High-pressure – High-temperature Synthesis of Na_6MnO_4

Steffen Pfeiffer and Martin Jansen

Max-Planck-Institut für Festkörperforschung, Heisenbergstraße 1, D-70569 Stuttgart, Germany

Reprint requests to Prof. Dr. Dr. h. c. Martin Jansen. Fax: ++49-0711-6891502.
E-mail: m.jansen@fkf.mpg.de

Z. Naturforsch. **2009**, *64b,* 487 – 490; received February 20, 2009

The title compound has been synthesized under 4 GPa and at 500 °C from Na_2O and MnO as starting materials. Rietveld refinement of the X-ray powder pattern indicates that Na_6MnO_4 is isostructural to Na_6ZnO_4 and thus is representing the second manifestation of an "isolated" $[MnO_4]^{6-}$ anion after $Na_{14}Mn_2O_9$. The compound crystallizes in the hexagonal system in space group $P6_3mc$ (no. 186) with a = 7.6631(2) and c = 5.9013(2) Å, V = 300.1 Å^3, and Z = 2.

Key words: Sodium Manganate(II), High-pressure – High-temperature Synthesis, Crystal Structure

Introduction

There are conspicuous parallels in the crystal chemistry of alkali oxomanganates(II) and oxozincates as well as oxocadmates. For example $Na_{10}Mn_4O_9$ [1] and $Na_2Mn_2O_3$ [2] are isostructural to $Na_{10}Zn_4O_9$ [3] and $Na_2Zn_2O_3$ [4], respectively, while $Na_{14}Mn_2O_9$ [5] and $K_2Mn_2O_3$ [6] are isostructural to the respective cadmates $Na_{14}Cd_2O_9$ [7] and $K_2Cd_2O_3$ [8]. Among the sodium zincates and the potassium cadmates, Na_6ZnO_4 and K_6CdO_4 are known to belong to the same structure type [9, 10]. As an obvious consequence one would expect the existence of the corresponding manganates, *e. g.* Na_6MnO_4. However, all attempts to prepare Na_6MnO_4 along the azide/nitrate route [11] failed. Instead, the known Compound $Na_{14}Mn_2O_9$ [5] was the main reaction product. A comparison of the densities of oxomanganates and oxozincates has revealed that $Na_{10}Zn_4O_9$ [3] has a density approximately 11 % higher than $Na_{10}Mn_4O_9$ [1]. By subtracting 11 % of the density from Na_6ZnO_4 [9], a value results that is still slightly higher than the density of $Na_{14}Mn_2O_9$ ($\equiv Na_7MnO_{4.5}$). Therefore it appeared to us promising to try to synthesize Na_6MnO_4 at elevated pressures.

Experimental Section

Na_6MnO_4 was synthesized from a mixture of Na_2O and "active" MnO in a belt press at 4 GPa and 500 °C. Na_2O was prepared by reacting sodium azide (Sigma-Aldrich, 99.5 %) and sodium nitrate (Aldrich, 99 %) according to Eq. 1 [12],

$$5\,NaN_3 + NaNO_3 = 3\,Na_2O + 8\,N_2\,(g), \qquad (1)$$

using specially designed containers [11], and a temperature schedule of: 25 → 260 °C (100 °C/h); 260 → 380 °C (5 °C/h); 380 °C (20 h) 380 → 25 °C (100 °C/h). Active "MnO_x" was prepared by thermal decomposition of manganese carbonate (Chempur, 99.9 %) at 400 °C for 12 h under vacuum (10^{-3} mbar) [13]. The starting materials were mixed in a glovebox in the molar ratio 3.1 : 1 and ground thoroughly in an agate mortar. The well homogenized starting materials were filled and compacted in a gold crucible (∅: 4 mm), which afterwards was tightly closed by pressing the lid carefully into the crucible. The filled crucible was placed in a belt press, and a pressure of 4 GPa was applied. Heating followed the temperature schedule 25 → 500 °C (1 h), 500 °C (24 h), 500 → 25 °C (63 h). The reaction product was a red, microcrystalline powder, which is very sensitive to humid air. Thus, the product was handled at strictly inert conditions. For the X-ray measurement the sample was filled and sealed in a glass capillary and placed on a Stoe Stadi P diffractometer with Mo$K_{\alpha 1}$ radiation (λ = 0.7093 Å). The powder pattern was indexed and refined based on the Na_6ZnO_4 structure type with a = 7.6631(2) and c = 5.9013(2) Å. Weak additional lines correspond to admixtures of 7 and 9 weight-% of Na_2O and $NaMnO_2$, respectively. Like for Na_6ZnO_4, the extinction conditions comply with the space group $P6_3mc$ (no. 186). For the final Rietveld refinement the atomic positions of the zincate were used as a starting model. The experimental and calculated profiles are given in Fig. 1.

Results and Discussion

Na_6MnO_4 has been prepared as a micro-crystalline powder, *via* high-pressure – high-temperature synthesis. The red product is extremely sensitive to air and

0932–0776 / 09 / 0500–0487 $ 06.00 © 2009 Verlag der Zeitschrift für Naturforschung, Tübingen · http://znaturforsch.com

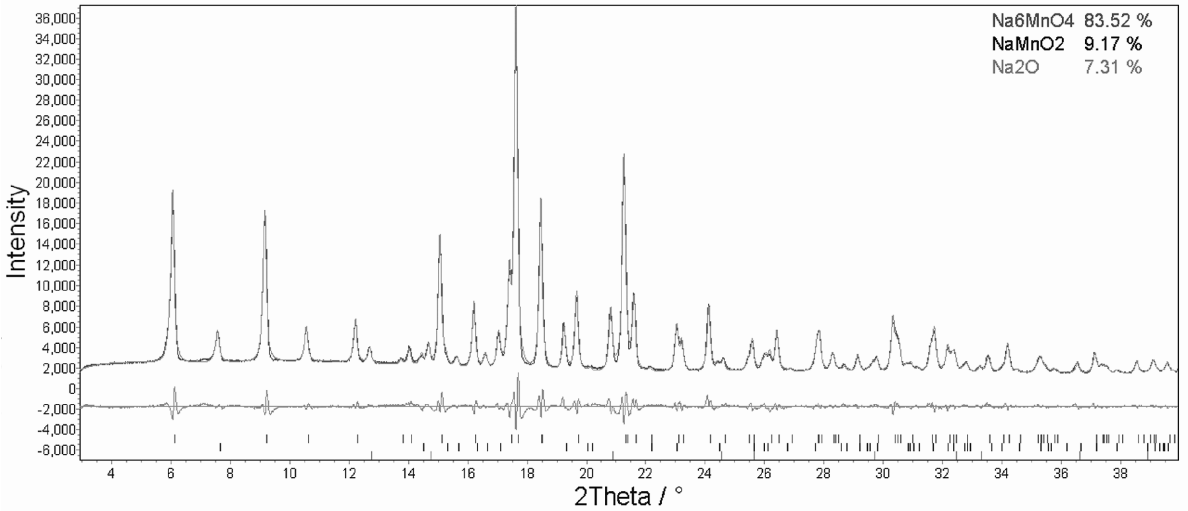

Fig. 1. Rietveld refinement of the X-ray powder pattern of Na_6MnO_4 and the difference curve showing the fit between the experimental and calculated data. The tickmarks below show the peak positions for Na_6MnO_4 (top), $NaMnO_2$ (middle) and Na_2O (bottom).

Table 1. Crystallographic data for Na_6MnO_4 [18].

Crystal data	
Crystal system	hexagonal
Space group, Z	$P6_3mc$ (no. 186), 2
Lattice constants (from powder data):	
a, Å	7.6631(2)
c, Å	5.9013(2)
Molar volume, $cm^3\ mol^{-1}$	150.06
Molar mass, $g\ mol^{-1}$	513.75
X-Ray density, $g\ cm^{-3}$	2.84
Data collection	
Diffractometer	STOE Stadi-P
Monochromator	Ge (111)
Radiation; λ, Å	Mo$K\alpha$, 0.7093
2θ range for data collection, deg	3 – 40
Structure refinement	
Used program	TOPAS
Crystallite size (Lorentz), nm	43
Strain	0.06(1)
R_{Bragg}	1.15
R_p	4.45
R_{wp}	6.17
Weight-% (Na_6MnO_4)	83.5
Weight-% ($NaMnO_2$)	9.1
Weight-% (Na_2O)	7.3

Table 2. Atomic positions and thermal displacement parameters for Na_6MnO_4.

Atom	Position	x	y	z	B_{iso} (pm^2)
Na_1	6c	0.1386(2)	−0.1386(2)	−0.0274(5)	1.14(5)
Na_2	6c	0.5373(2)	−0.5373(2)	0.1462(6)	1.14(5)
Mn_1	2b	1/3	2/3	1/4	0.67(6)
O_1	2b	1/3	2/3	0.9048(2)	0.99(9)
O_2	6c	0.8125(2)	−0.8125(2)	−0.1386(1)	0.99(9)

Table 3. Interatomic distances (in Å), coordination numbers (CN), effective coordination numbers (ECoN), and mean fictive ionic radii (MEFIR) for Na_6MnO_4.

Atom	O_1	O_2	CN	ECoN	MEFIR
Na_1	2.589 2.334 2.376	2.334	4	3.77	0.98
Na_2	2.286 3.073	2.487 2.487 2.740 2.740	6	4.4	1.05
Mn_1	2.037	2.049 2.049 2.049	4	4.0	0.65
CN	7	8			
ECoN	6.2	7.3			
MEFIR	1.38	1.42			

moisture and turns black immediately when exposed to humid air. X-Ray powder diffraction patterns can be indexed and refined based on the hexagonal crystal system. Na_6MnO_4 is isostructural to Na_6ZnO_4. For the crystallographic data, atomic positions and displacement factors as well as interatomic distances, coordination numbers (CN), effective coordination numbers (ECoN), and mean fictive ionic radii (MEFIR) [14] see Tables 1 – 3.

The main features of the structure are isolated MnO_4 tetrahedra (see Fig. 2) with one of their threefold symmetry axes aligned parallel to [001]. The tetrahedra are arranged following the motif of a hexagonal

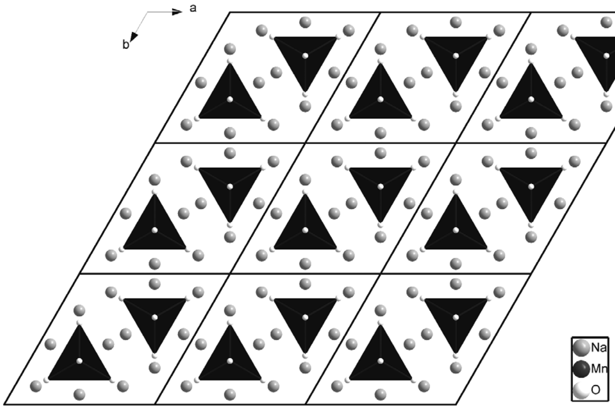

Fig. 2. Projection of the crystal structure of Na_6MnO_4 along [001].

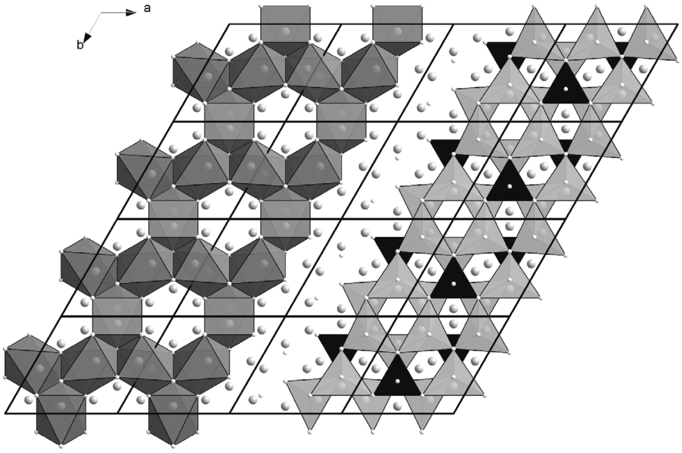

Fig. 3. Projection of the crystal structure of Na_6MnO_4 along [001]. On the left hand side the Na_2O_6 octahedra are emphasized, on the right hand side the Na1O4 (light grey) and the MnO_4 tetrahedra (black) are depicted.

close packing with the stacking sequence A, B, A, B, A… along [001]. Thus, Na_6MnO_4 is the second compound besides $Na_{14}Mn_2O_9$ [5] containing "isolated" $[MnO_4]^{6-}$ anions. There are two crystallographically independent oxygen positions, O_1 representing the apical position of the tetrahedron, and O_2 forming the base of the tetrahedron. The bond lengths Mn–O_1 and Mn–O_2 are 2.037 and 2.049 Å, respectively, the angles are in the range between 109.40 and 109.54°, indicating that the tetrahedra are rather regular. The bond lengths are in good agreement with the distances in other manganates(II), like for example Na_2MnO_2 [15] and $Na_{10}Mn_4O_9$ [1], but some of the O–Mn–O angles in these latter compounds deviate strongly from the ideal value of 109.4°. Like the tetrapnictidotitanates $Na_3M_3[TiX_4]$ with M = Na/Sr, Na/Eu and X = P, As [16], the structure can be described in terms of a hexagonal close packing of oxygen atoms with 3/4 of the octahedral voids being filled with sodium atoms, 3/8 of the tetrahedral voids being filled with sodium and 1/8 with manganese atoms according to: $(Na_3{}^{0})(Na_3{}^{t-}\ Mn^{t+})O_4$, with t+ and t− indicating the orientation of the tetrahedra parallel or antiparallel to the c axis (see Fig. 3). Na_6MnO_4 is one more example of the amazingly extensive family of solids of this structure type, which comprises ternary oxides and sulfides, or, as anti-types oxide halides like Ba_4OCl_6 [17].

Acknowledgement

We thank Dr. P. Balog and F. Falkenberg for their help in carrying out the high-pressure – high-temperature experiments.

[1] P. Amann, B. M. Sobotka, O. Fastje, A. Möller, *Z. Anorg. Allg. Chem.* **2007**, *633*, 2579 – 2586.
[2] S. Pfeiffer, M. Jansen, *Z. Kristallogr. NCS* **2009**, *224*, 163 – 164.
[3] D. Trinschek, M. Jansen, *Z. Anorg. Allg. Chem.* **1996**, *622*, 245 – 250.
[4] D. Trinschek, M. Jansen, *Z. Naturforsch.* **1996**, *51 b*, 917 – 921.
[5] G. Brachtel, R. Hoppe, *Z. Anorg. Allg. Chem.* **1978**, *438*, 97 – 104.
[6] E. Seipp, R. Hoppe, *Z. Anorg. Allg. Chem.* **1985**, *530*, 117 – 126.
[7] G. Brachtel, R. Hoppe, *Z. Anorg. Allg. Chem.* **1978**, *441*, 83 – 85.
[8] E. Vielhaber, R. Hoppe, *Z. Anorg. Allg. Chem.* **1971**, *382*, 270 – 280.
[9] P. Kastner, R. Hoppe, *Z. Anorg. Allg. Chem.* **1974**, *409*, 69 – 76.
[10] R. Baier, E. Seipp, R. Hoppe, *Monatsh. Chem.* **1987**, *118*, 677 – 690.
[11] D. Trinschek, M. Jansen, *Angew. Chem.* **1999**, *111*, 234 – 235; *Angew. Chem. Int. Ed.* **1999**, *38*, 133 – 135.
[12] E. Zintl, H. H. von Baumbach, *Z. Anorg. Allg. Chem.* **1931**, *198*, 88 – 101.
[13] M. Le Blanc, G. Wehner, *Z. Physik. Chem. A* **1934**, *168*, 59 – 78.
[14] R. Hoppe, *Z. Kristallogr.* **1979**, *150*, 23 – 52.
[15] S. Pfeiffer, M. Jansen, *Z. Anorg. Allg. Chem.* **2009**, *635*, 211 – 215.
[16] J. Nuss, W. Hoenle, H. G. von Schnering, *Z. Anorg. Allg. Chem.* **1997**, *623*, 1763 – 1768.
[17] B. Frit, B. Holmberg, J. Galy, *Acta Crystallogr.* **1970**, *B26*, 16 – 19.
[18] Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-informationsdienste.de/en/DB/icsd/depot_anforderung.html) on quoting the deposition number CSD-420410.