

[$s = (d_{\text{Mo-O}}/1.882)^{-6.0}$] and the Pauling bond order (PBO) equation $d_n = d_1 - 0.6 \log n$ (Pauling, 1960) for the Mo—Mo bonds, yields 14.0 (1) and 14.05 (5) e^- per Mo₄, respectively, which are in excellent agreement with the value of $14e^-$ based on the stoichiometry. Moreover, the number of antibonding electrons being one-half of the difference between the number of electrons per Mo₄ derived from PBO sums and that derived from the stoichiometry (McCarley, 1986), Ho₄Mo₄O₁₁ has no electrons in antibonding states. Thus this compound is perfectly bonded with all valence electrons of the Mo atoms involved in Mo—Mo or Mo—O bonding states.

Isostructural compounds are also formed with Nd, Sm, Gd, Tb, Dy, Er, Tm, Yb, Lu and Y as ternary element (Gall, Gougeon, Nagaki, Schimek & McCarley, 1990).

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Modulated Structure of Zirconium Titanate

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Abstract. Zr_{0.992}Hf_{0.008}TiO₄, $M_r = 203.81$, orthorhombic, $P2_1c2_1$, $a = 4.821$ (2), $b = 5.341$ (7), $c =$

5.022 (3) Å, $k = 0.43a^*$, $V = 129.31$ (1) Å³, $Z = 2$, $D_x = 5.2346$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 72.4$ cm⁻¹, $F(000) = 188.51$, $T = 298$ K, $R = 0.093$ for all, 0.067 for 565 main and 0.113 for 1082 first order satellite reflections. The structure can be

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regarded as an antiphase domain structure in which the cation sequences of Zr–Zr–Ti–Ti and Ti–Ti–Zr–Zr appear alternately with an average interval of $(1-2|k|)^{-1} \approx 7.14a$. Near the domain center, the Zr ion is coordinated by eight O atoms, while the Ti ion is coordinated by six. The domain boundary region takes a disordered structure.

Introduction. The lattice constants of ZrTiO_4 quenched from temperatures higher than *ca* 1473 K differ from those of slowly cooled specimens (Coughanour, Roth & De Presse, 1954; Cocco & Torriano, 1965). The differences in lattice constants have recently been attributed to an order–disorder phase transition (McHale & Roth, 1983, 1986; Ikawa, Iwai, Hiruta, Shimojima, Urabe & Udagawa, 1988; Ikawa, Shimojima, Yamada, Urabe & Udagawa, 1988). The high-temperature form quenched from temperatures higher than *ca* 1473 K has an $\alpha\text{-PbO}_2$ structure with space group *Pbcn* having disordered arrangements of Zr and Ti atoms (or Hf and Ti atoms) in octahedral cation sites (Newnham, 1967; Harari, Bocquet, Huber & Collongues, 1968). The low-temperature form, which is prepared by slow cooling and/or by prolonged heating at a temperature lower than *ca* 1423 K, has an ordered arrangement of atoms showing incommensurate satellite reflections along \mathbf{a}^* . The *b* parameter of the high-temperature form has been found to be anomalous (Ikawa, Iwai, Hiruta, Shimojima, Urabe & Udagawa, 1988; Ikawa, Shimojima, Yamada, Urabe & Udagawa, 1988) because it changes with quench temperature. Furthermore, a number of anomalies which cannot be explained by the normal concepts of crystal chemistry are observed for these compounds. Structural data are essential to understand the structure–property relationship of this crystal. Yamada, Urabe, Ikawa & Shimojima (1991) tried to analyze the modulated structure by using limited data – three normal diffractions of 200, 400 and 600, and three incommensurate diffractions near them – and suggested an ordered arrangement of cations such as Ti–Ti–Zr–Zr. Following this, the present study was undertaken to obtain a full analysis of the modulated structure.

Experimental. Single crystals of ZrTiO_4 were synthesized by a flux method. The mixture of ZrTiO_4 , Li_2MoO_4 and MoO_3 with a molar ratio of 1:2:5 was heated at 1573 K for 5 h, cooled slowly to 1073 K at 3 K h^{-1} and then quenched. A trace amount of Hf was detected in single crystals by means of energy-dispersive X-ray analysis (Hf/Zr = 0.008/0.992, Ikawa, Narita, Fukunaga & Newnham 1990). A single crystal $0.1 \times 0.1 \times 0.19 \text{ mm}$ in size was used for data collection on an automated four-circle diffractometer with a rotating anode X-ray tube

(Rigaku AFC-5R, graphite-monochromated $\text{Mo K}\alpha$, $\lambda = 0.71073 \text{ \AA}$). Lattice parameters were refined from 2θ values of strong reflections in the range $70 < 2\theta < 90^\circ$; 2θ – ω scan technique. Three standard reflections monitored every 50 reflections showed no intensity variation. No absorption correction was made. The intensities of reflections with the diffraction vector $\mathbf{h} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* + m\mathbf{k}$ within $m = 0, \pm 1$ and $2\theta < 90^\circ$ were collected, 2208 reflections of which 1649 were independent, $R_{\text{int}} = 0.012$. Merging of the observed [$I > 3\sigma(I)$] reflections gave 565 main and 1082 satellite reflections. The superspace group deduced from the observed reflection conditions, $l = 2n$ for $h0lm$, $k = 2n$ for $0k0l$, is $P_{111}^{Pbc_2}$. The structure refinement was carried out by REMOS (Yamamoto, 1982) with an initial model including one cation and two oxygen sites in the unit cell of the average structure, in which the cation site was occupied by Ti and Zr/Hf ions with occupation probabilities of $\frac{1}{2}$. The space group *Pbc* 2_1 has no special position, so that there is no restriction for the modulation function. The symmetry operations of the superspace group are given by $x, y, z, t; -x + \frac{1}{2}, y + \frac{1}{2}, z, -t; x, -y, z + \frac{1}{2}, t; -x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}, -t$. (The non-standard setting was employed for comparison with the high-temperature form.) The substitutional harmonic modulation of the Ti and Zr ions accompanied by a displacive modulation for each atom was assumed because the higher order satellite reflections were very weak. This model ($R = 0.20$) was modified based on the difference Fourier synthesis. In the final model, the split-atom approximation was employed; two positions were considered for the Ti-, Zr/Hf- and O-atom sites, one of which had an occupation probability *p* and the other $1-p$. In the harmonic approximation, the atom coordinates in the unit cell at \mathbf{X} are given by

$$x_i = \bar{x}_i + u_{0i} + u_{ci} \cos(2\pi\bar{x}_4) + u_{si} \sin(2\pi\bar{x}_4),$$

where $\bar{x}_4 = \mathbf{k} \cdot (\mathbf{x} + \mathbf{X})$, \mathbf{x} and \mathbf{k} being the positional vector of the fundamental structure and the wave vector of the modulation wave. The homogeneous deviation from the fundamental structure, u_{0i} , and the amplitudes of the modulation wave, u_{ci} , u_{si} ($i = 1, 2, 3$), are the refinable parameters. Similarly, the occupation probability of each atom is given by

$$p = p_0 + p_c \cos(2\pi\bar{x}_4) + p_s \sin(2\pi\bar{x}_4).$$

The model (split-atom approximation) requires correlated occupation probabilities for Ti and Zr/Hf, O(1) and O(2) or O(3) and O(4): the occupation probability of Zr/Hf, O(2) or O(4) is given by $1-p$ when that of Ti, O(1) or O(3) is *p*. In order to restrict the occupation probability within the physically reasonable range, $0 \leq p \leq 1$, the penalty function method was applied (Yamamoto, 1981). Since all the atoms are on general positions, there is no restriction

Table 1. Atomic positions of the fundamental structure

	Wyckoff position	x	y	z
Zr/Ti	4(a)	0.0	0.2872	0.25
O(1)/O(2)	4(a)	0.267	0.095	0.064
O(3)/O(4)	4(a)	0.773	0.585	0.445

for the modulation wave. The refinement with anisotropic temperature factors without modulation and unit weights gave an R factor of 0.093 for all ($wR = 0.094$, $S = 4.81$), 0.067 for 565 main and 0.113 for first-order satellite reflections. $(\Delta/\sigma)_{\max} = 0.03$, $(\Delta\rho)_{\max} = 3.2$ and $(\Delta\rho)_{\min} = -3.5 \text{ e } \text{Å}^{-3}$. Scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV). The structural parameters for the fundamental and modulated structures are listed in Tables 1 and 2.†

Discussion. The chemical formula obtained from the refinement is $(\text{Zr}_{0.992}\text{Hf}_{0.008})_{0.9}\text{Ti}_{1.1}\text{O}_4$. The structure has a Zr–Zr–Ti–Ti sequence as shown in Fig. 1. This sequence is interchanged with a Ti–Ti–Zr–Zr sequence by the insertion of a disordered boundary region. Therefore the structure can be regarded as an antiphase domain structure. The boundary region appears with an interval of $(1-2|k|)^{-1} \approx 7.14a$ because $k = 0.43a^*$. The local structure is different from the $\alpha\text{-PbO}_2$ structure but similar to that of $\text{Zr}_{0.83}\text{Ti}_{1.17}\text{O}_4$ ($\text{Zr}_5\text{Ti}_7\text{O}_{24}$) (Bordet, McHale, Santoro & Roth, 1986): the Ti atoms are coordinated by six O atoms while the Zr atoms are coordinated by eight O atoms. $\text{Zr}_{0.83}\text{Ti}_{1.17}\text{O}_4$ has, however, the Ti–Ti–Zr sequence in contrast to the Ti–Ti–Zr–Zr sequence in the present case. The structure will be discussed in detail elsewhere. The present result shows that the n -glide plane in the space group of the high-temperature form $Pbcn$ is lost at the phase transition to the low-temperature phase and the noncentrosymmetric superspace group $P_{111}^{Pbc_2}$, is realized.

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† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53982 (20 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

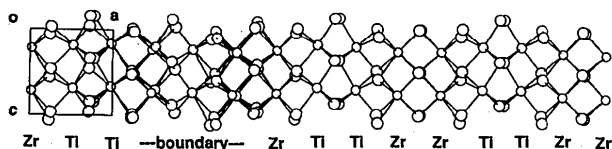


Fig. 1. The modulated structure of ZrTiO_4 . Atoms with an occupation probability greater than 0.4 are plotted. The plotted range ($7a$) corresponds to about one antiphase domain. The domain boundary is repeated with period $7.14a$.

Table 2. Structural parameters for the average structure and the modulation; the third column (corresponding to 1 in the heading) represents the parameters for the average structure (u_{0i} , B , p_0); the fourth and fifth columns are amplitudes for cosine and sine waves; the values have been multiplied by 10^3 for positional parameters and by 10^2 for thermal and occupational parameters; e.s.d.'s are in parentheses

$$B \equiv B_{\text{eq}} = (4/3)[\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2] \text{ \AA}^2.$$

		1	$\cos(2\pi t)^*$	$\sin(2\pi t)^*$
Zr/Hf	x	27 (1)	-9 (1)	-14 (1)
	y	-2 (1)	-5 (1)	-20 (1)
	z	0	-27 (1)	-39 (1)
	B	23 (2)		
	p	45 (1)	30 (1)	37 (1)
Ti	x	-21 (1)	-4 (1)	-5 (1)
	y	20 (1)	5 (1)	-14 (1)
	z	-39 (2)	66 (2)	37 (1)
	B	83 (3)		
	p	55	-30	-37
O(1)	x	11 (6)	8 (7)	30 (7)
	y	5 (5)	16 (5)	12 (6)
	z	-3 (5)	31 (5)	43 (7)
	B	71 (2)		
	p	55 (3)	11 (1)	-49 (2)
O(2)	x	-26 (12)	-10 (7)	28 (14)
	y	-10 (11)	9 (5)	-15 (14)
	z	-50 (12)	13 (8)	-85 (14)
	B	53 (2)		
	p	45	-11	49
O(3)	x	-14 (7)	-30 (9)	14 (6)
	y	-16 (6)	-2 (8)	-6 (5)
	z	5 (7)	-2 (9)	-8 (6)
	B	60 (2)		
	p	48 (5)	45 (7)	-17 (4)
O(4)	x	1 (6)	-1 (8)	-3 (4)
	y	30 (6)	-8 (8)	-13 (4)
	z	-79 (7)	57 (9)	4 (6)
	B	36 (1)		
	p	52	-45	17

* $t \equiv \bar{x}_4$.

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Structure of *fac*-Tricarbonyl[bis(2-diphenylphosphinoethyl)phenylphosphine]-tungsten(0)

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Abstract. $[\text{W}(\text{CO})_3\{\text{PhP}(\text{C}_2\text{H}_4\text{PPh}_2)_2\}]$, $[\text{W}(\text{CO})_3(\text{C}_{34}\text{H}_{33}\text{P}_3)]$, $M_r = 801.8$, monoclinic, $P2_1/n$ $a = 12.052$ (4), $b = 18.761$ (4), $c = 15.174$ (6) Å, $\beta = 106.77$ (3)°, $V = 3285$ (2) Å³, $Z = 4$, $D_m = 1.61$ (3), $D_x = 1.62$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.7093$ Å, $\mu = 37.7$ cm⁻¹, $F(000) = 1592$, $T = 298$ K, $R = 0.026$ for 4345 observed reflections. The title compound was prepared from $\text{W}(\text{CO})_6$ and $\text{PhP}(\text{C}_2\text{H}_4\text{PPh}_2)_2$ in *n*-decane. The three homologues, $M(\text{CO})_3[\text{PhP}(\text{C}_2\text{H}_4\text{PPh}_2)_2]$, $M = \text{Cr}$, Mo and W , have similar molecular structure and the Mo and W analogues are isomorphous.

Introduction. The tritertiary phosphine, bis(2-diphenylphosphinoethyl)phenylphosphine (pf-pf-pf), can react with suitable metals under different conditions to form monoligand monometallic, biligand monometallic, triligand monometallic, biligand bimetallic, triligand bimetallic and triligand trimetallic complexes (King, Kapoor & Kapoor, 1971). For the derivatives of metal carbonyls of Group VIb, the three triligand monometallic complexes $M(\text{CO})_3(\text{pf-pf-pf})$, $M = \text{Cr}$, Mo , and W , have been reported (Chatt & Watson, 1961; King, Kapoor & Kapoor, 1971; Favas, Kepert, Skelton & White, 1980). However, the crystal structure of the W complex has not, as yet, been published. In order to compare the structures and as part of a structural study on the derivatives of the metal carbonyls (Ueng & Hwang, 1991; Ueng & Leu, 1991), the crystal structure analysis of the title compound was undertaken.

Experimental. The title compound was prepared by refluxing stoichiometric amounts of $\text{W}(\text{CO})_6$ and $\text{PhP}(\text{C}_2\text{H}_4\text{PPh}_2)_2$ in purified *n*-decane under nitrogen for *ca* 5 h. The reaction medium for the thermolytic substitution reaction is *n*-decane instead of xylene or

decalin which have been previously reported (King, Kapoor & Kapoor, 1971; Favas, Kepert, Skelton & White, 1980). Crystal was prepared from $\text{CH}_2\text{Cl}_2/n$ -hexane by the diffusion method, crystal dimensions $0.08 \times 0.50 \times 0.50$ mm. D_m by flotation. CAD-4 diffractometer. Unit cell from 25 reflections, 2θ range 17.80 to 23.06° . $\theta/2\theta$ mode with θ scan width = $(0.65 + 0.35 \tan \theta)^\circ$. $\text{Mo } K\alpha$ radiation. Three standard reflections were monitored every 2 h: variation on $I \leq 4\%$. 6189 reflections measured ($1.0 \leq \theta \leq 49.8^\circ$; $h, k, l: -14$ to $13, 0$ to $22, 0$ to 18 , respectively), 5776 unique ($R_{\text{int}} = 0.012$), giving 4345 observed with $I \geq 2.0\sigma(I)$. Absorption corrections were made according to experimental ψ rotation (max., min. transmission factors = $0.464, 0.999$). Structure solved by heavy-atom method. Positions of H atoms of phenyl groups were calculated after isotropic refinement, the others found in difference Fourier map. $(\Delta/\sigma)_{\text{max}} = 0.10$. Peaks in final ΔF map 0.870 to -0.550 e Å⁻³. Secondary-extinction coefficient 0.451 (8) (length in μm). $w = 1/\sigma^2(F_o)$, with $\sigma(F_o)$ from counting statistics. The quantity minimized was $\sum w(KF_o - F_c)^2$, final R, wR and S are $0.026, 0.020$, and 1.49 . Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV). Computing programs: *NRCVAX* (Gabe & Lee, 1981) package and *ORTEP* from *Structure Determination Package* (Enraf-Nonius, 1979).

Discussion. Atomic positional parameters are given in Table 1† and selected bond lengths and bond angles of the title compound are listed in Table 2. The molecular structure is shown in Fig. 1.

† Lists of structure factors, anisotropic thermal parameters, H-atom parameters and full bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53925 (27 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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