Table 4. *The $P_2O_7$ group in the actual structure – interatomic distances (Å) and angles (°)*

| Neighbour *N* | P | O(1) | O(7) | O(8) | O(9) |
|---|---|---|---|---|---|
| P–*N* | 3·10 (1) | 1·57 (4) | 1·53 (4) | 1·43 (3) | 1·60 (1) |
| P–O(9)–*N* | 152 (2) | | | | |
| O(1)–P–*N* | | | 109 (2) | 110 (2) | 108 (2) |
| O(7)–P–*N* | | | | 113 (2) | 105 (2) |
| O(8)–P–*N* | | | | | 111 (2) |

explained by the fact that the perovskite slabs are narrower than for $n = 4$: in the [100] direction, there is only one octahedron ensuring the connection between the octahedra which share their corners with the $P_2O_7$ groups. It would be interesting to compare with the terms $n > 4$ and $n = 2$.

The W displacement from the centre of the octahedra can also be considered. It can be seen that W(2) is not displaced [0·05 (2) Å] while the displacements of W(1) [0·14 (3) Å] and W(3) [0·22 (3) Å] are rather large, involving for W(2) an ideal octahedral coordination while W(1) and W(3) are rather (4 + 2)-coordinated as in the term $n = 4$ (Table 3).

## Conclusion

The oxide $Rb_xP_8W_{24}O_{88}$ is the term $n = 3$ of the series $Rb_xP_8W_{8n}O_{24n+16}$ previously foreseen (Giroult, Goreaud, Labbé & Raveau, 1980).

The structural study of this term confirms the ability of the $P_2O_7$ group to accommodate an octahedral framework such as that of perovskite in spite of its rigidity. The latter, however, undergoes deformations by tilting of its octahedra.

The comparison of both structures $n = 3$ and $n = 4$ shows that the cages and tunnels with a distorted hexagonal section running along [010] are similar. The location of $Rb^+$ in eightfold sites, at the level where the $P_2O_7$ groups are missing, is a common character to both structures confirmed here by site-potential calculations. The evolution of the deformation of the octahedral framework, different in both structures, agrees with the different widths of the perovskite slabs.

The mixed valence of W allows us to expect, for this oxide, electrical properties which could be correlated to those of perovskite bronze, $Na_xWO_3$, but an anisotropic character should be observed.

## References

CROMER, D. T. (1965). *Acta Cryst.* **18**, 17–23.

CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104–109.

GIROULT, J. P., GOREAUD, M., LABBÉ, PH. & RAVEAU, B. (1980). *Acta Cryst.* B**36**, 2570–2575.

SUZUKI, T. (1960). *Acta Cryst.* **13**, 279.

---

*Acta Cryst.* (1981). B**37**, 1166–1170

# The Structure of Yttrium Tungstate ε-$Y_2WO_6$

BY O. BEAURY, M. FAUCHER AND G. TESTE DE SAGEY

*ER* 210, *CNRS*, 92190 *Meudon Bellevue, France*

(*Received* 23 *June* 1980; *accepted* 8 *December* 1980)

## Abstract

The high-temperature polymorph ε-$Y_2WO_6$ is orthorhombic, space group $P2_12_12_1$, with $a = 8{\cdot}591$ (5), $b = 20{\cdot}840$ (10), $c = 5{\cdot}233$ (5) Å, $Z = 8$, $D_m = 6{\cdot}38$, $D_c = 6{\cdot}49$ Mg m$^{-3}$. The structure was determined at room temperature from 454 diffractometer intensities and refined to $R = 0{\cdot}067$. The W atoms are octahedrally coordinated and far apart from each other. The four non-equivalent Y atoms have an eightfold (3) and sevenfold (1) coordination number. Reference is made to the fluorescence spectrum of the Eu-doped compound and a comparison is made with the homologous compounds $Ln_2WO_6$ (Ln = La to Lu).

## Introduction

Few structure determinations have been carried out on the mixed oxides of W and trivalent rare-earth elements and Y (Bevan & Summerville, 1979). However, their relationship with scheelite suggests efficient luminescent properties and this has stimulated interest for U-activated $Y_2WO_6$, $U^{6+}$ in particular (Blasse, Van den Heuvel & Van Hesteren, 1977). Doubtless, more knowledge of the structural features of tungstates would help in the interpretation of their optical spectra and mechanisms of site-to-site energy transfer.

The rare-earth tungstates with the composition $Ln_2WO_6$ previously investigated fall into three struc-

0567-7408/81/061166-05$01.00

tural groups: (*a*) $La_2WO_6$, structure unknown; (*b*) from $Ce_2WO_6$ to $Ho_2WO_6$; the compounds are monoclinic and scheelite-related – their space group is $C2/c$ and their structure has been solved by Polyanskaya, Borisov & Belov (1970); and (*c*) from Er to Lu; the rare earths form monoclinic tungstates with the $P2/m$ space group (Pokrovskii, Rybakov & Trunov, 1969) – their structure is unknown but their lattice parameters, $\mathbf{a}_m \equiv [210]_{\mathrm{sch}}$, $\mathbf{b}_m \equiv [00\frac{1}{2}]_{\mathrm{sch}}$ and $\mathbf{c}_m \equiv [\bar{1}10]_{\mathrm{sch}}$, also suggest a strong relationship with scheelite.

In the course of our crystallographic and optical studies on the $WO_3$–$Y_2O_3$ system (Beaury, Faucher & Caro, 1978; Beaury, Dexpert-Ghys, Faucher & Caro, 1979), we have synthesized two structural forms of $Y_2WO_6$. The first obtained for $T < 1773$ K was a polycrystalline sample of the $P2/m$ compound mentioned above, which we shall call $\beta$-$Y_2WO_6$ according to Brixner, Sleight & Foris (1973). The second was a pure phase which had not been obtained before and corresponded to the same formula. We shall refer to it as $\varepsilon$-$Y_2WO_6$. The present paper presents the structure determination of this new polymorph.

## Experimental

$\varepsilon$-$Y_2WO_6$ was prepared by solid-state reaction of pure oxides. A stoichiometric mixture of $Y_2O_3$ and $WO_3$ was heated for 12 h at 1973 K in a zirconia furnace. Small crystals, loosely aggregated, were obtained in the high-temperature zone of the furnace. They remained stable when quenched at room temperature. Their formula determined by microprobe analysis was (1·008 ± 0·01) $Y_2O_3.WO_3$. The dimensions of the orthorhombic unit cell were determined from rotation and moving-film photographs (Beaury, Faucher, Teste de Sagey & Caro, 1978). The conditions limiting possible reflections ($h00$: $h = 2n$; $0k0$: $k = 2n$; $00l$: $l = 2n$) prescribed the $P2_12_12_1$ space group. Taking into account the mean cationic volume (~37 Å$^3$) in similar compounds, the volume of the unit cell (937 Å$^3$) suggested $Z = 8$ (24 cations) in six 4(*c*) positions. Following this hypothesis, there should be two and four non-equivalent sites for W and Y respectively in the asymmetric unit. Additional evidence came from the analysis of the fluorescence spectrum (Beaury *et al.*, 1978, 1979) of Eu-doped $\varepsilon$-$Y_2WO_6$. The ionic radii of $Eu^{3+}$, $Y^{3+}$ and $W^{6+}$ are 1·01 (CN7), 0·96 (CN7), 0·6 Å (CN6) respectively (Shannon, 1976), so that triply-ionized Eu is unable to replace W; it is selectively substituted for Y and may occupy with equal chance any of the four crystallographic sites of the latter. Indeed, four sharp fluorescence lines are observed for the $^5D_0 \rightarrow {}^7F_0$ transition characteristic of the total number of local sites for Eu.

The small untwinned single crystal selected for the structure determination was about 0·05 × 0·05 × 0·1 mm (0·25 × $10^{-3}$ mm$^3$) with convex faces impossible to locate with respect to the crystallographic axes. The coincidence of the Mo $K\alpha$ wavelength with the absorption edge of Y precluded the use of this radiation. 492 independent reflexions were collected up to $\theta = 45°$ on an automatic four-circle Nonius diffractometer with Cu $K\alpha$ ($\lambda = 1{\cdot}5405$ Å) Ni-filtered radiation. 454 reflexions with $I > 2\sigma$ were declared observed and used in the analysis. The data were corrected for Lorentz and polarization effects.

For Cu $K\alpha$ radiation, absorption is very high ($\mu \sim 80$ mm$^{-1}$). The small dimensions and rather irregular form of the crystal prevented any precise analytical anisotropic correction. Prior to all calculations, we applied to the intensities a first absorption correction, approximating the crystal to a sphere ($\mu R \sim 3$) (*International Tables for X-ray Crystallography*, 1972). The aim of this treatment was to preserve a physical meaning for the thermal parameters. Corrections for anisotropic absorption were carried out during the refinement. Scattering factors of $Y^{3+}$, $W^{6+}$ and O were taken from *International Tables for X-ray Crystallography* (1974). Those of $Y^{3+}$ and $W^{6+}$ were corrected for complex anomalous dispersion.

## Structure determination

There were 18 atoms (2W, 4Y and 12O) to be placed in the asymmetric unit. *MULTAN* 77 (Main, Lessinger, Woolfson, Germain & Declercq, 1977) and *GIF* local programs were used to determine the structure. *NORM* and *MULTAN* provided 14 solutions with satisfactory figures of merit. The best set of phases was used for an $E$ map which displayed the heavy ions. The six metals with the same mean scattering factor $(2f_{\mathrm{Y}} + f_{\mathrm{W}})/3$ were used to phase a Fourier synthesis calculated with all the observed reflexions. In the resulting Fourier map, the six peaks were enhanced, two of them being much stronger than the others. They were attributed to W and $R$ fell to 0·24. By difference maps, we then located the twelve O atoms and $R$ fell to 0·16.

## Refinement

The program used for the refinement was a version of *ORFLS* (Busing, Martin & Levy, 1962) for full-matrix least-squares calculations, in the version modified by F. Dahan (Robert, Tézé, Hervé & Jeannin, 1980). In this program, the observed structure factors are weighted following the scheme proposed by Cruickshank (1965) and corrected for extinction. Anisotropic absorption is corrected by multiplying the observed structure factors by an empirical quantity: $\exp[-(A_1h^2 + A_2k^2 + A_3l^2 + A_4hk + A_5hl + A_6kl)]$ where the six $A_i$ parameters are refined by least squares.

Table 1. *Fractional atomic coordinates* ($\times 10^4$) *and thermal parameters*

The e.s.d.'s in parentheses refer to last decimal places.

| | $x$ | $y$ | $z$ | $B$ (Å$^2$) |
|---|---|---|---|---|
| W(1) | 5222 (2) | 1891 (1) | 143 (4) | 1·37 (9) |
| W(2) | 4811 (2) | 4427 (1) | 4358 (4) | 1·38 (9) |
| Y(1) | 7457 (5) | 3006 (1) | 5069 (7) | 1·55 (10) |
| Y(2) | 5839 (4) | 657 (1) | 5419 (9) | 1·58 (10) |
| Y(3) | 8953 (4) | 1647 (1) | 877 (7) | 1·51 (11) |
| Y(4) | 2556 (5) | 680 (1) | 380 (7) | 1·47 (10) |
| O(1) | 8765 (24) | 3624 (11) | 2181 (57) | 0·7 (4) |
| O(2) | 9623 (42) | 6187 (18) | 7103 (92) | 5·7 (8) |
| O(3) | 9402 (34) | 4982 (14) | 1932 (70) | 3·6 (6) |
| O(4) | 9046 (29) | 6179 (13) | 1790 (71) | 1·6 (5) |
| O(5) | 8812 (24) | 5003 (12) | 7138 (74) | 1·7 (6) |
| O(6) | 338 (25) | 2493 (12) | 2525 (56) | 1·4 (5) |
| O(7) | 3712 (29) | 2466 (11) | 1694 (52) | 1·6 (5) |
| O(8) | 1636 (34) | 6005 (12) | 1142 (55) | 1·9 (5) |
| O(9) | 1871 (22) | 2803 (9) | 7745 (42) | 0·0 (4) |
| O(10) | 1616 (34) | 3687 (11) | 1106 (50) | 1·4 (5) |
| O(11) | 4555 (31) | 1250 (14) | 2546 (72) | 3·1 (6) |
| O(12) | 6644 (27) | 9824 (10) | 2420 (47) | 0·0 (3) |

By varying the atomic coordinates and the individual isotropic temperature factors, $R$ dropped to 0·11. By varying in addition the extinction parameter and the $A_i$ parameters of anisotropic extinction, we obtained a final value $R = \sum ||F_o| - |F_c||/\sum |F_o| = 0{\cdot}067$ and $R_w = [\sum (F_o - F_c)^2/\sum wF_o^2]^{1/2} = 0{\cdot}098$. No determination of anisotropic thermal parameters was attempted. Final atomic coordinates and isotropic thermal parameters are reported in Table 1.* As expected, the precision of the determination of thermal parameters is poor.

## Discussion

The projection of a half unit cell on the *ab* plane is shown in Fig. 1. The first question which arises is that of a relationship with the fluorite structure. We have already mentioned that the three lattice parameters of the isomorph $\beta$-$Y_2WO_6$ suggest it is strongly scheelite-related. In $\varepsilon$-$Y_2WO_6$, it seems clear that the repetition sequence, at least in the **a** direction (8·59 Å), is disturbed with respect to the fluorite arrangement. So as to show how the cationic framework is built up, we have idealized it and projected it on the *ab* plane [Fig. 2(*a*)]. There appears a repetition of identical blocks such as those represented in Fig. 2(*b*), which consist of a superposition of simple cubic units with Y and W alternating on each row and face-centred units with mixed W–Y planes and unique Y planes. In the $Y_2WO_6$ unit cell, there are two such blocks twisted by $\pi$ and shifted by $a/2$ along **a** (glide axis). With this ideal arrangement, a W–Y distance repeated four times in the unit cell is too short and the true structure is distorted so that this distance attains 3·27 Å.

A remark must be made about the mean cationic volume ($V$/number of cations = m.c.v.) in the $Ln_2O_3$–$WO_3$ phases. In $Y_2O_3$ the m.c.v. is 37·2, $Y_6WO_{12}$ 36·6, $\alpha$-$Ho_2WO_6$ 37·9 Å$^3$ (space group $C2/c$; this form has not been observed for $Y_2WO_6$ although

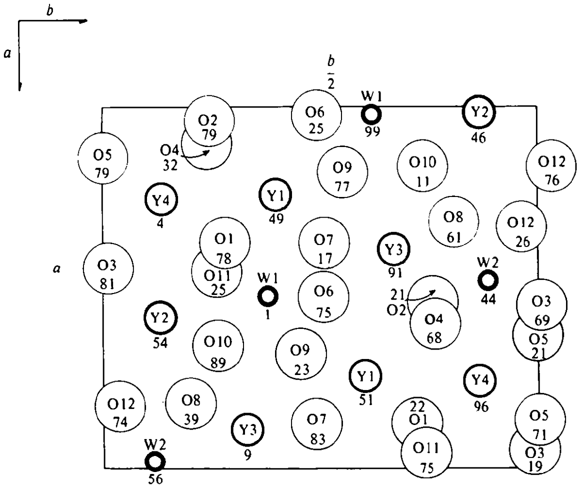


Fig. 1. Projection of a half unit cell of $\varepsilon$-$Y_2WO_6$ on the *ab* plane. The fractional coordinate $z$ is indicated adjacent to the atom label.

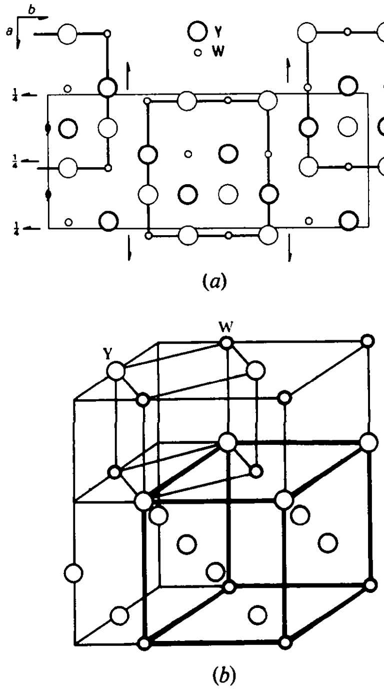


Fig. 2. (*a*) Projection on the *ab* plane of the idealized cationic framework of $\varepsilon$-$Y_2WO_6$. (*b*) Block constituting the structure.

---

* Lists of structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35931 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

the ionic radii of $Ho^{3+}$ and $Y^{3+}$ are nearly identical). For $\beta$-$Ho_2WO_6$ (high-pressure modification), it is 37·22 Å$^3$, and for $\beta$-$Y_2WO_6$, 37·15 Å$^3$.

In all these compounds, the cationic arrangement is close-packed (distorted c.f.c.) and the m.c.v. is nearly constant. The m.c.v. of $\varepsilon$-$Y_2WO_6$ is 39 Å$^3$ and that should imply a slightly looser cationic packing. This is indeed the case since the repetition blocks are made out of the superposition of face-centred units (close-packed) and simple cubic units (non-compact packing such as $WO_3$ whose room-temperature structure is a monoclinic distortion of a simple cubic packing from which it follows that the m.c.v. is 52·8 Å$^3$).

As in fluorite, the atoms (anions and cations) are well grouped in (041) planes which are the (011) planes of fluorite. Fig. 3 represents the occupation of one such plane. We have also represented the O atoms on each side of the plane close to W so as to show the coordination polyhedra of W(1) and W(2). The distance of the other atoms to the mean plane is <0·2 Å. O atoms form strings along [100]. W is octahedrally coordinated and the octahedra are isolated. The W atoms are arranged as far apart as possible. The shortest W···W distances range between 4·99 and 6·12 Å. The smallest Y···W distance is W(1)···Y(3) = 3·27 Å.

Table 2 reports some interatomic distances and angles. Retaining in the coordination polyhedra O atoms not farther than 3 Å, we find that the coordination number of Y(1), Y(2) and Y(4) is 8 while that of Y(3) is 7. The immediate anionic environments of the four Y atoms are represented in Fig. 4. The shortest Y—O distance is 2·12 Å [Y(3)—O(8)]. Similar distances have been found in $U_6WO_{12}$ (Bartram, 1966) and $Y_6WO_{12}$ (Beaury *et al.*, 1978). Some short O···O distances are found in the coordination polyhedra of W(1) and W(2): O(2)···O(4) = 2·50, O(3)···O(5) = 2·56, O(5)···O(12) = 2·47, O(8)···O(12) = 2·54 Å for W(2); O(9)···O(10) = 2·56, O(1)···O(11) = 2·58 Å for W(1). Such a fact has already been stated by Polyanskaya *et al.* (1970) concerning $Nd_2WO_6$.

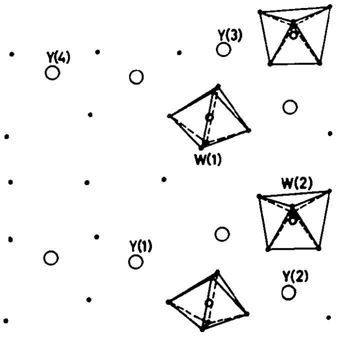
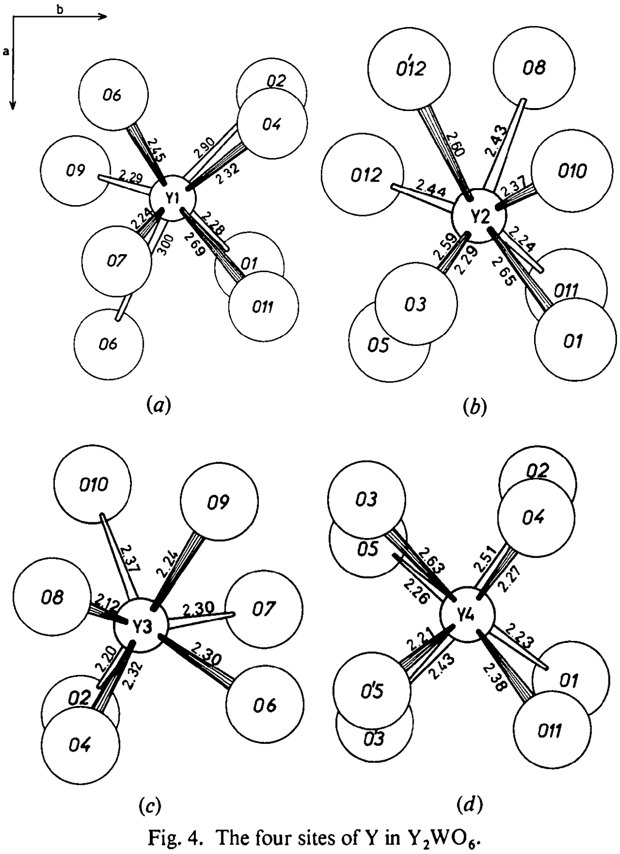


Fig. 3. Arrangement of atoms in a mean (041) plane. O atoms are small points. O atoms before and behind the plane are represented so as to show the octahedral coordination of W(1) and W(2).

Table 2. *Interatomic distances* (Å) *and angles* (°)

The standard errors in the *M*—O distances and O—*M*—O angles are 0·03 Å and 1° respectively.

| | | | Cation coordination |
|---|---|---|---|
| O(7)—W(1)—O(11) | 1·94, 1·92 | 88 | 6 |
| O(9)—W(1)—O(6) | 1·91, 1·90 | 99 | |
| O(10)—W(1)—O(1) | 1·82, 2·05 | 81 | |
| O(12)—W(2)—O(8) | 1·76, 1·80 | 91 | 6 |
| O(3)—W(2)—O(4) | 1·95, 2·04 | 78 | |
| O(2)—W(2)—O(5) | 1·81, 2·04 | 83 | |
| O(1)—Y(1)—O(6) | 2·28, 3·00 | 60 | 8 |
| O(4)—Y(1)—O(2) | 2·32, 2·90 | 56 | |
| O(6)—Y(1)—O(9) | 2·45, 2·29 | 82 | |
| O(7)—Y(1)—O(11) | 2·24, 2·69 | 65 | |
| O(11)—Y(2)—O(12) | 2·24, 2·44 | 96 | 8 |
| O(8)—Y(2)—O′(12) | 2·43, 2·60 | 75 | |
| O(10)—Y(2)—O(1) | 2·37, 2·65 | 60 | |
| O(3)—Y(2)—O(5) | 2·29, 2·59 | 69 | |
| O(6)—Y(3)—O(8) | 2·30, 2·12 | 109 | 7 |
| O(2)—Y(3)—O(4) | 2·20, 2·32 | 77 | |
| O(9)—Y(3)—O(7) | 2·24, 2·30 | 73 | |
| O(9)—Y(3)—O(10) | 2·24, 2·37 | 67 | |
| O(11)—Y(4)—O(1) | 2·38, 2·23 | 68 | 8 |
| O(2)—Y(4)—O(4) | 2·51, 2·27 | 72 | |
| O(3)—Y(4)—O′(3) | 2·63, 2·43 | 112 | |
| O(5)—Y(4)—O′(5) | 2·26, 2·21 | 101 | |



(*a*) (*b*)

(*c*) (*d*)

Fig. 4. The four sites of Y in $Y_2WO_6$.

The mean e.s.d. in O···O distances is 0·04 Å. The mean Y—O distances are 2·52, 2·45 and 2·36 Å for Y(1), Y(2) and Y(4) respectively, and 2·26 Å for Y(3). These values fall into the range of observed Y—O distances in other compounds. For $Y_6WO_{12}$ (CN7), the mean Y—O is 2·32 Å. In yttrium orthovanadate (CN8) (Milligan & Vernon, 1952), it is 2·42 Å.

We showed previously (Beaury *et al.*, 1978) the aspect of the $^5D_0 \rightarrow {}^7F_0$ transition (four lines) in the fluorescence spectrum of ε-$Y_2WO_6$: $Eu^{3+}$ under UV excitation. The first line (highest in energy; $\lambda$ = 5799·8 Å) was far stronger than the others. By resonant laser excitation at this wavelength, we observed a fluorescence spectrum with the strongest electric dipole lines ($^5D_0 \rightarrow {}^7F_0$, $^5D_0 \rightarrow {}^7F_2$) of the observed overall spectrum under UV excitation. This means that the corresponding Eu site is the most efficient. It might be that heptacoordinated Eu substituted for Y(3) since rare-earth atoms substituted in CN7 sites are rather efficient phosphors (*e.g.* $Y_2O_2S$: $Eu^{3+}$ or *B*-$Gd_2O_3$: $Eu^{3+}$), the corresponding site-symmetry giving rise to high crystal-field parameters.

## Conclusion

Three structural forms have been described for rare-earth tungstates of formula $Ln_2WO_6$. In addition, a high-temperature tetragonal form has been synthesized by Yoshimura, Sibieude, Rouanet & Foex (1975) as well as a $\delta$ metastable phase. Among all these compounds, the only resolved structure is that of $Nd_2WO_6$ (occurring from $CeWO_6$ to $HoWO_6$). In the neighbouring series $Ln_2MoO_6$, the situation is clearer since only the structure of $Ce_2MoO_6$ has not been established. From $La_2MoO_6$ to $Sm_2MoO_6$ (Ce excepted) the symmetry is $I\bar{4}2m$, while from $Dy_2MoO_6$ to $Lu_2MoO_6$ (including $Y_2MoO_6$) the structure is $C2/c$, isomorphous with $Nd_2WO_6$.

The presently reported structure of ε-$Y_2WO_6$ has little relationship with these two compounds: $La_2MoO_6$ (like $Bi_2WO_6$ or koechlinite $Bi_2MoO_6$) is a layer-type compound ($La_2O_2$ layers alternating with $MoO_4$, or $Bi_2O_2$ with $WO_4$); $Nd_2WO_6$ is intermediate between a layer-type compound and a scheelite one (mixed planes). Besides, for both phases, the cationic arrangement is face-centred, even if distorted.

In ε-$Y_2WO_6$, a portion of the cationic framework is face-centred and the remainder is primitive cubic (very distorted). The result is a slightly less dense structure.

W atoms occupy two non-equivalent octahedrally coordinated sites while the four sites of Y are sevenfold (1) and eightfold coordinated (3).

The authors thank F. Villain (Laboratoire d'Etudes des Structures Organiques Dissymétriques) who collected the data on the automatic diffractometer of the Faculté de Pharmacie (Chatenay–Malabry); A. Chiaroni, J. Guilhem, C. Riche and C. Pascard (Laboratoire de Cristallochimie, Institut de Chimie des Substances Naturelles, Gif s/Yvette) who provided access to *MULTAN* 77 and to *GIF* local programs; F. Dahan and F. Robert who furnished their modified version of *ORFLS*; and M. Fromaget for technical assistance in the preparation of the manuscript.

### References

BARTRAM, S. F. (1966). *Inorg. Chem.* **5**, 749–754.

BEAURY, O., DEXPERT-GHYS, J., FAUCHER, M. & CARO, P. (1979). *J. Lumin.* **18–19**, 249–252.

BEAURY, O., FAUCHER, M. & CARO, P. (1978). *Mater. Res. Bull.* **13**, 175–185.

BEAURY, O., FAUCHER, M., TESTE DE SAGEY, G. & CARO, P. (1978). *Mater. Res. Bull.* **13**, 953–957.

BEVAN, D. J. M. & SUMMERVILLE, E. (1979). *Handbook of the Chemistry and Physics of Rare Earths*, edited by K. A. GSCHNEIDER JR & L. EYRING, pp. 401–524. Amsterdam: North Holland.

BLASSE, G., VAN DEN HEUVEL, G. P. & VAN HESTEREN, J. J. A. (1977). *J. Solid State Chem.* **21**, 99–103.

BRIXNER, L. H., SLEIGHT, A. W. & FORIS, C. M. (1973). *J. Solid State Chem.* **7**, 418–421.

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.

CRUICKSHANK, D. W. J. (1965). *Computing Methods in Crystallography*. Oxford: Pergamon Press.

*International Tables for X-ray Crystallography* (1972). Vol. II, p. 300. Birmingham: Kynoch Press.

*International Tables for X-ray Crystallography* (1974). Vol. IV, pp. 71–98; pp. 148–151. Birmingham: Kynoch Press.

MAIN, P., LESSINGER, L., WOOLFSON, M. M., GERMAIN, G. & DECLERCQ, J.-P. (1977). *MULTAN 77. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

MILLIGAN, W. O. & VERNON, L. W. (1952). *J. Phys. Chem.* **56**, 145–148.

POKROVSKII, A. N., RYBAKOV, V. K. & TRUNOV, V. K. (1969). *Zh. Neorg. Khim.* **14**, 2344–2345. Engl. trans. *J. Inorg. Chem.* (*USSR*) (1969). **14**, 1233–1234.

POLYANSKAYA, T. M., BORISOV, S. V. & BELOV, N. V. (1970). *Dokl. Akad. Nauk SSSR*, **193**, 83–86. Engl. trans. *Proc. Acad. Sci. USSR* (1971). **15**, 636–639.

ROBERT, F., TÉZÉ, A., HERVÉ, G. & JEANNIN, Y. (1980). *Acta Cryst.* B**36**, 11–15.

SHANNON, R. D. (1976). *Acta Cryst.* A**32**, 751–767.

YOSHIMURA, M., SIBIEUDE, F., ROUANET, A. & FOEX, M. (1975). *Rev. Int. Hautes Temp. Refract.* **12**, 215–219.