substance: Mn_2O_3
property: phase diagram, crystal structure, lattice parameters of low temperature phase

phase diagram: see Fig. 1.

low-temperature phase ($T \leq 302$ K):

crystal structure: orthorhombically distorted bixbyite structure, space group D_{2h}^{15} – Pcab, $Z = 16$ [71G, 67N]. Bixbyite structure: Fig. 2. Mn_2O_3 is the only sesquioxide having this structure, the origin is thought to lie in the expected substantial Jahn-Teller distortion associated with the d^4 Mn^{3+} ion.

lattice parameters

a	9.4137 Å	*T* = 298 K	temperature dependence, see Fig. 3	71G
b	9.4233 Å			
c	9.4047 Å			
a	9.4118(8) Å	*T* = 298 K		67N
b	9.4177(7) Å			
c	9.4233(7) Å			

In the undistorted bixbyite structure there are two distinguishable Mn sites at the 8(a) and 24(d) positions. In the setting shown in Fig. 2, the 8(a) sites are at 1/4 1/4 1/4; 1/4 3/4 3/4; 3/4 1/4 3/4; 3/4 3/4 1/4 + b.c. and the 24(d) sites are at ± (*u* 0 1/4; 0 1/4 *u*; –*u* 1/2 1/4; 1/4–*u* 1/2; 1/2 1/4 -*u*) + b.c. The oxygen atoms occupy the 48(e) sites described by the parameters ± (*x y z*; *x* –*y* 1/2–*z*; 1/2–*x y* –*z*; –*x* 1/2–*y z*; *z x y*; 1/2–*z x* -*y*; -*z* 1/2–*x y*; *z* –*x* 1/2–*y*; *y z x*; –*y* 1/2–*z x*; *y* –*z* 1/2–*x*; 1/2–*y z* –*x* + b.c. In the mineral bixbyite itself, $(Mn,Fe)_2O_3$, $u = -0.035$, $x = 0.384$, $y = 0.147$ and $z = 0.382$ [71G], for the composition $(Mn_{0.98}Fe_{0.017})_2O_3$. The high-temperature form of Mn_2O_3 itself is discussed in the following document. For the low-temperature form, there are five distinguishable Mn sites, two derived from the 8(a) sites and three from the 24(d) sites. The sets derived from 8(a) are the 4(a) at (1/4, 1/4, 1/4) ..... and the 4(b) which arise by loss of b.c. and are at (1/4, 1/4, 3/4).... The 24(d) sites split into three sets of 8(c).

average Mn – O distances in the low-temperature form

d(Mn(1)–O)	2.003(87) Å	numbers of the Mn atoms as	71G
d(Mn(2)–O)	2.002(87) Å	in Fig.2	
d(Mn(3)–O)	2.043(408) Å		
d(Mn(4)–O)	2.043(380) Å		
d(Mn(5)–O)	2.042(384) Å		

References:

65O Otto, E. M.: J. Electrochem. Soc. 112 (1965) 367.
67N Norrestam, R.: Acta Chem. Scand. 21 (1967) 2871.
67S Shenouda, F., Aziz, S.: J. Appl. Chem. 17 (1967) 258.
70G Geller, S., Espinosa, G. P.: Phys. Rev. Bi (1970) 3763.
71G Geller, S.: Acta Crystallogr. 27 (1971) 821.
75W Wells, A. F.: Structural Inorganic Chemistry, OUP 1975.

Fig. 1.

Phase diagram for the systems MnO_2/Mn_2O_3 and Mn_2O_3/Mn_3O_4 drawn from the data of [65O, 67S].

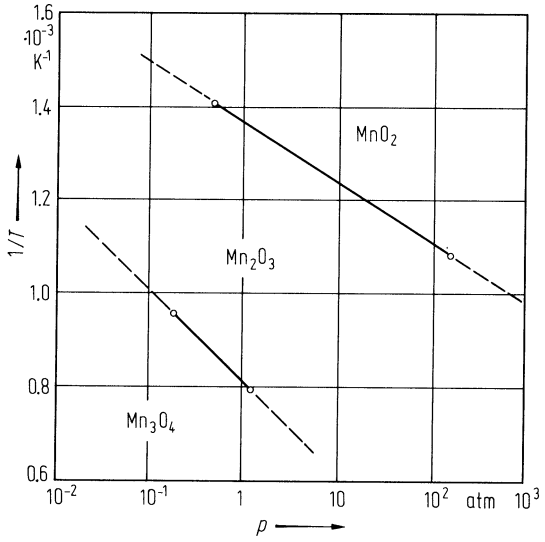

Fig. 2.

Mn_2O_3. (a) The cubic bixbyite structure and its relationship to (b) fluorite. The dotted circles show the oxygen atoms that have been removed from the fluorite structure; the oxygen atoms forming the two types of the Mn site 8(a) and 24(d) described in the text, are shown shaded [75W].

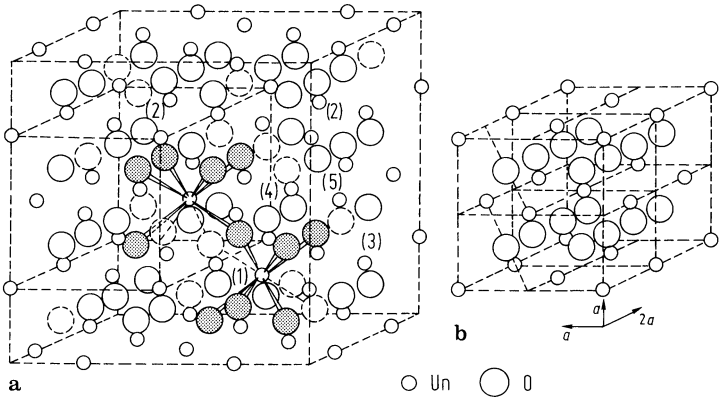

Fig. 3.

Mn_2O_3. Lattice parameters vs. temperature [70G].