

## High Pressure Synthesis and Crystal Structure of $\text{NaMn}_7\text{O}_{12}$

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A new compound,  $\text{NaMn}_7\text{O}_{12}$ , with the perovskite-like arrangement has been synthesized at 80 kbar and  $1000^\circ\text{C}$ . This compound is cubic,  $a = 7.3036 \text{ \AA}$ , space group  $Im\bar{3}$  with four formula weights per unit cell. The structure has been solved by Patterson and Fourier synthesis and refined by least-squares based on 142 reflections. The final  $R$  and  $wR$  factors were 0.025 and 0.033, respectively. The A sites of the perovskite structure are occupied by sodium and manganese atoms in an ordered fashion. The sodium atoms are each surrounded by a 12-oxygen polyhedron whereas the manganese atoms have four nearest oxygens at  $1.909 \text{ \AA}$  forming a square and four more at  $2.688 \text{ \AA}$  forming a rectangle perpendicular to the square. The distortion of the oxygen network from the ideal perovskite structure is similar to that found for  $\text{In}(\text{OH})_3$  and  $\text{Sc}(\text{OH})_3$ .

### Introduction

This paper reports the high pressure synthesis and crystal structure of  $\text{NaMn}_7\text{O}_{12}$  which represents a new distortion of the perovskite structure. The  $\text{ABO}_3$  perovskite arrangement can be considered a cubic close-packed array of oxygens and A cations with the smaller B cations occupying one-quarter of the octahedral sites, namely, those made up only of oxygen atoms. The ratio of the ionic radii of the two cations is very critical for an  $\text{ABO}_3$  compound to crystallize with this structure. The range of existence has been enlarged in recent years by doing the synthesis under high pressure. The undistorted perovskite structure is cubic with one molecule per unit cell. The A and B cations are surrounded by 12 and 6 equidistant oxygens, respectively. Several distortions are known for this structure and a complete list can be found in the review published by Goodenough and Longo (1).

### Experimental

The apparatus and the procedure of the high pressure experiments have been described in the preceding paper (2). A powder sample of  $\text{Mn}_2\text{O}_3$ , prepared by firing  $\text{MnO}_2$  in air at  $700^\circ\text{C}$ , was

packed into a platinum capsule together with a few drops of a dilute NaOH solution, and subjected to 80 kbar and  $1000^\circ\text{C}$  for 1 hr. The quenched material contained dark brown single crystals and a brown powder. X-Ray powder analysis showed that the quenched material contained the starting compound  $\text{Mn}_2\text{O}_3$ ,  $\text{MnOOH}$  (manganite) and a body-centered cubic phase. In order to improve the yield of the cubic phase, other experimental conditions were tried and they are summarized in Table I. As can be seen a pure cubic phase has not yet been obtained. Precession photographs taken with  $\text{MoK}\alpha$  radiation proved that the single crystals were cubic with the  $m\bar{3}$  Laue symmetry. Since the systematic absences among the reflections were  $h + k + l = 2n + 1$ , the space group symmetry was either  $Im\bar{3}$ ,  $I2_1\bar{3}$  or  $I23$ . The lattice parameter,  $a = 7.3036 \pm 0.0002 \text{ \AA}$ , was determined by least-squares refinement of data from a powder film taken with a 114.6-mm diameter Debye-Scherrer camera and  $\text{CrK}\alpha$  ( $K\alpha_1 = 2.28962 \text{ \AA}$ ) radiation. It was readily seen from the precession photographs that the structure of this cubic compound contained a subcell whose volume was 1/8th of the cubic cell and that the subcell had the perovskite arrangement.

TABLE I  
HIGH-PRESSURE EXPERIMENTS

| Experimental conditions | Starting material                        | Phases present in the quenched material  |
|-------------------------|--|--|
| 80 kbar<br>400°C        | Mn <sub>2</sub> O <sub>3</sub> +<br>NaOH | γ-MnOOH<br>(100%)  |
| 80 kbar<br>600°C        | "  | γ-MnOOH +<br>(80%)<br>cubic phase<br>(20%)   |
| 80 kbar<br>750°C        | "  | γ-MnOOH +<br>(80%)<br>cubic phase<br>(20%)   |
| 80 kbar<br>900°C        | "  | Mn <sub>2</sub> O <sub>3</sub> + γ-MnOOH +<br>(10%) (45%)<br>cubic phase<br>(45%)    |
| 80 kbar<br>1000°C       | "  | Mn <sub>2</sub> O <sub>3</sub> + γ-MnOOH +<br>(50%) (traces)<br>cubic phase<br>(50%) |
| 80 kbar<br>950°C        | MnO+MnO <sub>2</sub><br>NaOH             | Mn <sub>2</sub> O <sub>3</sub> + γ-MnOOH +<br>(33%) (33%)<br>cubic phase<br>(33%)    |

The intensity measurements were made by use of a G.E. XRD-5 paper-tape controlled automatic diffractometer with Zr-filtered Mo radiation. The procedure for the collection of the intensity data has been described in detail elsewhere (3). The specimen was a sphere whose average radius was 0.010 cm. This crystal was oriented with the [111] zone axis parallel to the  $\phi$  axis of the goniostat. All possible reflections of the upper hemisphere up to  $2\theta = 80^\circ$  were measured. A total of 1177 reflections were observed of which 142 were independent. The spherical absorption ( $\mu R = 1.12$ ), Lorentz, and polarization corrections were applied to the intensities in order to convert them to structure factors.<sup>1</sup>

### Solution of the Structure

A three-dimensional Patterson synthesis was carried out by using the program FOUR (4).

<sup>1</sup> A table of structure factor data has been deposited as Document No. NAPS 01874 with the ASIS National Auxiliary Publications Service, c/o CCM Information Corp., 909 Third Avenue, New York, NY 1002. A copy may be secured by citing the document number and by remitting \$5 for photocopies or \$2 for microfiche.

The squares of 460 structure factors on an arbitrary scale were the input terms. The strongest peaks could be explained by placing manganese atoms in the cation positions in a perovskite structure with a doubled lattice parameter and 8 formulas per unit cell. The medium peaks could be explained as the Mn–O vectors of a perovskite-like structure. This strongly indicated that the ratio cation/oxygen was 2:3. A three-dimensional Fourier synthesis computed with the signs corresponding to the cation contribution gave the positions of the oxygen atoms. We observed that the Fourier peak at the origin was approximately half the intensity of the other cation peaks. This indicated that the (0,0,0) position was either partially occupied by manganese or fully occupied by an atom with approximately half the number of electrons. Space groups  $I23$  and  $I2_13$  were readily eliminated by trial refinements. However, a good refinement was obtained in space group  $Im\bar{3}$  by placing the atoms in the following positions:  $x$  manganese in positions  $2a$  (0,0,0), 6 manganese in  $6b$  (0,  $\frac{1}{2}$ ,  $\frac{1}{2}$ ), 8 manganese in  $8c$  ( $\frac{1}{4}$ ,  $\frac{1}{4}$ ,  $\frac{1}{4}$ ), and 24 oxygens in  $24g$  ( $x, y, 0$ ) with  $x \approx 0.18$  and  $y \approx 0.31$ . The least-squares refinements were carried out by the program written by C. T. Prewitt (5). In this program the site occupancy can be varied along with the secondary extinction coefficient. The atomic scattering tables (for neutral atoms) and real and imaginary anomalous dispersion coefficients were taken from the values reported by Cromer and Waber (6) and by Cromer (7), respectively. The positions  $2a$  were initially filled with manganese atoms. After four cycles of refinement, in which a secondary extinction coefficient, a scale factor, two positional parameters, four isotropic temperature factors, and the occupancy parameter of the  $2a$  sites were varied, convergence was attained. Three more cycles of refinement were done after the anisotropic temperature factors were introduced. After the final cycle the occupancy parameter had decreased to  $0.468 \pm 0.001$ . This indicated, in agreement with the Fourier synthesis, that the  $2a$  sites were either slightly less than half occupied or completely filled by an atom with approximately 11 electrons. However, the final value of the temperature parameter for the manganese in this site was anomalously large when compared with the other temperature parameters. Furthermore, the Mn( $2a$ )–O separation was by far too large for a Mn<sup>2+</sup>–O distance. Since the chemical synthesis was carried out in a NaOH flux it was

likely that the  $2a$  positions were filled with sodium atoms. A refinement carried out with two sodium atoms in the  $2a$  positions yielded a lower  $R$  factor, lower standard deviations, and a reasonable temperature parameter for the sodium atoms. The positional parameters remained unchanged. In the final cycle all the occupancy factors were varied and they all remained equal to unity within their standard deviations. We therefore concluded that the formula of a unit cell was  $\text{Na}_2\text{Mn}_6\text{Mn}_8\text{O}_{24}$ . In addition, this formula seems to be corroborated by the compounds,  $\text{Ca}_{0.5}\text{Cu}_{1.5}\text{Ti}_2\text{O}_6$  and the cadmium counterpart, which have been reported by Deschavres et al. (8) to be cubic and perovskite-like. However, no structural details were given. It is quite likely that these compounds are isostructural with  $\text{NaMn}_7\text{O}_{12}$ .

The final positional and thermal parameters for  $\text{NaMn}_7\text{O}_{12}$  together with the final  $R$  and  $wR$  factors are reported in Table II. The interatomic distances and angles with their standard deviations were calculated by the program ORFFE (9), and are reported in Table III.

## Discussion

The oxide  $\text{NaMn}_7\text{O}_{12}$  has the perovskite-like arrangement in which  $1/4$  and  $3/4$  of the A sites are occupied by the Na and Mn(1) atoms, respectively. The B sites are occupied by Mn(2)

TABLE II

FINAL POSITIONAL AND THERMAL PARAMETERS<sup>a</sup>

|                | Na        | Mn(1)     | Mn(2)      | O         |
|----------------|-----------|-----------|------------|-----------|
| $x$            | 0         | 0         | 0.25       | 0.1828(2) |
| $y$            | 0         | 0.5       | 0.25       | 0.3132(2) |
| $z$            | 0         | 0.5       | 0.25       | 0         |
| $\beta_{11}^b$ | 0.0060(3) | 0.0020(1) | 0.00190(7) | 0.0036(2) |
| $\beta_{22}$   | 0.0060    | 0.0060(1) | 0.00190    | 0.0036(2) |
| $\beta_{33}$   | 0.0060    | 0.0019(1) | 0.00190    | 0.0040(2) |
| $\beta_{12}$   | 0         | 0         | 0.00011(3) | 0.0018(2) |
| $\beta_{13}$   | 0         | 0         | 0.00011    | 0         |
| $\beta_{23}$   | 0         | 0         | 0.00011    | 0         |

<sup>a</sup>  $R = (\sum | \Delta F | / \sum | F_0 |) = 2.5\%$ ,  $wR = 3.3\%$ .

<sup>b</sup> By symmetry,

$\beta_{11} = \beta_{22} = \beta_{33}$ , and  $\beta_{12} = \beta_{13} = \beta_{23} = 0$  for Na,

$\beta_{12} = \beta_{13} = \beta_{23} = 0$  for Mn(1),

$\beta_{11} = \beta_{22} = \beta_{33}$ , and  $\beta_{12} = \beta_{13} = \beta_{23}$  for Mn(2),

$\beta_{13} = \beta_{23} = 0$  for O.

TABLE III

INTERATOMIC DISTANCES (Å) AND ANGLES (°)

|   |                        |
|---|------------------------|
| Na-Polyhedron   |                        |
| Na-O  | $= 2.649(2) \times 12$ |
| O <sup>i</sup> -O <sup>iii</sup>                          | $= 2.815(2) \times 24$ |
| O <sup>vi</sup> -O <sup>xiii</sup>                        | $= 2.670(2) \times 6$  |
| O <sup>vi</sup> - $\tilde{\text{Na}}$ -O <sup>xiii</sup>  | $= 60.54(9) \times 6$  |
| O <sup>vii</sup> - $\tilde{\text{Na}}$ -O <sup>x</sup>    | $= 119.46(9) \times 6$ |
| O <sup>i</sup> - $\tilde{\text{Na}}$ -O <sup>iii</sup>    | $= 64.19(2) \times 24$ |
| Mn(1)-Polyhedron  |                        |
| Mn(1)-O <sup>v</sup>                                      | $= 1.909(2) \times 4$  |
| Mn(1)-O <sup>i</sup>                                      | $= 2.688(2) \times 4$  |
| O <sup>v</sup> -O <sup>vii</sup>                          | $= 2.729(2) \times 2$  |
| O <sup>i</sup> -O <sup>v</sup>                            | $= 2.689(2) \times 8$  |
| O <sup>i</sup> -O <sup>ii</sup>                           | $= 2.670(2) \times 4$  |
| O <sup>i</sup> - $\tilde{\text{Mn}}$ (1)-O <sup>iii</sup> | $= 119.01(9) \times 2$ |
| O <sup>i</sup> - $\tilde{\text{Mn}}$ (1)-O <sup>ii</sup>  | $= 60.99(9) \times 2$  |
| O <sup>v</sup> - $\tilde{\text{Mn}}$ (1)-O <sup>vi</sup>  | $= 88.77(9) \times 2$  |
| O <sup>v</sup> - $\tilde{\text{Mn}}$ (1)-O <sup>vii</sup> | $= 91.23(9) \times 2$  |
| O <sup>i</sup> - $\tilde{\text{Mn}}$ (1)-O <sup>v</sup>   | $= 69.21(3) \times 8$  |
| Mn(2)-Octahedron  |                        |
| Mn(2)-O   | $= 1.946(1) \times 6$  |
| O-O   | $= 2.689(2) \times 6$  |
| O-O   | $= 2.815(2) \times 6$  |
| O-Mn(2)-O   | $= 92.63(7) \times 6$  |
| O-Mn(2)-O   | $= 87.37(7) \times 6$  |

atoms only. The cation network is undistorted. The departure from the monomolecular cubic perovskite structure, namely, the doubling of the lattice parameter, is due only to the distortion of the oxygen network. Even though this distortion is large, the oxygen atoms move from (0.25, 0.25, 0) to (0.1828, 0.3132, 0); the structure distorts within the cubic symmetry. A similar distortion of the oxygen network was found in the structure of  $\text{Sc}(\text{OH})_3$  and  $\text{In}(\text{OH})_3$ . These compounds are cubic, space group  $Im\bar{3}$ , with  $a \approx 7.8$  Å (10). The trivalent cations and the oxygen atoms occupy essentially the same positions as Mn(2) and oxygen in  $\text{NaMn}_7\text{O}_{12}$ . The hydrogen ions are arranged within the 12-oxygen polyhedra formed around the A sites.

The Na and Mn(1) atoms occupy crystallographically independent sites and therefore they have different coordination polyhedra. The sodium atoms are surrounded by 12 equidistant oxygen atoms at 2.649 Å. A sketch of this polyhedron is shown in Fig. 1. In the undistorted perovskite the A-polyhedron can be considered to be built up of three mutually perpendicular equal squares of oxygen atoms, whereas in the

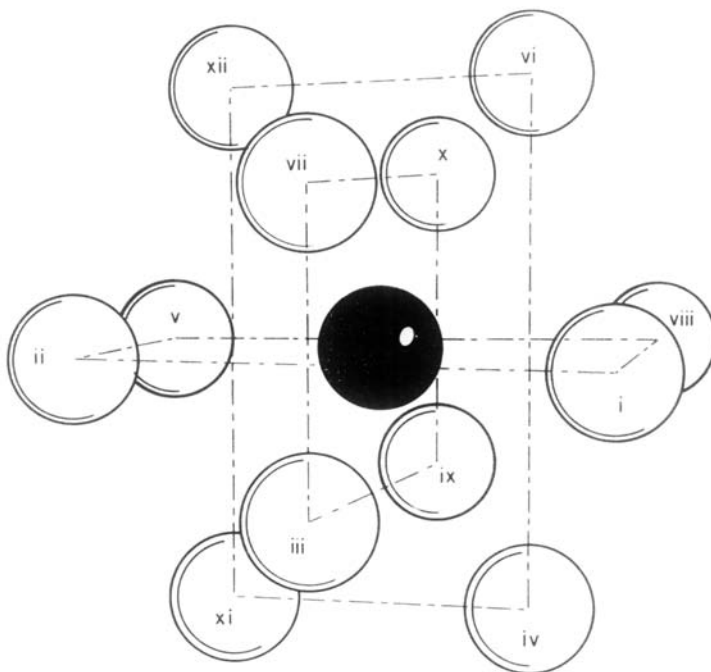


FIG. 1. The oxygen polyhedron around the central sodium ion consists of three mutually perpendicular equal rectangles. These rectangular planes are lightly outlined in the figure.

present compound the polyhedron is built up of three mutually perpendicular equal rectangles. As far as we know, this is the first oxide compound in which the sodium atoms are 12-coordinated. This high coordination for the sodium atoms is due to the fact that this compound was synthesized at 80 kbar.

The Mn(1) atoms are also surrounded by 12-oxygen polyhedra, but not all the oxygens surrounding the Mn(1) atoms can be considered nearest neighbors. Four of the twelve oxygens are very close at 1.909 Å, four are at 2.688 Å and four at 3.256 Å. Two of the three squares of the undistorted A polyhedron have contracted and enlarged, while one has distorted to a rectangle. It is difficult to determine the cation coordination number when the cation-oxygen distances vary over such a large range. Despite this, it is clear that the four oxygens at 3.256 Å must be considered second-nearest neighbors. A sketch of this polyhedron is shown in Fig. 2 where these second-nearest neighbors have been omitted.

The arrangement around Mn(1) atoms is the same as that of Pd<sup>2+</sup> ions in PdCl<sub>2</sub> and in a way similar to the apically elongated oxygen octahedra surrounding Jahn-Teller Mn<sup>3+</sup> (h.s.) ions in other oxide compounds. In NaMn<sub>7</sub>O<sub>12</sub>, instead of having this apical elongation, the polyhedron consists of two mutually perpendicu-

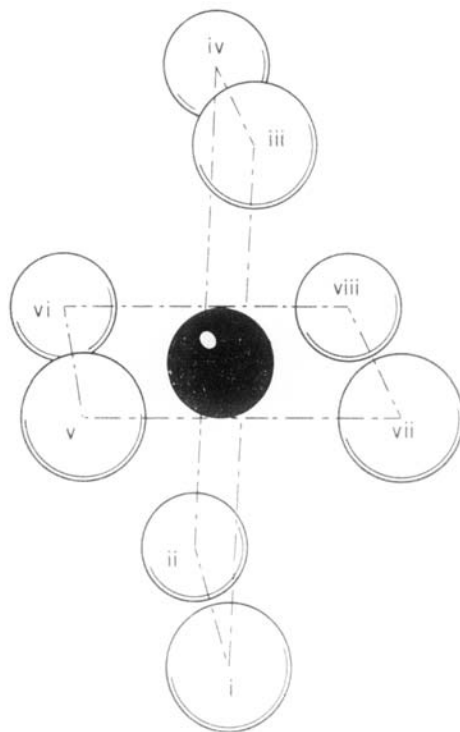


FIG. 2. The oxygen polyhedron around the central manganese ion consists of a small square plane perpendicular to a larger rectangular plane shown lightly outlined. The second-nearest oxygen neighbors have been omitted for clarity.

TABLE IV  
THERMAL DATA

|       |   | R.M.S.   | Angles With |        |        |
|-------|---|----------|-------------|--------|--------|
|       |   |          | X           | Y      | Z      |
| Na    |   | 0.127(2) | —           | —      | —      |
| Mn(1) | 1 | 0.072(2) | 90.00       | 90.00  | 180.00 |
|       | 2 | 0.074(2) | 0.00        | 90.00  | 90.00  |
|       | 3 | 0.127(2) | 90.00       | 180.00 | 90.00  |
| Mn(2) | 1 | 0.070(2) | 66(1)       | 66(1)  | 145(1) |
|       | 2 | 0.070(2) | 114(1)      | 114(4) | 35(1)  |
|       | 3 | 0.076(2) | 125(1)      | 125(1) | 125(1) |
| O     | 1 | 0.070(4) | 135(2)      | 45(2)  | 90.00  |
|       | 2 | 0.103(3) | 90.00       | 90.00  | 0.00   |
|       | 3 | 0.121(3) | 135(2)      | 135(2) | 90.00  |

lar planes, one containing four oxygens nearly forming a square at a distance of 1.909 Å from Mn(1), and the other containing four oxygens forming a rectangle at 2.688 Å.

The Mn(2) atoms are surrounded by six equidistant oxygens arranged as an octahedron. The Mn(2)–O distance is 1.946 Å, giving an ionic radius of 0.56 Å for Mn(2). The oxygen coordination in this structure is fivefold and therefore an effective radius of 1.39 Å was assumed for the O<sup>2-</sup> ions. The oxygen octahedron around Mn(2) is distorted, but its distortion (~2.5%) is by far less than the distortion of the polyhedra around the Na and the Mn(1) ions. This is usually true for any perovskite-like compound (11, 12).

The thermal data are reported in Table IV. The sodium atoms vibrate isotropically as dictated by the point-symmetry and the Mn(2) atoms vibrate nearly isotropically. Both the Mn(1) atoms and the oxygens have strongly anisotropic thermal vibration. The longest principal axis of the Mn(1) ellipsoid is normal to the square formed by the four nearest oxygens. The magnitude of this anomalously large axis is the same as the sodium isotropic value.

The uncertainty in the ionic radii of manganese, particularly for the Mn<sup>3+</sup> ion in a distorted eightfold coordination, does not allow one to determine unambiguously the charge distribution among the manganese sites. However, one model, which fits the observed interatomic distances quite well, assumes that the Mn(1) sites are

completely occupied by high-spin Mn<sup>3+</sup> ions while the Mn(2) sites are filled in equal proportions by low-spin Mn<sup>3+</sup> and Mn<sup>4+</sup> ions. The short 1.909-Å Mn(1)–O distances of the near-square plane are also found in the Jahn–Teller distorted octahedra of the high-spin manganese oxide compounds. The average calculated distance between Mn<sup>4+</sup>–O and Mn<sup>3+(l.s.)</sup>–O is 1.95 (13) which compares very well with the observed Mn(2)–O distance of 1.946 Å. This model yields the following charge distribution:



The new Na–O distance can be used to obtain a reliable value of 1.26 Å for the effective radius of a 12-coordinated sodium ion. Since the values for sodium with coordination numbers other than six are uncertain (13), this latest experimental value together with the value for 6-coordinated sodium (obtained from a regular octahedron) allows one to interpolate the values for intermediate coordination numbers. The linear dependence of the ionic radius and coordination number is a good approximation for the alkali and alkaline-earth cations.

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