

## High Pressure Synthesis and Crystal Structure of a New Series of Perovskite-Like Compounds $\text{CMn}_7\text{O}_{12}$ (C = Na, Ca, Cd, Sr, La, Nd)

B. BOCHU, J. CHENAVAS, J. C. JOUBERT, AND M. MAREZIO

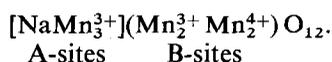
*Laboratoire des Rayons X—C.N.R.S., B.P. 166—Centre de Tri, 38042—Grenoble—Cedex, France*

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A new series of perovskite-like compounds  $\text{CMn}_7\text{O}_{12}$  have been synthesized under high pressure and high temperature conditions. C is a large divalent or trivalent cation such as Ca, Cd, Sr, La and Nd. The structures of the quenched materials have been determined from powder X-ray data. They are distortions of the  $\text{NaMn}_7\text{O}_{12}$  cubic structure. The  $[\text{C}^{2+}\text{Mn}_3^{3+}](\text{Mn}_3^{3+}\text{Mn}^{4+})\text{O}_{12}$  compounds are trigonal ( $R\bar{3}$ ). The  $\text{C}^{2+}$  and  $\text{Mn}^{3+}$  as well as the  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  cations are ordered on the corresponding A and B sites of the perovskite structure, respectively. The  $[\text{C}^{3+}\text{Mn}_3^{3+}](\text{Mn}_4^{3+})\text{O}_{12}$  compounds are monoclinic ( $I2/m$ ). In these compounds the order exists only in the A sites. It is shown that the lower symmetry may be the result of a cooperative Jahn–Teller effect of the  $\text{Mn}^{3+}$  cations occupying the B sites.

### Introduction

$\text{NaMn}_7\text{O}_{12}$  (1) is a perovskite-like compound in which the sodium and 3/7 of the manganese atoms occupy the A-sites of the perovskite structure, while the rest of the manganese atoms occupy the B-sites. Thus its formula can be written as follows:



The structure was found to be cubic at ambient temperature  $a = 7.3036 \text{ \AA}$ , space group  $Im\bar{3}$ , and 2 formulae ( $\text{NaMn}_7\text{O}_{12}$ ) per unit cell. The  $\text{Na}^{+1}$  and the  $\text{Mn}^{+3}$  corresponding to the A cations occupy 2 crystallographically independent sites. The sodium atoms are surrounded by 12 equidistant oxygen atoms arranged as a slightly distorted icosahedron. The  $\text{Mn}^{3+}$  cations are also surrounded by 12 oxygen atoms. However, the distortion of this polyhedron is so large that only 8 oxygen atoms can be considered as first neighbours. Four of these 8 oxygens are very close and form a square while the others form a rectangle perpendicular to

the square. As far as we know this is the first example of an 8-coordinated Jahn–Teller  $\text{Mn}^{3+}$  cation. The octahedral B-sites are occupied at random by  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  cations in equal proportion. The doubling of the perovskite unit cell is due to the order on the A-sites and to the distortion of the oxygen sublattice.

Because in the  $\text{NaMn}_7\text{O}_{12}$  compound the B-sites of the perovskite structure are occupied by  $\text{Mn}^{4+}$  and  $\text{Mn}^{3+}$  cations, it was thought that one could synthesize  $\text{CMn}_7\text{O}_{12}$  compounds with C being a large divalent and trivalent cation. The valence variation would be balanced by a change in the  $\text{Mn}^{3+}/\text{Mn}^{4+}$  ratio of the cations occupying the octahedral sites. This paper reports the high pressure synthesis and crystal structures of the Ca, Cd, Sr, La and Nd compounds.

### Experimental

The apparatus and the procedure of the high pressure experiments have been described in a preceding report (2). The experimental conditions used for the preparations of the

TABLE I  
EXPERIMENTAL CONDITIONS

C cation	Starting materials	High pressure conditions (1 hr)	Phases present in the quenched products
$\text{Ca}^{2+}$	$\text{CaO} + 3\text{Mn}_2\text{O}_3 + \text{MnO}_2$	80 kbar 1000°C	$\text{CaMn}_7\text{O}_{12}$ + trace of $\text{Mn}_2\text{O}_3$
	$\text{CaO} + 2\text{Mn}_2\text{O}_3 + 3\text{MnO}_2$	80 kbar 1000°C	$\text{CaMn}_7\text{O}_{12}$ + trace of $\text{MnO}_2$
$\text{Cd}^{2+}$	$\text{CdO} + 3\text{Mn}_2\text{O}_3 + \text{MnO}_2$	80 kbar 1000°C	$\text{CdMn}_7\text{O}_{12}$ + trace of an $X$ unknown phase
$\text{Sr}^{2+}$	$\text{Sr}(\text{OH})_2, 8\text{H}_2\text{O} + 3\text{Mn}_2\text{O}_3 + \text{MnO}_2$	50 kbar 1000°C	$\text{SrMn}_7\text{O}_{12}$ + traces of $\text{Mn}_2\text{O}_3$ and of a $Y$ unknown phase
$\text{La}^{3+}$	$\text{La}_2\text{O}_3 + 7\text{Mn}_2\text{O}_3$	40 kbar 1000°C	$\text{LaMn}_7\text{O}_{12}$
$\text{Nd}^{3+}$	$\text{Nd}_2\text{O}_3 + 7\text{Mn}_2\text{O}_3$	40 kbar 1000°C	$\text{NdMn}_7\text{O}_{12}$ (poorly crystallized)
$\text{Nd}^{3+}$	$\text{Nd}_2\text{O}_3 + 7\text{Mn}_2\text{O}_3$	80 kbar 1000°C	$\text{NdMn}_7\text{O}_{12}$ (well crystallized)

different compounds are reported in Table I. The powder X-ray photographs of the quenched materials were taken with a 360 mm circumference Guinier focusing camera,  $\text{FeK}\alpha$  radiation, ( $\lambda_x = 1.9373 \text{ \AA}$ ), and KCl as an internal standard. The lattice parameters of each compound were obtained by least-squares refinement.

## Results

It is readily seen from the powder photographs that the  $\text{CMn}_7\text{O}_{12}$  compounds are all  $\text{NaMn}_7\text{O}_{12}$ -like and that their symmetry is lower than cubic when C is a large divalent or trivalent cation. The powder patterns were indexed on a trigonal cell for the  $\text{C}^{2+}\text{Mn}_7\text{O}_{12}$  compounds whereas they were indexed on a monoclinic cell for the  $\text{C}^{3+}\text{Mn}_7\text{O}_{12}$  compounds. A comparison between the observed and calculated interplanar spacing together with the observed relative intensities is given in Table II for  $\text{NaMn}_7\text{O}_{12}$ ,  $\text{CaMn}_7\text{O}_{12}$ , and  $\text{LaMn}_7\text{O}_{12}$ . The lattice parameters along with the space groups and the number of molecules per unit cell of all compounds prepared until now, are reported in Table III.

The systematic absences among the  $(hkl)$  reflections of the trigonal patterns were  $-h + k + l \neq 3n$ . These absences indicated a rhombohedral space group. The fact that the only trigonal subgroups of the cubic  $m\bar{3}$  point group are  $3$  and  $\bar{3}$ , led us to choose  $R\bar{3}$  and  $R3$

as possible space groups for the  $\text{C}^{2+}\text{Mn}_7\text{O}_{12}$  structure. Since the structure of  $\text{NaMn}_7\text{O}_{12}$  is centrosymmetrical we have decided to describe the structure of  $\text{C}^{2+}\text{Mn}_7\text{O}_{12}$  in the  $R\bar{3}$  space group. The matrix of transformation between the cubic and trigonal cell expressed in terms of hexagonal axes is:

$$\begin{pmatrix} a \\ b \\ c \end{pmatrix}_{\text{Hex}} = \begin{pmatrix} 1 & 0 & 1 \\ 0 & 1 & \bar{1} \\ \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \end{pmatrix} \begin{pmatrix} a \\ b \\ c \end{pmatrix}_{\text{cubic}} \quad \Delta = \frac{3}{2}.$$

The atomic arrangement of  $\text{C}^{2+}\text{Mn}_7\text{O}_{12}$  calculated from that of cubic  $\text{NaMn}_7\text{O}_{12}$  is given in Table IV.

The systematic absences among the  $(hkl)$  reflections of the monoclinic patterns of the  $\text{C}^{3+}\text{Mn}_7\text{O}_{12}$  compounds are  $h + k + l \neq 2n$ , which lead to the possible space groups  $I2/m$ ,  $I2$ , and  $Im$ . It was decided to describe this structure in a body-centered space group rather than in the standard C-centered one because with the  $I$ -cell it is easier to understand the relationship between the cubic structure and the monoclinic distortion. In Table IV the calculated atomic arrangement is reported for the centrosymmetrical  $I2/m$  space group.

As can be seen in Table III the lattice parameters  $a$  and  $c$  for each monoclinic cell are equal. On the powder films one could not distinguish any splitting between the  $(hkl)$  and  $(lkh)$  reflections. A consequence of this equality is that there exists an orthorhombic

TABLE II

OBSERVED AND CALCULATED INTERPLANAR SPACINGS IN  $\text{NaMn}_7\text{O}_{12}$ ,  $\text{CaMn}_7\text{O}_{12}$ , AND  $\text{LaMn}_7\text{O}_{12}$  COMPOUNDS

$\text{CaMn}_3^+(\text{Mn}_3^+\text{Mn}_4^+)\text{O}_{12}$				$\text{NaMn}_3^+(\text{Mn}_2^+\text{Mn}_2^+)\text{O}_{12}$				$\text{LaMn}_3^+(\text{Mn}_4^+)\text{O}_{12}$												
$hkl$	$d_{\text{obs}}$	$d_{\text{calcd}}$	$I_{\text{obs}}^a$	$hkl$	$d_{\text{obs}}$	$d_{\text{calcd}}$	$I_{\text{obs}}^a$	$hkl$	$d_{\text{obs}}$	$d_{\text{calcd}}$	$I_{\text{obs}}^a$									
1 1 0}	5.217	5.230	vw}	1 1 0	5.166	5.165	w	1 0 $\bar{1}$	5.379	5.374	vw									
1 0 1}		5.196	w}	0 1 1				5.266				5.264	M							
0 2 1		3.689	3.686	w				0 0 2				3.762	3.757	vw						
2 1 1	3.014	3.013	w	2 1 1	2.981	2.982	w	2 1 $\bar{1}$	3.082	3.081	w									
2 2 0				2.617				2.615				vS}	1 2 $\bar{1}$	3.040	3.041	w				
2 0 2				2.597				2.598				vS}	1 2 1	3.017	3.019	vw				
1 3 1	2.338	2.336	M}	2 2 0	2.581	2.582	vS	2 0 $\bar{2}$	2.686	2.687	S									
1 2 2				2.327				2.327				M}	3 1 0	2.310	2.310	M	2 0 2	2.628	2.627	vS
4 0 1				2.132				2.133				w}	2 2 2				2.109	2.108	w	1 0 $\bar{3}$
0 0 3	2.1138	2.1144	w}	3 2 1	1.952	1.952	M	0 1 3	2.371	2.372	M									
1 4 0}	1.9763	1.9766	M}	4 0 0				1.825	1.826	S	1 0 3	2.361	2.360	vw						
3 2 1}		1.9748		M}							3 3 0}	1.722	1.722	vw	0 3 1	2.339	2.337	M		
3 1 2		1.9702			1.9693	M}	4 2 0				1.633				1.633	vw	2 2 $\bar{2}$	2.172	2.172	w
1 1 3	1.9596	1.9603	M}		3 3 2	1.557	1.557	vw	2 2 2	2.139							2.140	w		
0 4 2	1.8434	1.8430	S	4 2 2	1.490				1.491	vS		2 1 $\bar{3}$	2.024	2.025			w			
3 3 0}				1.7424							1.7432	w}	4 3 1}	1.431	1.431	vw	3 2 $\bar{1}$	2.007	2.007	w
0 5 1}				1.7420		1.7420	w}	5 1 0}			1.410	1.410	vw				2 3 $\bar{1}$	1.9892	1.9905	M
3 0 3	1.7322	1.7319	w}	4 3 0}	1.400	1.400	vw	1 2 3	1.9880	1.9880							M			
2 4 1	1.6529	1.6527	w}	4 3 1}				1.400	1.400	vw				1 3 2	1.9782	1.9780	vw			
2 2 3	1.6440	1.6441	w}	4 3 2}							1.400	1.400	vw	0 0 4	1.8786	1.8785	S			
5 1 1	1.5751	1.5759	vw}	4 3 3}	1.400	1.400	vw							0 4 0	1.8445	1.8440	S			
1 0 4	1.5620	1.5620	vw}	4 3 4}				1.400	1.400	vw				1 1 $\bar{4}$	1.7785	1.7782	vw			
6 0 0	1.5101	1.5097	S}	4 3 5}							1.400	1.400	vw	1 1 4	1.7607	1.7604	vw			
4 2 2	1.5062	1.5064	S}	4 3 6}	1.400	1.400	vw							1 4 1	1.7404	1.7399	vw			
0 2 4	1.4968	1.4967	S}	4 3 7}				1.400	1.400	vw				2 0 4	1.6639	1.6652	vw			
				4 3 8}							1.400	1.400	vw	2 3 $\bar{3}$	1.6001	1.5995	vw			
				4 3 9}	1.400	1.400	vw							4 2 $\bar{2}$	1.5406	1.5406	S			
				4 3 10}				1.400	1.400	vw				2 4 2	1.5189	1.5177	S			
				4 3 11}							1.400	1.400	vw	2 4 2	1.5097	1.5093	M			
				4 3 12}	1.400	1.400	vw							3 1 $\bar{4}$	1.4878	1.4882	vw			
				4 3 13}				1.400	1.400	vw				0 1 5	1.4723	1.4726	vw			
				4 3 14}							1.400	1.400	vw	4 3 $\bar{1}$	1.4685	1.4691	vw			
				4 3 15}	1.400	1.400	vw							1 3 4	1.4593	1.4591	vw			
				4 3 16}				1.400	1.400	vw				1 4 3	1.4527	1.4531	vw			
				4 3 17}							1.400	1.400	vw	0 5 1	1.4476	1.4475	vw			

<sup>a</sup> vw (very weak); w (weak); M (medium); S (strong); vS (very strong).

cell related to the monoclinic one by the matrix:

$$\begin{pmatrix} a \\ b \\ c \end{pmatrix}_{\text{Orthor.}} = \begin{pmatrix} 1 & 0 & \bar{1} \\ 1 & 0 & 1 \\ 0 & \bar{1} & 0 \end{pmatrix} \begin{pmatrix} a \\ b \\ c \end{pmatrix}_{\text{mon.}} \quad \Delta = 2.$$

which can fully index the powder pattern.

However, the possible point groups  $mmm$ ,  $2mm$ , and  $222$  corresponding to the orthorhombic cell are not subgroups of the cubic  $m\bar{3}$ , because two of the three orthorhombic axes ( $a_o$  and  $c_o$ ) are along the diagonals of the ac plane of the cubic cell. The (101) and ( $\bar{1}01$ ) planes and the [101] and [ $\bar{1}01$ ] axes of the

TABLE III  
LATTICE PARAMETERS AND SPACE GROUPS OF CMn<sub>7</sub>O<sub>12</sub> COMPOUNDS

	C <sup>1+</sup> Mn <sub>7</sub> O <sub>12</sub> cubic	C <sup>2+</sup> Mn <sub>7</sub> O <sub>12</sub> trigonal	C <sup>3+</sup> Mn <sub>7</sub> O <sub>12</sub> monoclinic
Na <sup>+</sup>	$a = 7.3036 \text{ \AA}$ ( $a_{Rh} = 6.325 \text{ \AA}$ ; $\alpha = 109.47^\circ$ )* $V = 389.6 \text{ \AA}^3$		
Cd <sup>2+</sup>		$\{a = 6.394 \text{ \AA} \ a_{hex} = 10.453 \text{ \AA}$ $\alpha = 109.65^\circ \ c_{hex} = 6.336 \text{ \AA}$ $V = 199.8 \text{ \AA}^3$	
Ca <sup>2+</sup>		$\{a = 6.401 \text{ \AA} \ a_{hex} = 10.464 \text{ \AA}$ $\alpha = 109.65^\circ \ c_{hex} = 6.343 \text{ \AA}$ $V = 200.5 \text{ \AA}^3$	
Sr <sup>2+</sup>		$\{a = 6.430 \text{ \AA} \ a_{hex} = 10.509 \text{ \AA}$ $\alpha = 109.61^\circ \ c_{hex} = 6.384 \text{ \AA}$ $V = 203.5 \text{ \AA}^3$	
La <sup>3+</sup>			$\{a = 7.516(2) \text{ \AA}$ $b = 7.376(2) \text{ \AA}$ $c = 7.516(2) \text{ \AA}$ $\beta = 91.30^\circ$ $V = 416.6 \text{ \AA}^3$
Nd <sup>3+</sup>			$\{a = 7.504(2) \text{ \AA}$ $b = 7.366(2) \text{ \AA}$ $c = 7.504(2) \text{ \AA}$ $\beta = 91.18^\circ$ $V = 414.7 \text{ \AA}^3$
	* Primitive cell.		

orthorhombic cell are not symmetry elements of the  $m\bar{3}$  point group. Therefore, the symmetry of C<sup>3+</sup>Mn<sub>7</sub>O<sub>12</sub> compounds is truly monoclinic.

### Discussion

In the cubic [NaMn<sub>3</sub><sup>3+</sup>](Mn<sub>2</sub><sup>3+</sup>Mn<sub>2</sub><sup>4+</sup>)O<sub>12</sub> structure the Mn<sup>3+</sup> and Mn<sup>4+</sup> ions occupying the octahedral sites are completely disordered at room temperature. As determined by X-ray diffraction, the point symmetry of these sites is  $\bar{3}$ , therefore the octahedra are trigonally distorted and the 6 Mn–O distances are equal. In Ref. (1) it was speculated that the 6 coordinated Mn<sup>3+</sup> were in the low-spin state. The argument was based solely on the fact that the average octahedral Mn–O distance for the octahedral sites was found to be too small when compared with the reported [Mn<sup>3+</sup>(h.s.)–O + Mn<sup>4+</sup>–O]/2 value (3). The distortions of the CMn<sub>7</sub>O<sub>12</sub> compounds with C being a divalent or a trivalent cation and the preliminary results at low temperature on NaMn<sub>7</sub>O<sub>12</sub> seem to indicate that Mn<sup>3+</sup> ions

occupying the octahedral sites are in the high spin state.

In the trigonal [C<sup>2+</sup>Mn<sub>3</sub><sup>3+</sup>](Mn<sub>3</sub><sup>3+</sup>Mn<sup>4+</sup>)O<sub>12</sub> compounds 75% of the B-sites of the perovskite structure are occupied by Mn<sup>3+</sup> cations and 25% by Mn<sup>4+</sup> cations. It seems logic to assume that the 9d and the 3b positions of the  $R\bar{3}$  space group are occupied by the Mn<sup>3+</sup> and the Mn<sup>4+</sup> cations, respectively. The 9d positions have a  $\bar{1}$  point symmetry, therefore they can be Jahn–Teller distorted and accommodate the Mn<sup>3+</sup> cations in the high spin state. The 3b positions have the same point symmetry as the equivalent sites in the cubic structure namely,  $\bar{3}$ . They do not need to be further distorted as they accommodate Mn<sup>4+</sup> ions. The C<sup>2+</sup>Mn<sub>7</sub>O<sub>12</sub> are perovskite-like compounds in which an order 1:3 is established on the A-sites as well as on the B-sites. As far as we know it represents the first example where an order is established on both sites of the perovskite structure. As can be seen from Table III the lattice distortion on going from the cubic structure of NaMn<sub>7</sub>O<sub>12</sub>

TABLE IV

EXPERIMENTAL ATOMIC ARRANGEMENT FOR  $\text{NaMn}_7\text{O}_{12}$  AND THE CALCULATED ONE FOR  $\text{CaMn}_7\text{O}_{12}$  AND  $\text{LaMn}_7\text{O}_{12}$ 

Compounds	$[\text{CaMn}_3^{3+}](\text{Mn}_3^{3+}\text{Mn}^{4+})\text{O}_{12}$			$[\text{NaMn}_3^{3+}](\text{Mn}_2^{3+}\text{Mn}_2^{4+})\text{O}_{12}$			$[\text{LaMn}_3^{3+}](\text{Mn}_4^{3+})\text{O}_{12}$		
Number of molecules per unit cell	3			2			2		
Space group	Hexagonal axes			$R\bar{3}$			$Im\bar{3}$		
									$I2/m$
C	3a	(0 0 0)	$\bar{3}$	2a	(0 0 0)	$m\bar{3}$	2a	(0 0 0)	$2/m$
$\text{Mn}^{3+}$	9e	(1/2 0 0)	$\bar{1}$	6b	(0 1/2 1/2)	$mmm$	2b	(0 1/2 0)	$2/m$
$(\text{Mn}^{3+})$	9d	(1/2 0 1/2)	$\bar{1}$				2c	(0 0 1/2)	$2/m$
$(\text{Mn}^{4+})$	3b	(0 0 1/2)	$\bar{3}$	8c	(1/4 1/4 1/4)	$\bar{3}$	2d	(0 1/2 1/2)	$2/m$
							4e	(1/4 1/4 3/4)	$\bar{1}$
							4f	(1/4 1/4 1/4)	$\bar{1}$
							4i	$(x_1 0 z_1)$	$m$
								$x_1 \sim 0.31$	
								$z_1 \sim 0.18$	
							4i	$(x_2 0 z_2)$	$m$
								$x_2 \sim 0.31$	
								$z_2 \sim -0.18$	
0	18f	$(x y z)$	1				8j	$(x_3 y_3 z_3)$	1
		$x \sim 0.23$						$x_3 \sim 0.0 z_3 \sim 0.31$	
		$y \sim 0.27$						$y_3 \sim 0.18$	
		$z \sim 0.09$						$z_3 \sim 0.18$	
				24g	$(x y 0)$	$m$	8j	$(x_4 y_4 z_4)$	1
					$x = 0.1828$			$x_4 \sim 0.18 z_4 \sim 0.0$	
					$y = 0.3132$			$y_4 \sim 0.31$	
	18f	$(x y z)$	1						
		$x \sim 0.35$							
		$y \sim 0.52$							
		$z \sim 0.34$							

to the trigonal of  $\text{CaMn}_7\text{O}_{12}$  consists in a slight opening of the angle  $\alpha$ . It is  $109.47^\circ$  in the primitive cubic cell and  $109.65^\circ$  in the rhombohedral one.

In the  $[\text{C}^{3+}\text{Mn}_3^{3+}](\text{Mn}_4^{3+})\text{O}_{12}$  compounds, the distortion to the monoclinic symmetry is due to the fact that all the octahedral sites are now occupied by high spin  $\text{Mn}^{3+}$  Jahn-Teller cations. In this structure all the octahedral sites have a  $\bar{1}$  point symmetry. The monoclinic lattice distortion consists in the opening of the  $\beta$  angle and in the shortening of the parameter along the twofold axis.

As the symmetry lowers from cubic to trigonal and from cubic to monoclinic, also the sites containing the C cations and the 8 coordinated Jahn-Teller  $\text{Mn}^{3+}$  cations become more distorted. The point symmetry of the sites occupied by the C cations lowers from  $m\bar{3}$  to  $\bar{3}$  and from  $m\bar{3}$  to  $2/m$  on going from  $\text{C}^{+1}\text{Mn}_7\text{O}_{12}$  to  $\text{C}^{2+}\text{Mn}_7\text{O}_{12}$  and from  $\text{C}^{+1}\text{Mn}_7\text{O}_{12}$  to  $\text{C}^{3+}\text{Mn}_7\text{O}_{12}$ , respectively. In

the same way, the point symmetry of the sites occupied by the  $\text{Mn}^{3+}$  cations lowers from  $mmm$  to  $\bar{1}$  and from  $mmm$  to  $2/m$ .

Preliminary results show that the cubic  $\text{NaMn}_7\text{O}_{12}$  compound undergoes a phase transition at  $\sim 180^\circ\text{K}$  and that this transition is accompanied by a lowering of the cubic symmetry. This could be the result of a crystallographic order taking place among the  $\text{Mn}^{4+}$  and  $\text{Mn}^{3+}$  cations in the octahedral sites.

These results seem to indicate that in the  $\text{CMn}_7\text{O}_{12}$  compounds all the  $\text{Mn}^{3+}$  cations are in the high-spin state. The discrepancy between the experimental octahedral Mn-O average distance (1.946 Å) and the calculated value (1.98 Å) in  $\text{NaMn}_7\text{O}_{12}$  can be due to the inaccuracy of the ionic radius of the high spin  $\text{Mn}^{3+}$  cations. This value has been deduced (3) from well refined structures such as  $\text{Mn}_2\text{O}_3$  (4). In this orthorhombic compound there are 5 crystallographically independent

octahedral sites for the  $\text{Mn}^{3+}$  cations. Two of these octahedra are less apically elongated than the other 3. The average Mn–O distances of these first 2 octahedra are 2.003 and 2.002 Å, whereas those of the other 3 are 2.043, 2.042, and 2.043 Å, respectively. These values indicate that the average Mn–O distance varies considerably with the distortion of the oxygen octahedron and that it becomes larger as the distortion increases. In  $[\text{NaMn}_3(\text{Mn}_2^{3+}\text{Mn}_2^{4+})\text{O}_{12}]$  the octahedral sites have a high local symmetry and the 6 Mn–O distances are equal. Consequently, one should expect a smaller  $\text{Mn}^{3+}$ –O distance than the value calculated from the ionic radii.

$\text{LaMn}_7\text{O}_{12}$  and  $\text{NdMn}_7\text{O}_{12}$  represent new compounds in the binary systems  $\text{La}_2\text{O}_3/\text{Mn}_2\text{O}_3$  and  $\text{Nd}_2\text{O}_3/\text{Mn}_2\text{O}_3$ . Until now, only the 1:1 perovskite-like compounds  $\text{LaMnO}_3$  and  $\text{NdMnO}_3$  were known. High

pressure is needed to synthesize the 1:7 compounds because they contain 3/7 of the  $\text{Mn}^{3+}$  cations in high-coordinated sites. The relative volume variation between the  $\text{LaMnO}_3 + 3\text{Mn}_2\text{O}_3$  mixture and  $\text{LaMn}_7\text{O}_{12}$  is  $-4.8\%$ .

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#### References

1. M. MAREZIO, P. D. DERNIER, J. CHENAVAS, AND J. C. JOUBERT, *J. Solid State Chem.* **6**, 16 (1973).
2. J. CHENAVAS. Thèse, Grenoble, 1973. C.N.R.S.-A.O. No. 8691.
3. R. D. SHANNON AND C. T. PREWITT, *Acta Cryst.* **B25**, 925 (1969); **B26**, 1046 (1970).
4. S. GELLER, *Acta Cryst.* **B27**, 821 (1971).