SHORT STRUCTURAL PAPERS

Papers intended for publication under this heading must be in the format prescribed in Notes for Authors, *Acta Cryst.* (1973). **B29**, 154

Acta Cryst. (1974). B**30**, 1872

Sodium Tungstate

By K. Okada, H. Morikawa, F. Marumo and S. Iwai

Research Laboratory for Engineering Materials, Tokyo Institute of Technology, Meguro-ku, Tokyo, Japan

(*Received* 29 *November* 1973; *accepted* 12 *January* 1974)

Abstract. Na_2WO_4: cubic, $Fd3m$, $a=9·133$ (3) Å, $Z=8$. The crystal is a normal spinel with W–O and Na–O distances 1·819 (8) and 2·378 (8) Å respectively. The u parameter is 0·3650 (9).

Introduction. Crystals of Na_2WO_4 were kindly provided by Dr S. Yamaoka of the National Institute for Researches in Inorganic Materials. The crystals are prismatic, colourless and transparent. The cell dimension obtained from Weissenberg photographic data is in agreement with the value given by Swanson, Morris, Stinchfield & Evans (1962).

A prismatic crystal with dimensions of about $0·1\times0·1\times0·15$ mm was used for intensity collection. Intensities were measured on a Rigaku automated four-circle diffractometer with Mo $K\alpha$ radiation, monochromated with graphite, up to $2\theta=70°$ by the ω–2θ scan technique. The scan speed was 2° min^{-1} in ω and scanning was repeated up to three times when the standard deviation of a structure amplitude due to the counting statistics, $\sigma(|F|)$, was larger than 2% of the amplitude, $|F|$. The scan width was determined according to the formula $1·7+0·8°\tan\theta$. The intensities were corrected for Lorentz, polarization and absorption factors assuming a sphere of 0·14 mm in diameter for the crystal shape. No corrections were made for extinction. In total 92 independent intensity data were obtained and used for the structure determination.

The structure was refined by the full-matrix least-squares procedure to a conventional R value of 0·034. The atomic scattering factors and dispersion correction factors were taken from *International Tables for X-ray Crystallography* (1962). Unit weights were assigned for all the terms. Coordinates and anisotropic thermal parameters for all atoms are listed in Table 1.* Interatomic distances and bond angles are given in Table 2 with their estimated standard deviations in parentheses.*

Table 2. *Interatomic distances and bond angles*

W–O	1·819 (8) Å	Na–O—Na	85·5 (3)°
O—O	2·970 (11)	O—Na–O	85·7 (3)
Na–O	2·378 (8)	O—Na–O	94·3 (3)
O—O	3·234 (11)	Na–O—W	128·4 (4)
O—O	3·488 (11)		
Na–Na	3·229 (1)		

Discussion. A crystallographic description of Na_2WO_4 crystals was first given by Lindqvist (1950) on the basis of an X-ray powder diffraction study, reporting that the crystals had a spinel-type structure with $a=8·99$ Å, $u=0·375$. More recently a precise measurement of the cell dimension was carried out by Swanson, Morris, Stinchfield & Evans (1962) and the value $a=9·1297$ Å was obtained. In normal spinel-type compounds there are three types of cation combinations, (1) $A_2^{3+}B^{2+}O_4^{2-}$, (2) $A_2^{2+}B^{4+}O_4^{2-}$ and (3) $A_2^{1+}B^{6+}O_4^{2-}$. Many compounds of type (1), and some of type (2), have been investigated with the X-ray diffraction technique, and the structural parameters are given for those compounds. No precise structure investigation has been made, however, of a type (3) compound before the present study of sodium tungstate.

Table 1. *Final atomic parameters*

Positional parameters are given as fractions of cell edges. Anisotropic temperature factors are expressed as

$$\exp\left[-(h^2B_{11}+k^2B_{22}+l^2B_{33}+2hkB_{12}+2klB_{23}+2hlB_{13})\right],\ \text{where } B_{11}=B_{22}=B_{33},\ B_{12}=B_{13}=B_{23}\,.$$

	x	y	z	B_{11}	B_{12}
O	0·3650 (9)	0·3650 (9)	0·3650 (9)	0·0025 (6)	−0·0001 (6)
W	0	0	0	0·0019 (1)	0
Na	0·625	0·625	0·625	0·0051 (7)	−0·0002 (6)

---

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30341 (2 pp.). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

The structure is of normal spinel type, having Na atoms in octahedral and W atoms in tetrahedral sites. In a spinel structure, oxygen ions are in an ideal cubic closest-packed arrangement when the *u* parameter is 0·375. However, the *u* parameters are almost always equal to or larger than 0·375 in normal spinels stable at atmospheric pressure. The only exception reported is Ag_2MoO_4, which has the value 0·364 (Donohue & Shand, 1947). In the present study, the *u* parameter of Na_2WO_4 was found to be 0·365, a value significantly smaller than 0·375. The *u* parameters of normal spinels are plotted against the cation ionic radii ratios, r_A/r_B, in Fig. 1. All spinels are distributed nearly along a simple curve as shown in the figure. The *u* parameters, as well as the cation ionic radii ratios, also have an interesting correlation with the types of cation combinations. In the type (1) spinels, r_A/r_B's are smaller than 1·3 and the *u* parameters are distinctly larger than 0·375. In the type (2), r_A/r_B's are around 1·5 and the *u* parameters are close to 0·375. In the type (3), r_A/r_B's are larger than 1·5 and the *u* parameters are markedly smaller than 0·375. As discussed by Kamb (1968), the *u* value is closely related to the stability of the spinel, since the condition $u > 0·375$ indicates the shortening of shared edges in coordination octahedra.

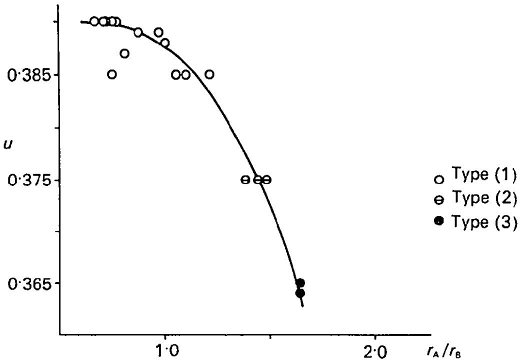

Fig. 1. A plot of *u* parameters against cation ionic radii ratios for normal spinels. r_A and r_B are ionic radii of cations in octahedral and tetrahedral sites, respectively. Type (1) represents $A_2^{3+}B^{2+}O_4^{2-}$ compounds, type (2) $A_2^{2+}B^{4+}O_4^{2-}$ and type (3) $A_2^{1+}B^{6+}O_4^{2-}$.

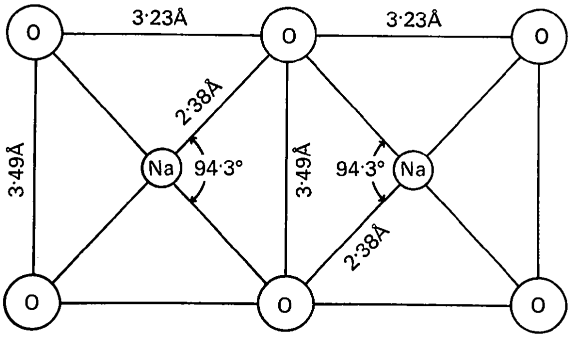

Fig. 2. Bond distances and angles in the NaO_6 octahedra.

The fact that most of the normal spinels have *u* parameters larger than 0·375 can be explained by this shortening of shared edges. Since the *u* parameter of Na_2WO_4 is as small as 0·365, the shared edges of NaO_6 octahedra (3·49 Å) are remarkably longer than the unshared ones (3·23 Å) (Fig. 2), and consequently the interatomic distance between two Na atoms in neighbouring octahedral sites is shortened compared with the case where the coordination octahedron is regular and has the identical Na–O distance to the observed. Ag_2MoO_4 is in the same situation. Kamb (1968) attributed the stabilization of Ag_2MoO_4 to the covalent character of the Ag–O bonds. In the case of Na_2WO_4, however, we cannot expect considerable covalent character in Na–O bonds, and we have to seek the stabilizing factor in other directions. Probably one of the important factors is that the increase in repulsion between two A cations in neighbouring octahedral sites caused by shortening of the A–A distance is relatively small in type (3) spinels, since A cations have relatively large ionic radii and small positive charges in this type of spinel.

We are very grateful to Professor Y. Saito for his kindness in making available an automatic four-circle diffractometer. Computations were carried out on HITAC 8700 computer at the Computer Center of Tokyo Institute of Technology using the UNICS program system (Sakurai, 1967).

References

DONOHUE, J. & SHAND, W. JR (1947). *J. Amer. Chem. Soc.* **69**, 222.

International Tables for X-ray Crystallography (1962). Vol. III, pp. 201–216. Birmingham: Kynoch Press.

KAMB, B. (1968). *Amer. Min.* **53**, 1493.

LINDQVIST, I. (1950). *Acta Chem. Scand.* **4**, 1066.

SAKURAI, T. (1967). Universal Program System for Crystallographic Computations. Cryst. Soc. Japan.

SWANSON, H. E., MORRIS, M. C., STINCHFIELD, R. P. & EVANS, E. H. (1962). *NBS Monograph No.* 25, sec. 1, p. 47.