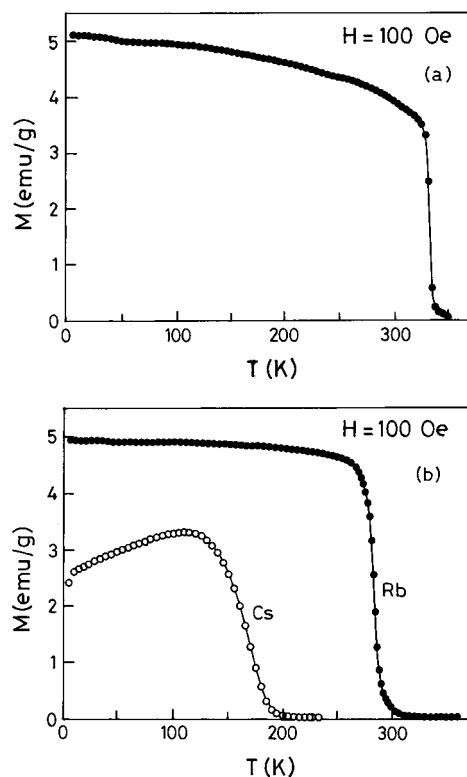
Considering that the oxygen deficiency  $y$  in  $\text{ALaMn}_2\text{O}_{6-y}$  is close to 0.5 in A = K and Rb phases, we expected that the superstructure of these manganites could be related to the oxygen-deficient perovskites of the kind  $\text{Ba}_2\text{Ln}_2\text{Cu}_2\text{M}_2\text{O}_{11}$  (Ln = La or rare earth; M = Sn or Ti).<sup>16</sup> These oxides possess a quadruple perovskite structure,  $1a_p \times 1a_p \times 4a_p$ , where the oxygen vacancies and Ba/Ln atoms are ordered to give rise to a layered structure consisting of  $\text{CuO}_{5/2}$  square pyramids and  $\text{MO}_{6/2}$  octahedra. We have generated the X-ray powder pattern of  $\text{ALaMn}_2\text{O}_{5.5}$  (A = K, Rb) manganites assuming the quadruple perovskite structure model ( $\text{Ba}_2\text{Ln}_2\text{Cu}_2\text{Ti}_2\text{O}_{11}$ ), replacing Ba by K/Rb, Ln by La, and Cu/Ti by Mn. The generated pattern, however, did not match the observed XRD pattern of  $\text{ALaMn}_2\text{O}_{5.5}$  (A = K, Rb). The observed XRD pattern did not match that of  $\text{Ca}_4\text{Ti}_2\text{Fe}_2\text{O}_{11}$ <sup>17</sup>, either, which is another possible perovskite superstructure for the composition  $\text{A}_2\text{La}_2\text{Mn}_4\text{O}_{11}$ .

A comparison of both the XRD patterns and the lattice parameters of  $\text{ALaMn}_2\text{O}_{5.5}$  (A = K, Rb) manganites with those of the various oxygen-deficient perovskite oxides known so far<sup>16</sup> has revealed a similarity between  $\text{ALaMn}_2\text{O}_{5.5}$  and  $\text{La}_2\text{Ni}_2\text{O}_5$ .  $\text{La}_2\text{Ni}_2\text{O}_5$  possesses a tetragonal ( $a = 7.816$ ,  $c = 7.468$  Å) perovskite superstructure<sup>16a,18</sup> where  $\text{NiO}_{6/2}$  octahedra and  $\text{NiO}_{4/2}$  square planes alternate along the  $c$ -direction. Addition of 0.5 extra oxygen per formula unit would convert the square planes to square pyramids giving a new tetragonal superstructure of  $\text{AA}'\text{M}_2\text{O}_{5.5}$  composition (Figure 2), which is a likely structure for  $\text{ALaMn}_2\text{O}_{5.5}$  (A = K, Rb). This structure is consistent with the coordination preferences (octahedral and square pyramidal) of Mn(III) and Mn(IV) in perovskite oxides. This three-dimensional structure is also consistent with the large ferromagnetic  $T_c$  values (see later) observed for these oxides. A quadruple perovskite structure for  $\text{ALaMn}_2\text{O}_{5.5}$  would have given a much lower  $T_c$  because of its layered character.

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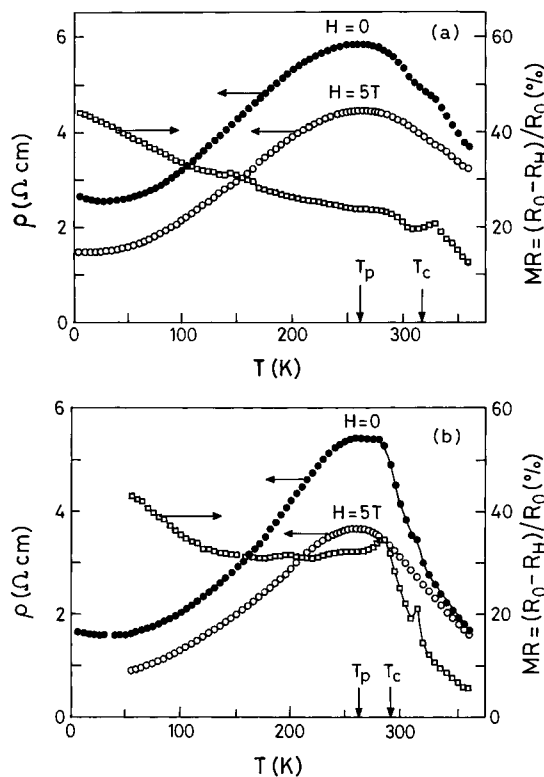
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**Figure 3.** Magnetization vs temperature plots for  $\text{ALaMn}_2\text{O}_{6-y}$ . (a) A = K. (b) A = Rb and Cs.

The orthorhombic distortion of  $\text{CsLaMn}_2\text{O}_{6-y}$  ( $y < 0.5$ ) phases likely arises because of insertion of extra oxygens into the  $\text{ALaMn}_2\text{O}_{5.5}$  superstructure that would destroy the perfect square pyramidal  $\text{MnO}_{5/2}$  and octahedral  $\text{MnO}_{6/2}$  alternation in the superstructure (Figure 2); the large size of Cs also could play a role in the structural distortion. Determination of the actual structure of  $\text{ALaMn}_2\text{O}_{6-y}$  manganites is required to confirm the structural model proposed.

Considering the presence of mixed-valent manganese [Mn(III) and Mn(IV)] and an ordered perovskite-related structure for  $\text{ALaMn}_2\text{O}_{6-y}$ , we expected that these oxides would exhibit ferromagnetic and conducting properties including CMR, similar to  $\text{La}_{1-x}\text{A}_x\text{MnO}_3$  (A = Ca, Sr, Ba). Measurements of electrical and magnetic properties of  $\text{ALaMn}_2\text{O}_{6-y}$  indeed reveal that they are ferromagnetic conductors similar to the CMR manganites. The K and Rb phases of  $\text{ALaMn}_2\text{O}_6$  are ferromagnetic with  $T_c$ 's of  $327 \pm 1$  and  $290 \pm 3$  K, respectively (Figure 3). The experimentally measured values of saturation magnetization,  $M_s$ , are equal to  $74 \pm 2$  and  $64 \pm 2$  emu/g, respectively. These values are smaller than the corresponding values, 104.6 and 91.1 emu/g, calculated using the formula  $M_s = g\mu_B\langle S \rangle$ , where  $g = 2$  is Lande g factor,  $\mu_B$  is the Bohr magneton, and  $\langle S \rangle$  is the average spin value, for the appropriate Mn(III) and Mn(IV) content (Table 1). The discrepancy could in part be due to the presence of alkali cations which render the samples sensitive to atmospheric  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . We tried to minimize this possibility by preserving the samples in evacuated sealed tubes until the measurements were made. Another possibility is that these oxides possess a canted ferromagnetic structure. Although  $\text{CsLaMn}_2\text{O}_{5.59}$  exhibits the onset of the spontaneous magnetization around 170 K, the transition is



**Figure 4.** Electrical resistivity vs temperature plots at  $H = 0$  and  $H = 5\text{ T}$  for (a)  $\text{KLaMn}_2\text{O}_{6-y}$ , and (b)  $\text{RbLaMn}_2\text{O}_{6-y}$ . The MR ratio is also indicated.

very broad, and zero-field-cooled temperature dependence of the magnetization (Figure 3b) is similar to the

spin glass behavior. So,  $\text{CsLaMn}_2\text{O}_{5.59}$  most probably does not have a long-range ferromagnetic order at low temperature.

Zero-field electrical resistivity data for the K and Rb phases are typical of ferromagnetic manganites showing a peak in the resistivity-temperature plots near  $T_c$  (Figure 4). Nevertheless, the peak temperature,  $T_p$  is significantly lower than the Curie temperature for these compounds, which was not observed for other manganites. Measurement of magnetoresistance at an applied field of  $H = 5\text{ T}$  shows a clear suppression of resistivity (Figure 4) indicating the presence of a CMR effect in the K and Rb phases. Unlike other manganites in which  $T_p$  increases with an increase of magnetic field, in  $\text{KLaMn}_2\text{O}_{5.43}$  and  $\text{RbLaMn}_2\text{O}_{5.53}$  there is no noticeable change in  $T_p$ . Considerable magnetoresistance (MR) at low temperature can be attributed to the grain boundary effects in ceramic samples.  $\text{CsLaMn}_2\text{O}_{5.59}$ , which has a higher Mn(IV) content ( $\sim 70\%$ ), is semiconducting. Another sample of  $\text{CsLaMn}_2\text{O}_{5.80}$ , which has a still higher Mn(IV) content ( $\sim 86\%$ ), also shows semiconducting behavior. The results indicate that a higher Mn(IV)/Mn(III) ratio in  $\text{CsLaMn}_2\text{O}_{6-y}$  suppresses the long-range ferromagnetic ordering and the CMR property.

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