JOURNAL OF MATERIALS SCIENCE 31 (1996) 2873–2877

# Neutron powder diffraction study of the scintillator material $ZnWO_4$

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With a view to the technological applications of $ZnWO_4$ crystals, we have performed Rietveld profile refinement of medium-resolution, time-of-flight, neutron powder diffraction data of synthetic $ZnWO_4$ to improve the quality of the current crystal structure derived from single crystal X-ray techniques that produced a final solution with an *R* factor of only 10%. The new structural data for $ZnWO_4$, monoclinic space group *P2/c*, lattice parameters of 0.469263(5), 0.572129(7), 0.492805(5) nm for *a, b* and *c* respectively, and a β angle of 90.6321(9)° with two formula units per unit cell. The $ZnO_6$ octahedra contain 3 pairs of Zn–O bonds of 0.2026(2), 0.2090(2) and 0.2227(3) nm and the $WO_6$ octahedra contain 3 pairs of W–O bonds 0.1789(2), 0.1914(2) and 0.2133(3) nm. These new data confirm the basic structure of $ZnWO_4$ and provide accurate off-centring magnitudes for the Zn and W cations.

## 1. Introduction

The rare mineral sanmartinite, $ZnWO_4$, is a member of a large group of monoclinic, divalent-transition-metal tungstates of the general form $AWO_4$, [1] in which the ionic radius of the divalent cation is no larger than that of $Cd^{2+}$. Since the study of Broch [2] several tungstates, often referred to as wolframite-type or $NiWO_4$-type tungstates, have been structurally characterized, i.e. A = Mg, Mn, Fe, Co, Ni, Zn, Cd, and, in addition, some high pressure molybdates have also been shown to exhibit this structure for which A = Mg, Mn, Co, Ni and Zn [3]. The wolframite structure type, see Fig. 1, comprises of infinite zig–zag chains of either $AO_6$ octahedra or $WO_6$ octahedra, running parallel to the *z* axis. These chains are formed by edge–sharing octahedra, with each chain of $AO_6$ octahedra being corner linked to four chains of edge–sharing $WO_6$ octahedra.

Crystals of $ZnWO_4$ are of significant technological importance in areas such as scintillation detectors, photoanodes and masers. It is as a result of this that a large number of studies have been carried out on their physical properties. van Uitert *et al.* [4] and Földvári *et al.* [5] have explored the growth of $ZnWO_4$ single crystals, while the characteristics of impurity charge balancing by $OH^-$ in such single crystals was studied by Földvári *et al.* [6]. Various thermodynamic properties have been calculated [7, 8] and the elastic, acoustic [9] and optical properties [10] have been fully characterized. In addition various electrical properties such as the dielectric constants [11], the electronic and ionic conductivities [12] and magnetic properties [13] have also been measured. The scintillation properties [14, 15] have been well documented and with such technological applications in mind there is a vast literature dedicated to the effects of various chemical dopants, on both the Zn and the W sites, and any subsequent charge mismatching on these physical properties.

$ZnWO_4$ was shown to be structurally analogous to the other wolframite type phases by Filipenko *et al.* [16] using single crystal X-ray diffraction techniques. Subsequent studies of the cell parameters have shown some marked differences from those of Filipenko *et al.*, as shown in Table I, and certain inconsistencies associated with the structural parameters and metal–oxygen bond lengths have recently come to light. Schofield *et al.* [17] found significant difference between their extended X-ray absorption fine structure [EXAFS] derived bond lengths and those of Filipenko *et al.*, over and above the expected inherent bond shortening of the EXAFS data. They pointed out that the refinement of Filipenko *et al.* was carried out on a deep red crystal whilst the sample of their study, and this study, was white and was found to contain no chemical impurity. No discussion was given by Filipenko *et al.* with respect to the purity of their starting materials and the final single crystal grown, the X-ray intensities were visually estimated with no mention of the thermal vibration assumptions being given. Such vibrations may indeed be very significant in these compounds as Abrahams [18], for example, showed for the refinement of α-$ZnMoO_4$, in which anisotropic thermal vibrations had to be assumed. It is possible that a combination of some, or all, of these factors may be responsible for the relatively

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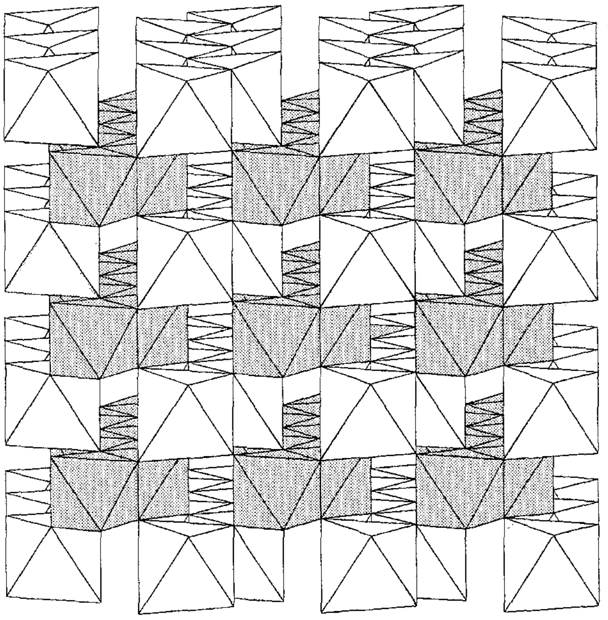

*Figure 1* The crystal structure of $ZnWO_4$ viewed along the $z$ axis, with the $x$ axis vertical and the $y$ axis horizontal. The filled octahedra represent $WO_6$ octahedra and the unfilled octahedra represent the $ZnO_6$ octahedra.

high final $R$ factor of 10% determined for the single crystal study. It has also been noted recently [19] that certain inconsistencies exist in the quoted bond lengths of Filipenko *et al.*

These problems, coupled with the technological applications of these crystals, and the large amount of work still being carried out on the various properties of pure and doped crystals of $ZnWO_4$, makes it seem remarkable that no more recent structural refinement has been carried out to improve the structural model of Filipenko *et al.* As a result we have used Rietveld profile refinement of medium-resolution, time-of-flight, neutron powder diffraction data to try to improve this position.

## 2. Experimental procedure

### 2.1. Synthesis

The $ZnWO_4$ powder was synthesized by direct precipitation, a method which has been employed for other tungstate end members [20] and also for tungstate solid solutions [21–23]. Stoichiometric amounts of analytical grade $ZnSO_4 \cdot 7H_2O$ and $Na_2WO_4 \cdot 2H_2O$ were dissolved in 250 ml of deionized water according to the equation:

$$ZnSO_4 \cdot 7H_2O(aq) + Na_2WO_4 \cdot 2H_2O(aq) \rightarrow ZnWO_4(s) + Na_2SO_4(aq) + 9H_2O$$

The solution of $ZnSO_4 \cdot 7H_2O$ was brought to the boil and to this, the solution containing $Na_2WO_4 \cdot 2H_2O$ was added. A white precipitate appeared instantly and was allowed to settle. After separation from the remaining solution the precipitate was washed, dried and ground before annealing in a muffle furnace at 600 °C for 88 h. Characterization using a Huber 620 high-resolution Guinier X-ray powder diffraction camera, with Cu $K_{\alpha_1}$ radiation, and a Philips EM400 analytical TEM showed that the sample was indeed $ZnWO_4$ and revealed the presence of no chemical impurity. A small amount of ZnO is present, however, as a second phase and is a result of the synthesis technique.

### 2.2. Neutron diffraction

Neutron time-of-flight powder diffraction data were collected on the medium-resolution diffractometer POLARIS [24] at the ISIS neutron spallation source [25]. Data in the time-of-flight range 3500–19700 μs, corresponding to a d-spacing range of 0.069–0.389 nm, and binned as $\Delta t/t = 1 \times 10^{-3}$, were background subtracted, corrected for the incident flux distribution using a vanadium standard and finally corrected for absorption and self scattering. These data were subsequently used in the Rietveld profile refinement.

## 3. Structure refinement

Profile refinement was carried out using the dedicated time-of-flight Rietveld package TF14LS [26] based on the Cambridge crystallographic subroutine library. The starting model was the refined structural coordinates of Filipenko *et al.* and the scattering lengths used in the analysis were, Zn 5.680 fm, W 4.77 fm and O 5.805 fm [27]. Convergence was rapid from this model and resulted in the following agreement factors, $R_p = 0.045$, $R_{wp} = 0.037$, $R_E = 0.015$, $\chi^2 = 5.9$ for 1723 observations and 31 variables. The final fit to the data is shown in Fig. 2, with the observed data as dots, calculated as a full line and the residual (difference/esd) shown separately. The dotted lines on the residual plot are $\pm 3\sigma$ and it can be seen that the fit

TABLE I Cell parameters for $ZnWO_4$ from this study compared with those of other studies

| | Filipenko *et al.* (1968) | Sleight (1972) | Schofield and Redfern (1992) | This study |
|---|---|---|---|---|
| space group | *P*2/*c* | *P*2/*c* | *P*2/*c* | *P*2/*c* |
| $a \times 10^{-1}$ nm | 4.72 (1) | 4.690 (1) | 4.6913 (3) | 4.69263 (5) |
| $b \times 10^{-1}$ nm | 5.700 (5) | 5.718 (1) | 5.7199 (3) | 5.72129 (7) |
| $c \times 10^{-1}$ nm | 4.950 (5) | 4.926 (1) | 4.9271 (3) | 4.92805 (5) |
| β/degrees | 90.08 (3) | 90.32 (2) | 90.615 (5) | 90.6321 (9) |
| volume $\times 10^{-3}$ nm$^3$ | 133.2 (3) | 132.10 (5) | 132.205 (9) | 132.300 (2) |

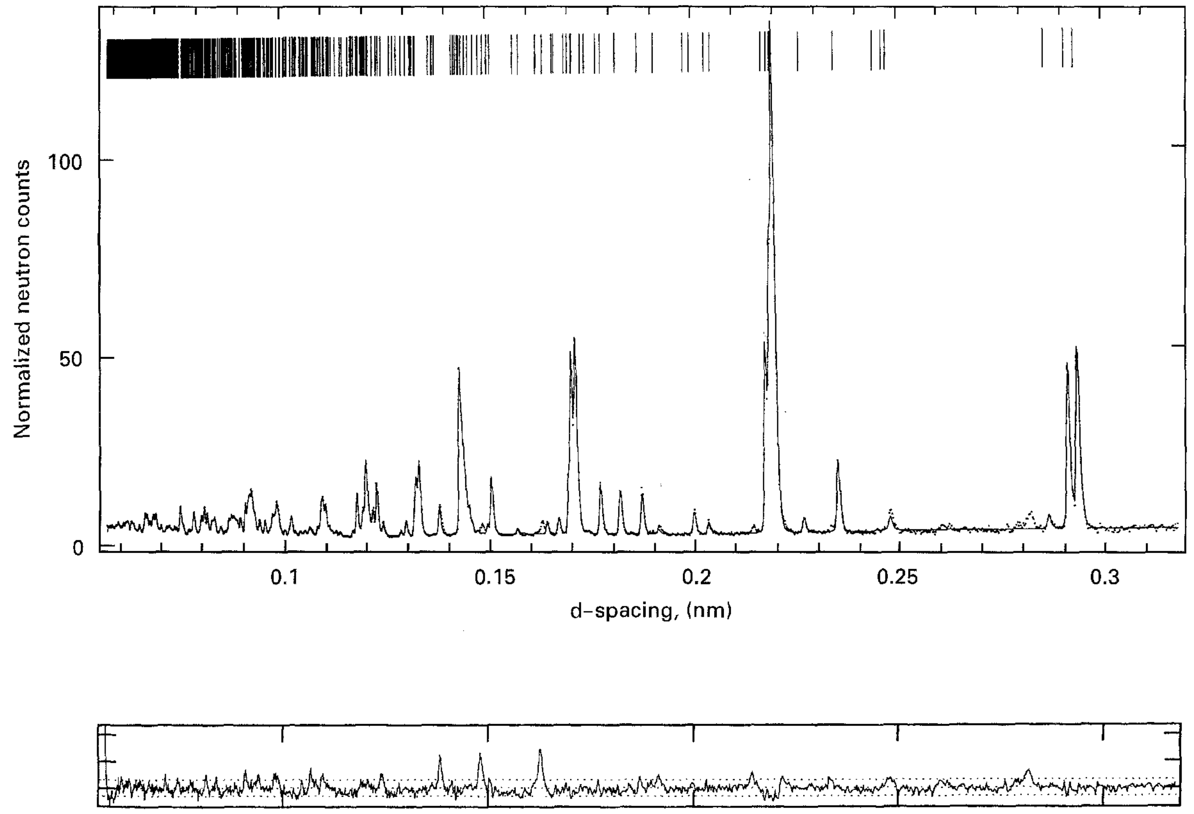

*Figure 2* Neutron powder diffraction profile of $ZnWO_4$ with the dots representing the observed data and the line representing the calculated model. The limits on the residual plot are $\pm 3\sigma$ and the residual peaks are from the secondary phase ZnO.

TABLE II Final structural parameters for $ZnWO_4$

| Atom | $x$ | $y$ | $z$ | $B_{iso}$ ($\times 10^{-2}$ $nm^2$) |
|---|---|---|---|---|
| Zn | 0.50000 | 0.68325 (43) | 0.25000 | 0.415 (33) |
| W | 0.00000 | 0.18233 (48) | 0.25000 | 0.215 (36) |
| O1 | 0.21707 (29) | 0.89547 (27) | 0.43599 (30) | 0.357 (24) |
| O2 | 0.25474 (31) | 0.37717 (29) | 0.40049 (33) | 0.451 (23) |

$R_p = 0.045$, $R_{wp} = 0.037$, $R_E = 0.015$, $\chi^2 = 5.9$ for 1723 observations and 31 variables.

TABLE III Metal–oxygen bond lengths and oxygen–metal–oxygen bond angles within $ZnWO_4$

| Zn octahedra | | W octahedra | |
|---|---|---|---|
| Zn–O1 (nm) | 0.2026 (2) | W–O2 (nm) | 0.1789 (2) |
| Zn–O2 (nm) | 0.2090 (2) | W–O1 (nm) | 0.1914 (2) |
| Zn–O2 (nm) | 0.2227 (3) | W–O1 (nm) | 0.2133 (3) |
| $O2_{-a}$–Zn–$O1_a$ | 94.82 (7) | $O1_{-a}$–W–$O1_a$ | 74.31 (9) |
| $O2_{-a}$–Zn–$O1_b$ | 96.56 (7) | $O1_{-a}$–W–$O1_b$ | 84.99 (10) |
| $O2_{-a}$–Zn–$O2_b$ | 82.09 (8) | $O1_{-a}$–W–$O2_b$ | 96.94 (8) |
| $O2_{-a}$–Zn–$O2_a$ | 82.96 (8) | $O1_{-a}$–W–$O2_a$ | 99.72 (8) |
| $O2_{-a}$–Zn–$O2_{-b}$ | 160.96 (15) | $O1_{-a}$–W–$O1_{-b}$ | 153.11 (18) |
| $O1_a$–Zn–$O1_b$ | 106.35 (13) | $O1_a$–W–$O1_b$ | 79.41 (11) |
| $O1_b$–Zn–$O2_b$ | 88.68 (6) | $O1_b$–W–$O2_b$ | 89.29 (7) |
| $O2_b$–Zn–$O2_a$ | 76.32 (10) | $O2_b$–W–$O2_a$ | 102.94 (16) |
| $O2_a$–Zn–$O1_a$ | 88.68 (6) | $O2_a$–W–$O1_a$ | 89.29 (7) |

Zn Site Octahedral Angle Variance = 74.07 degrees squared; W Site Octahedral Angle Variance = 100.77 degrees squared.

generally lies between these limits with the exception of regions of the pattern where a low level of ZnO as an impurity phase may be observed. The refined structural coordinates and thermal parameters are shown in Table II, and the calculated bond lengths and angles are given in Table III.

## 4. Discussion

Neutron scattering lengths are not dependent upon atomic number and the neutron scattering length magnitudes have a small dynamic range. Hence, the atomic positions of light atoms in the presence of heavy atoms may be determined with high precision. This has indeed been shown to be critical for the accurate structure determination of similar tungstate compounds [28]. The $x$ and $z$ positions of the Zn and W atoms are both fixed by symmetry constraints, however, the $y$ coordinates are found to be greater, with respect to those of the single crystal X-ray study, by a value amounting to some $6 \times 10^{-3}$ nm and $1.7 \times 10^{-3}$ nm respectively, in the $y$ direction. All the O parameters are found to vary from those of Filipenko *et al.* especially in the $z$ direction where the variations reflect a positional difference along $z$ of some $-7 \times 10^{-3}$ nm and $5 \times 10^{-3}$ nm for O1 and O2 respectively.

The crystal structure of $ZnWO_4$, as refined here, is displayed in Fig. 1. As briefly outlined earlier the structure can be considered as a chain structure with zig–zag chains composed entirely of either edge–sharing $ZnO_6$ octahedra or edge–sharing $WO_6$ octahedra running parallel to the $z$ axis. Each $ZnO_6$ (or $WO_6$) octahedron shares two edges; one with each of the two neighbouring $ZnO_6$ (or $WO_6$) octahedra in the chain. Each chain of $ZnO_6$ octahedra is corner linked to

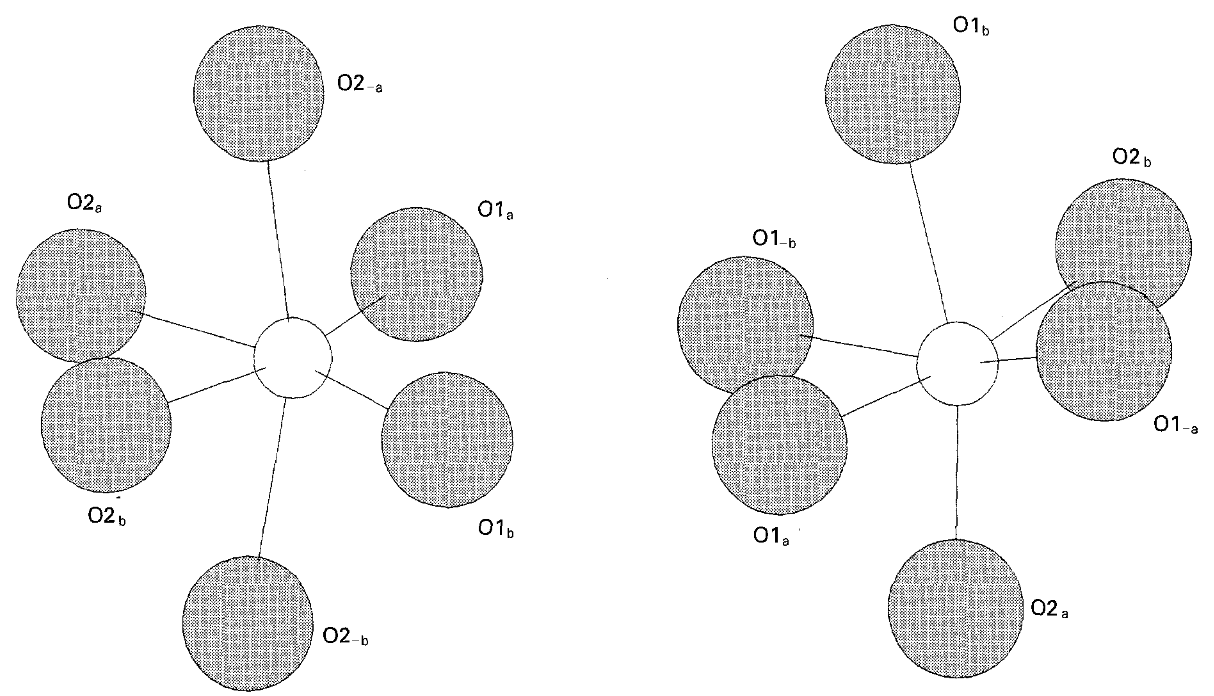

*Figure 3* Ball and stick representations of the $ZnO_6$ octahedra (left) and the $WO_6$ octahedra (right).

four chains of $WO_6$ octahedra and *vice-versa*. As a result open channels, also running parallel to the *z* axis, are left in the structure. The octahedral geometries about the Zn and the W are shown in Fig. 3 and the octahedral bond lengths and bond angles are given in Table III. These distances are, in general, similar to those of Filipenko *et al.* and reflect more accurately determined atom coordinates. The longest Zn–O bond, 0.2227 nm, however, is found to be much larger than 0.214 nm as given by Filipenko *et al.*

The $ZnO_6$ octahedra possess three pairs of equivalent Zn–O bonds with two pairs in the nominal square plane of the octahedra and one pair as the axial bonds of the octahedra. The angle between the two axial Zn–O bonds is 160.96°, significantly less than the ideal 180°, however these two bonds still lie on the plane containing the Zn cation and bisecting the remaining two pairs of Zn–O bonds. Mirror symmetry is not operational, however, due to the non-equivalent bond angles $O2_{-a}$–Zn–$\phi$ (where $\phi$ is an oxygen within the nominal square plane of the octahedra) either side of this plane. The $ZnO_6$ octahedral angular variance is 74.04 degrees squared and the Zn atom itself is displaced from the centre of these octahedra by 0.029 nm along the *y* axis, towards the two O1 oxygens of the nominal square plane. The $WO_6$ octahedra are similar to the $ZnO_6$ octahedra in geometry, with an angular variance of 100.77 degrees squared. The $WO_6$ octahedra contain three pairs of equivalent bonds and a non-centred cation, with the W cation displaced by 0.032 nm also along the *y* axis.

## 5. Conclusions

In comparison to the previously reported structure, a substantially improved structural refinement of $ZnWO_4$ has been achieved from the data presented here. The advantages of time-of-flight neutron powder diffraction, coupled with well characterized $ZnWO_4$, have resulted in a higher degree of accuracy for all structural parameters. This in turn has clarified some of the inconsistencies present in the literature, and has led to a more accurate understanding of the overall $ZnWO_4$ structure.

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*Received 12 May*
*and accepted 19 September 1995*