

# Structural Changes in the System $\text{Zn}_{1-x}\text{Cd}_x\text{WO}_4$ , Determined from Single Crystal Data

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Dahlborg, M. Å. and Svensson, G., 1999. Structural Changes in the System  $\text{Zn}_{1-x}\text{Cd}_x\text{WO}_4$ , Determined from Single Crystal Data. – Acta Chem. Scand. 53: 1103–1109. © Acta Chemica Scandinavica 1999.

The solid solution system  $\text{Zn}_{1-x}\text{Cd}_x\text{WO}_4$  has been studied using single-crystal diffraction. Crystals, with sizes up to 1 cm in length and compositions in the range  $x=0.0$ – $1.0$ , have been grown from  $\text{Na}_2\text{W}_2\text{O}_7$  fluxes. The composition  $x$  of the crystals deviates substantially from the composition in the flux. A linear relation between the composition  $x$  and the unit-cell parameters  $a$  and  $c$  has been found, but not for  $b$  and  $\beta$ . The structure consists of six-coordinated W and Zn/Cd ions in oxygen octahedra, which forms the wolframite structure type. The movement of the Zn/Cd ion in the octahedra is comparable with the effect of an increased pressure on the wolframite structure. The net result, when  $x$  increases, is that the wolframite structure deforms towards the scheelite structure type. The deformation of the octahedra in the structure increases with increasing  $x$ .

Divalent metal ion tungstates ( $\text{MWO}_4$ ) are of interest for their luminescent properties.<sup>1</sup> Tungstate single crystals find their applications as detector materials for high-energy radiation and particles.  $\text{CdWO}_4$  is used as the X-ray detector in Computed Tomography (CT),<sup>2</sup> and the new Large Hadron Collider (LHC) detector<sup>3</sup> at CERN is being built of  $\text{PbWO}_4$  single crystals. Tungstates can also be used as matrices for optical generators,<sup>4</sup> as host lattices in paramagnetic studies,<sup>5</sup> as conductive sensors<sup>6</sup> for gases and in other semiconductor applications.

One advantage with tungstate materials is that the luminescence is an intrinsic property. The electron transfer takes place within the  $\text{WO}_4^{2-}$  (or  $\text{WO}_6^{6-}$ ) unit. Growth of high-quality single crystals in a reproducible way is then simplified, since there is no need for doping or other defects that affect the crystal quality and homogeneity. The scintillation properties of tungstate crystals are fairly well documented, but there is still a lot of work going on in this field.<sup>1,2</sup> Special attention is being paid to mixed  $\text{A}_{1-x}\text{B}_x\text{WO}_4$  crystals. With those mixed crystals one can combine advantageous properties from the pure components. Optimal luminescent properties for one compound are combined with good mechanical strength from the other compound.

In this paper we present a single-crystal structure study of the  $(\text{Zn,Cd})\text{WO}_4$  system whose end members are well known scintillators.<sup>7–10</sup> All crystals have been grown

using  $\text{Na}_2\text{W}_2\text{O}_7$  as flux.<sup>5</sup> The phase diagram shows no miscibility gap.<sup>11</sup>

Tungstate crystals of composition  $\text{MWO}_4$ , where the ionic radius<sup>12</sup> of the cation  $\text{M}$  is smaller than 1 Å, as is the case for Mg, Mn, Fe, Co, Ni, Zn and Cd, belong to the wolframite structure type<sup>13</sup> with monoclinic unit cells. In the wolframite structure the oxygens can be described as hexagonal close-packed with  $\text{M}$  and  $\text{W}$  ions in octahedral coordination.

The  $\text{MWO}_4$  crystals where  $\text{M}=\text{Ca}$ ,  $\text{Sr}$ ,  $\text{Ba}$ ,  $\text{Pb}$  or  $\text{Eu}$ , are the ones with ionic radius of  $\text{M} > 1$  Å.<sup>14</sup> They belong to the scheelite<sup>15</sup> structure type with tetragonal unit cells. The scheelite structure can be described as a cubic close-packed system consisting of  $\text{M}^{2+}$  and  $\text{WO}_4^{2-}$  ions. Each tungsten ion is coordinated by four oxygen atoms in a tetrahedral arrangement, while  $\text{M}$  ions are coordinated by eight oxygens in a cube.

A summary of some crystallographic data for simple  $\text{MWO}_4$  structures is presented in Table 1. Cuproscheelite,<sup>16</sup>  $\text{CuWO}_4$ , has a structure closely related to the wolframite structure type, but Jahn–Teller distortion of the  $\text{CuO}_6$  octahedron makes the unit cell triclinic.

$\text{ZnWO}_4$  and  $\text{CdWO}_4$  both belong to the wolframite structure type (Table 1). Considering the great technological importance of these compounds, together with the large amount of work being carried out on characterisation of various properties, it is remarkable that accurate single-crystal structure determinations have not yet been done. The need for precise crystal data in order to clarify the mechanisms involved in the electron excitation

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Table 1. AWO<sub>4</sub> crystal structures at room temperature and at ambient pressure.

Wolframites, Space group <i>P2<sub>1</sub>/c</i> , <i>Z</i> =2, monoclinic								
	<i>a</i> /Å	<i>b</i> /Å	<i>c</i> /Å	$\beta$ /°	<i>V</i> /Å <sup>3</sup>	<i>R</i> /%	Ref.	Comments
Mg	4.696(2)	5.683(2)	4.945(3)	90.83(5)	132.0	2.45	18	XDS <sup>a</sup>
Mn	4.830(1)	5.760(1)	4.994(1)	91.14(2)	138.8	3.23	18	XDS <sup>a</sup>
Mn	4.823(0)	5.753(1)	4.992(1)	91.1(0)	138.5	8.9	30	TEM, NDP, MAG
Fe	4.730	5.703	4.952	90.08	133.6	—	31	NDP
Co	4.670(1)	5.687(2)	4.951(2)	90.03	131.5	3.0	31	NDP
Ni	4.599(1)	5.661(1)	4.907(1)	90.00	127.7	5.7	31	NDP
Zn	4.6926(1)	5.7213(1)	4.9281(1)	90.63(0)	132.3	4.5	27	NDP
Cd	5.013(7)	5.090(10)	5.866 (9)	91.5(1)	149.6	7.6	11	XDS, <i>D<sub>m</sub></i> =7.83 g cm <sup>-3b</sup>
Scheelites, Space group <i>I4<sub>1</sub>/a</i> , <i>Z</i> =4, tetragonal								
	<i>a</i> /Å	<i>c</i> /Å	<i>V</i> /Å <sup>3</sup>	<i>R</i> /%	Ref.	Comments		
Ca	5.243(0)	11.374(1)	312.6	2.3	14	XDS		
Sr	5.4168	11.951	350.7	—	32	NDS		
Ba	5.614(3)	12.719(3)	400.9	16	33	XDP		
Ba	5.6134	12.72	400.8	—	32	NDS		
Pb	5.456(2)	12.020(2)	357.2	5.0	34	Other phase exists <sup>c</sup>		
Eu	5.411(1)	11.936(1)	349.4	—	35	No structure known		

XDS, X-Ray diffraction, single crystal. XDP, X-Ray diffraction, powder. NDS, Neutron diffraction, single crystal. NDP, Neutron diffraction, powder. TEM, Transmission electron microscopy. MAG, Magnetic structure.

<sup>a</sup>Crystal grown from Na<sub>2</sub>W<sub>2</sub>O<sub>7</sub> flux. <sup>b</sup>Crystal grown from NaF flux. <sup>c</sup>Raspite *P2<sub>1</sub> a*.<sup>36</sup>

relaxation and energy transfer to scintillation centres has prompted the work presented in this paper. The excitation experiments, performed at the synchrotron sources MAX 1 in Lund, Sweden, and DESY at HASYLAB in Hamburg, Germany, are presented in separate<sup>17</sup> and in forthcoming papers.

The Zn<sub>1-x</sub>Cd<sub>x</sub>WO<sub>4</sub> system has previously been studied by Morell *et al.*<sup>11</sup> They determined the unit-cell parameters using powder data. Macavei and Shulz<sup>18</sup> have done a high-pressure single-crystal study up to 8.2 GPa of several tungstates including CdWO<sub>4</sub>.

Some mixed A<sub>1-x</sub>B<sub>x</sub>WO<sub>4</sub> systems have also been investigated.<sup>19,20</sup> In this paper we present the first elaborate crystallographic structure investigation of an A<sub>1-x</sub>B<sub>x</sub>WO<sub>4</sub> system using single-crystal data.

## Experimental

Powders of Zn<sub>1-x</sub>Cd<sub>x</sub>WO<sub>4</sub> with *x*=0.0, 0.1, 0.4, 0.6, 0.9 and 1.0 were prepared from stoichiometric amounts of ZnO (Merck, min 99%), CdCO<sub>3</sub> (Kebo, pa) and WO<sub>3</sub> (Johnson & Matthey, 99.7%). The powders were

annealed at 773 K for 3 h and then sintered at 1273 K for 10 h. The products were examined by powder diffraction, using a Guinier-Hägg camera with monochromatised Cu K<sub>α</sub> radiation. Analysis using PCPIRUM<sup>21</sup> verified the results by Morell *et al.*<sup>11</sup>

Single crystals of ZnWO<sub>4</sub>, CdWO<sub>4</sub> and Zn<sub>x</sub>Cd<sub>1-x</sub>WO<sub>4</sub> (Table 2) were flux grown in Pt crucibles. Starting materials were ZnO and CdCO<sub>3</sub> and equimolar amounts of WO<sub>3</sub> and Na<sub>2</sub>WO<sub>4</sub> (Johnson & Matthey, 95%). The M<sup>2+</sup> molar content (Zn + Cd) was half of the W content. When heated to about 1000 K, Na<sub>2</sub>WO<sub>4</sub> and WO<sub>3</sub> formed the flux, Na<sub>2</sub>W<sub>2</sub>O<sub>7</sub>. Each batch was heated to 1523 K in 10 h. The melt was then left for 10 h after which the temperature was decreased by 2.5 K h<sup>-1</sup> down to 973 K and then to room temperature through self-cooling. The flux was removed, preferably mechanically, and then dissolved in concentrated NaOH to convert it to water-soluble Na<sub>2</sub>WO<sub>4</sub>. Colourless crystals up to 1 cm in length were grown. Scanning electron microscopy electron probe microsond analysis (SEM-EPMA) using either energy dispersive spectroscopy (EDS) or wavelength dispersive spectroscopy (WDS) was used to detect

Table 2. Unit cell parameters for Zn<sub>1-x</sub>Cd<sub>x</sub>WO<sub>4</sub> from 25 reflections.

Flux <sup>a</sup> <i>x</i>	0	0.10	0.30	0.50	0.70	0.90	1.00
	0	0.04(2)	0.11(2)	0.60(2)	0.884(14)	0.96(2)	1
<i>a</i> /Å	4.6986(8)	4.7267(8)	4.7472(7)	4.9192(11)	5.0053(13)	5.0290(6)	5.0400(8)
<i>b</i> /Å	5.7293(8)	5.7491(6)	5.7670(6)	5.8430(15)	5.8615(7)	5.8692(3)	5.8701(6)
<i>c</i> /Å	4.9367(11)	4.9487(10)	4.9629(6)	5.0301(22)	5.0664(7)	5.0741(18)	5.0841(7)
$\beta$ /°	90.615(25)	90.790(22)	90.862(13)	91.505(23)	91.467(21)	91.519(16)	91.476(19)
<i>V</i> /Å <sup>3</sup>	132.89(4)	134.46(7)	135.85(3)	144.53(8)	148.59(5)	149.71(6)	150.37(4)

<sup>a</sup>Start composition in the flux defined as [Cd]/([Cd] + [Zn]).

any impurities and to measure the composition of the crystals. No impurities were found (the detection limit for  $\text{Na}^+$  is about 0.1%). Different colours of both  $\text{ZnWO}_4$  and  $\text{CdWO}_4$  have often been reported in the literature.<sup>5,11,22</sup> This seems to be an effect of either impurities or the growth technique used. The crystals in this study are all colourless.

Crystal data pertinent to the intensity data collection and least-square refinements are given in Table 2. Unit cell parameters were refined using LATCON.<sup>23</sup> Data reduction was made with XTAL<sup>24</sup> programs including absorption correction using ABSORB<sup>25</sup> and box-shaped crystals with six faces. The structures were refined in space group  $P2_1/c$  using SHELXL-93.<sup>26</sup> All structures were refined with anisotropic displacement parameters for all atoms. Starting atomic positions in the refinements were taken from the literature.<sup>11,27</sup> The Cd occupancy,  $x$ , was refined restraining both Zn and Cd to the same position with full total occupancy. The same anisotropic thermal parameters were used for both Cd and Zn. The occupancy,  $x$ , was also confirmed with SEM-EPMA

measurements using EDS. The Zn/Cd ratio deviated substantially from that of the starting materials in the flux (Fig. 1).

The highest rest electron density peaks ( $\Delta\rho_{\text{max}}$ , Table 3) are always located 0.6–0.8 Å from the tungstate ion, and there are usually some ripples close to the Zn/Cd ion. Atomic parameters can be found in Table 4. Selected bond distances and angles are given in Table 5. Lists of all structure factors, anisotropic displacement parameters and figures similar to Fig. 2 for all structures can be obtained from the authors.

### Description of the structure

The unit cell with coordination for Zn/Cd and W is shown in Fig. 2. A polyhedral drawing of  $\text{CdWO}_4$  (the wolframite structure type) is shown in Fig. 3. The structure can be described as a chain structure with interconnected zigzag chains of  $\text{MO}_6$  ( $\text{M}=\text{Cd}/\text{Zn}$ ) octahedra and  $\text{WO}_6$  octahedra, respectively. Both types of chains run parallel to  $c$ . All chains of  $\text{MO}_6$  octahedra are corner-

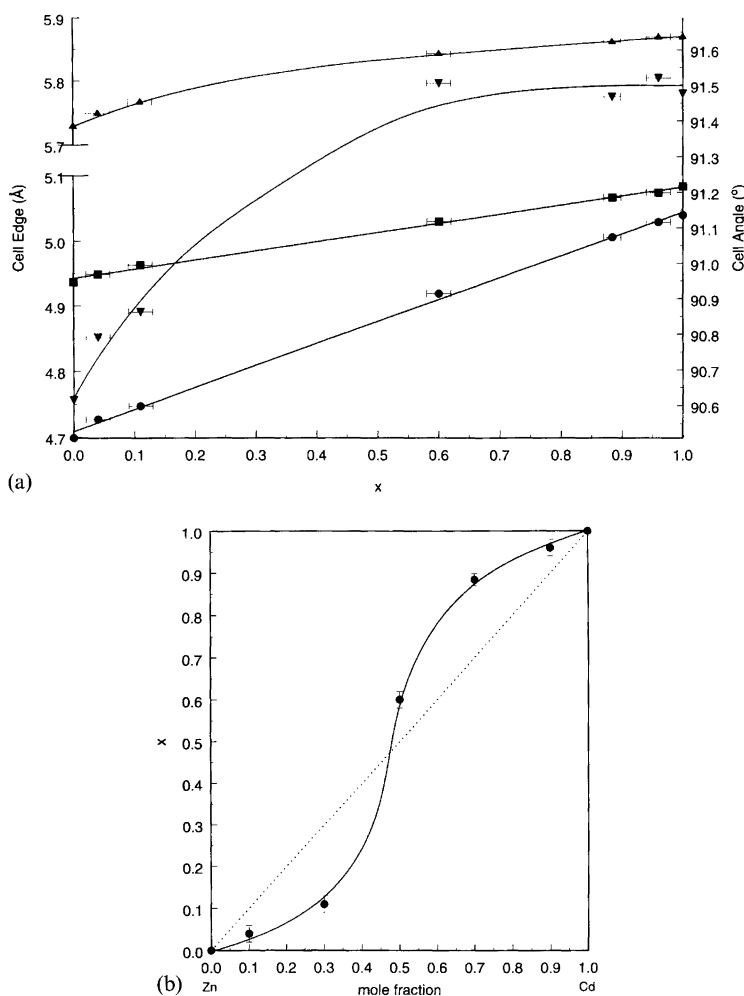


Fig. 1. (a) Cell parameters vs.  $x$  in  $\text{Zn}_{1-x}\text{Cd}_x\text{WO}_4$ . Error bars are  $\pm 1$  e.s.d., error bars in unit cell parameters are within the dots,  $\bullet$ ,  $a$ ;  $\blacktriangle$ ,  $b$ ;  $\blacksquare$ ,  $c$ ;  $\blacktriangledown$ ,  $\beta$ . (b) Mole fraction =  $[\text{Cd}] / ([\text{Cd}] + [\text{Zn}])$  in starting material vs.  $x$  in  $\text{Zn}_{1-x}\text{Cd}_x\text{WO}_4$ . The dotted line,  $x = \text{mole fraction}$ , is for guidance only. Error bars are  $\pm 1$  e.s.d., error bars for the mole fraction are within the dots.

Table 3. Crystal data and refinement parameters for  $Zn_{1-x}Cd_xWO_4$  from Enraf-Nonius CAD-4 intensity data.

x in $Zn_{1-x}Cd_xWO_4$	0	0.04	0.11	0.60	0.884	0.96	1
$D_x/g\text{ cm}^{-3}$	7.828	7.852	8.002	7.738	7.735	7.866	7.957
$\mu/\text{mm}^{-1}$	52.059	51.347	50.622	47.395	45.908	45.383	45.104
Crystal size/ $10^6\text{ mm}^3$	$5 \times 3 \times 10$	$5 \times 5 \times 8$	$9 \times 3 \times 13$	$9 \times 8 \times 24$	$9 \times 3 \times 8$	$6 \times 9 \times 16$	$11 \times 2 \times 5$
Grid, absorption corr.	$8 \times 6 \times 12$	$8 \times 8 \times 16$	$8 \times 6 \times 24$	$8 \times 8 \times 24$	$12 \times 6 \times 8$	$6 \times 8 \times 16$	$12 \times 6 \times 8$
Transmission $T_{\min}$	0.1025	0.0904	0.0280	0.0236	0.0671	0.0312	0.1008
$T_{\max}$	0.2238	0.1795	0.2005	0.0921	0.2445	0.1226	0.4027
Scan width/ $^\circ$ ( $a/^\circ$ )	0.70	0.80	0.60	0.80	0.80	0.80	0.70
$\Delta\omega = a + b \times \tan \theta$ ( $b/^\circ$ )	0.34	0.50	0.34	0.50	0.50	0.50	0.34
No. of reflections							
Measured	1220	1228	1241	1334	1371	1383	1383
Unique	583	588	593	637	656	661	661
Observed, $I > 2\sigma(I)$	538	563	581	611	623	638	603
$R_{\text{int}}$	0.0419	0.0252	0.0668	0.0616	0.0291	0.0518	0.0342
Least-squares weight							
$w = [\sigma^2(F_o^2) + (aP)^2]^{-1}$							
where $P = (F_o^2 + 2F_c^2)/3$ (a)	0.044	0.0393	0.0510	0.0609	0.0499	0.0593	0.0430
R	0.0335	0.0264	0.0376	0.0374	0.0297	0.039	0.0317
$R_{\text{obs}}[F, I > 2\sigma(I)]$	0.0293	0.0238	0.0369	0.0360	0.0276	0.0376	0.0254
$R_w(F^2)$	0.0706	0.0608	0.0816	0.0995	0.0676	0.1035	0.0657
S	1.126	1.131	1.157	1.212	1.068	1.158	1.065
No. of parameters refined	30	31	31	31	31	31	30
$\Delta\rho_{\text{max}}/e\text{ \AA}^{-3}$	4.467	3.904	6.382	4.187	5.468	5.885	4.680
$\Delta\rho_{\text{min}}/e\text{ \AA}^{-3}$	-4.531	-3.695	-6.520	-4.569	-3.948	-5.009	-2.469
Extinction correction <sup>26</sup>	0.019(2)	0.008(2)	0.034(4)	0.017(3)	0.031(3)	0.076(6)	0.043(2)
Space group	$P2_1/c$ , (No. 13) $Z=2$						
No. of faces	6, {100}, {010} and {001}						
Absorption correction	Numerical integration						
Radiation	0.710 69 Å (Mo K $\alpha$ )						
Monochromator	Graphite						
Maximum scan time	120 s						
Scan type	$\omega/2\theta$ scan						
$\theta$ -range for data collection	$3 < \theta < 35^\circ$						
Refinement on	$F^2$						
$(\Delta/\rho)_{\text{max}}$	< 0.001						

Table 4. Atomic positional parameters and  $U_{\text{eq}}$  for  $Zn_{1-x}Cd_xWO_4$ . Parameters for structures with  $x=0.04(2)$  and  $x=0.96(2)$  are omitted for clarity.

Wyckoff positions			$ZnWO_4$ ( $x=0$ )	$x=0.11(2)$	$x=0.60(2)$	$x=0.884(14)$	$CdWO_4$
W	2(e)	y	0.18258(6)	0.18172(4)	0.17981(5)	0.17879(4)	0.17855(4)
		$U_{\text{eq}}/\text{\AA}^2$	0.00456(14)	0.0079(2)	0.0080(2)	0.00600(14)	0.00523(12)
Zn/Cd	2(f)	y	0.6840(2)	0.68590(13)	0.69470(14)	0.69664(10)	0.69729(9)
		$U_{\text{eq}}/\text{\AA}^2$	0.0078(2)	0.0107(6)	0.0095(4)	0.0084(3)	0.00820(13)
O1	4(g)	x	0.2169(10)	0.2137(8)	0.2069(9)	0.2031(7)	0.2018(8)
		y	0.1051(9)	0.1042(7)	0.0983(9)	0.0965(6)	0.0955(7)
		z	-0.0637(9)	-0.0608(7)	-0.0534(10)	-0.0522(7)	-0.0496(8)
		$U_{\text{eq}}/\text{\AA}^2$	0.0074(7)	0.0105(6)	0.0115(8)	0.0085(6)	0.0083(7)
O2	4(g)	x	0.2565(10)	0.2537(8)	0.2444(11)	0.2425(7)	0.2420(8)
		y	0.3777(8)	0.3739(8)	0.3743(10)	0.3725(7)	0.3703(7)
		z	0.3996(10)	0.3983(9)	0.3905(11)	0.3856(7)	0.3839(8)
		$U_{\text{eq}}/\text{\AA}^2$	0.0074(7)	0.0119(6)	0.0141(9)	0.0105(6)	0.0098(7)

<sup>a</sup> 2(e), (0, y, 1/4); 2(f), (1/2, y, 1/4).

linked to four chains of  $WO_6$  octahedra and *vice versa*. The arrangement of the chains gives open channels in the structure, also running parallel to  $c$  (Fig. 3).

The W–O bond distances in the  $WO_6$  octahedra are

constant through all compositions while the W–W–W angle in the  $WO_6$  chains increases from 99.43(2) to 100.98(2) $^\circ$  when going from  $ZnWO_4$  to  $CdWO_4$ . The shortest W–W distance increases from 3.2357(6) to

Table 5. Selected atomic distances (in Å) and angles (in °) for  $Zn_{1-x}Cd_xWO_4$ .<sup>a,b</sup>

	ZnWO <sub>4</sub>	x=0.11	x=0.60	x=0.884	CdWO <sub>4</sub>
W-M <sup>ii</sup>	3.4744(9)	3.4924(5)	3.5480(11)	3.5903(8)	3.6074(7)
W <sup>i</sup> -M <sup>ii</sup>	3.5100(9)	3.5428(5)	3.6384(11)	3.6796(8)	3.6978(7)
W-M <sup>xiii</sup>	3.6983(10)	3.7162(7)	3.7529(9)	3.7751(7)	3.7857(6)
W-M	3.7113(10)	3.7534(7)	3.8859(10)	3.9343(7)	3.9526(6)
W-W <sup>iv</sup>	3.2357 (6)	3.2482(4)	3.2773(10)	3.2881(4)	3.2949(5)
M-M <sup>ii</sup>	3.2467(15)	3.2795(10)	3.3914(14)	3.4253(8)	3.4390(8)
W-O <sub>2</sub>	1.797(5)	1.787(4)	1.786(5)	1.787(4)	1.782(4)
W-O <sub>1</sub>	1.915(5)	1.912(4)	1.917(5)	1.921(3)	1.917(4)
W-O <sub>1</sub> <sup>iv</sup>	2.140(5)	2.145(4)	2.146(5)	2.142(3)	2.146(4)
M-O <sub>1</sub> <sup>ii</sup>	2.025(5)	2.057(4)	2.143(5)	2.182(3)	2.203(4)
M-O <sub>2</sub> <sup>x</sup>	2.094(5)	2.115(5)	2.213(6)	2.261(4)	2.278(4)
M-O <sub>2</sub>	2.226(5)	2.274(5)	2.374(5)	2.406(4)	2.426(4)
W <sup>iv</sup> -W-W <sup>vi</sup>	99.43(2)	99.63(2)	100.25(3)	100.79(2)	100.98(2)
M <sup>xiv</sup> -M-M <sup>ii</sup>	98.98(6)	98.34(4)	95.74(5)	95.40(3)	95.32(3)
W-M <sup>ii</sup> -W <sup>xv</sup>	154.59(4)	154.75(3)	156.14(3)	156.53(2)	156.69(2)
O <sup>ii</sup> -M-O <sup>vii</sup>	106.7(3)	107.9(2)	111.3(3)	112.5(2)	113.0(2)
O <sup>viii</sup> -M-O <sup>xi</sup>	82.1(2)	81.81(15)	78.8(2)	78.07(12)	78.03(13)
O <sup>vii</sup> -M-O <sub>2</sub>	164.5(2)	163.7(2)	161.9(2)	161.13(14)	160.66(14)
O <sub>1</sub> -W-O <sub>2</sub> <sup>v</sup>	99.9(2)	100.1(2)	102.1(2)	102.8(2)	103.2(2)
O <sub>1</sub> -W-O <sub>1</sub> <sup>iv</sup>	74.3(2)	73.8(2)	72.6(2)	72.1(2)	71.8(2)
O <sub>1</sub> -W-O <sub>1</sub> <sup>v</sup>	153.2(3)	153.0(3)	151.3(3)	150.9(2)	150.5(2)

<sup>a</sup>Parameters for structures with  $x=0.04(2)$  and  $x=0.96(2)$  are omitted for clarity. <sup>b</sup>Symmetry codes used, <sup>i</sup> $x+1, y, z$ ; <sup>ii</sup> $x, -y+1, z+1/2$ ; <sup>iii</sup> $x+1, -y+1, z+1/2$ ; <sup>iv</sup> $-x, -y, -z$ ; <sup>v</sup> $-x, y, -z+1/2$ ; <sup>vi</sup> $x, -y, z+1/2$ ; <sup>vii</sup> $-x+1, -y+1, -z$ ; <sup>viii</sup> $-x+1, y, -z+1/2$ ; <sup>ix</sup> $x, y, z+1$ ; <sup>x</sup> $x, -y+1, z-1/2$ ; <sup>xi</sup> $-x+1, -y+1, -z+1$ ; <sup>xii</sup> $-x+1, y, -z+3/2$ ; <sup>xiii</sup> $x, y-1, z+1$ ; <sup>xiv</sup> $x, -y+1, z-1/2$ ; <sup>xv</sup> $x+1, y, z+1$ .

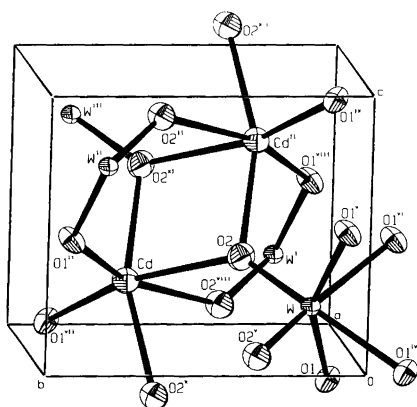


Fig. 2. Crystal structure of CdWO<sub>4</sub>. Atoms are displayed as displacement ellipsoids at a probability level of 90%. Symmetry codes are from Table 5.

3.2949(5) Å. The average shift in the O-W-O angles in the WO<sub>6</sub> octahedra is about 3°; some are increasing and others decreasing.

In the MO<sub>6</sub> octahedra the M-O distances increase by approximately 0.2 Å. This is in agreement with the increasing ionic radius<sup>28</sup> of six-coordinated Zn<sup>2+</sup> and Cd<sup>2+</sup>, 0.74 and 0.95 Å, respectively. Consequently when going from Zn to Cd the closest M-M distance increases from 3.2467(15) to 3.4390(8) Å, with the M-M-M angle in the MO<sub>6</sub> chain decreasing from 98.98(6) to 95.32(3)°. The W-M distance increases from 3.4744(9) to 3.6074(7) Å and the W-M-W angle from 154.59(4) to 156.69(2)°. There are four different W-M distances shorter than 4 Å in the structure (Table 5).

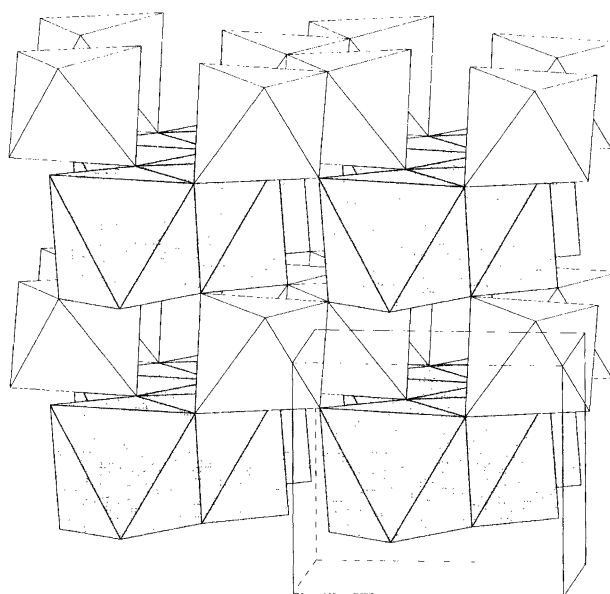


Fig. 3. The wolframite structure (CdWO<sub>4</sub>) viewed along  $c$ . The white octahedra represent WO<sub>6</sub> and the grey octahedra represent MO<sub>6</sub>.

## Discussion

As can be seen from Fig. 1a there are linear relationships between composition and unit cell parameters  $a$  and  $c$ , i.e. Vegard's law is obeyed. For  $b$  and the monoclinic angle  $\beta$ , however, there is no such relation. The linear correlation coefficients are 0.999, 0.985 and 0.998 for  $a$ ,  $b$  and  $c$ , respectively. In a powder diffraction study

Morell *et al.*<sup>11</sup> found a linear relation between  $b$  and composition, although no data are given in the paper.

The structure of the end member  $\text{ZnWO}_4$  is in good agreement with a neutron powder study by Schofield *et al.*<sup>27</sup> Their Rietveld refinements result in a very accurate structure solution, although they do not use a pure powder. The displacement  $d$  of the Zn and W atoms from the centre of the oxygen octahedra (Fig. 2) may be commented on. The centre of the octahedron is at the same  $x$  and  $z$  coordinate as the W and the Zn ion. The displacement of the W and the Zn ion from this centre is exactly along  $b$ , and can be calculated as the difference:

$$d_{\text{Zn}} = b[y(\text{Zn}/\text{Cd}) - \{y(\text{O1}^{\text{ii}}) + y(\text{O2})\}/2]$$

$$d_{\text{W}} = b[y(\text{W}) - \{y(\text{O2}) + y(\text{O1}^{\text{vi}})\}/2]$$

In our study these displacements are 0.273(7) and 0.265(5) Å for Zn and W, respectively. The corresponding values given in the study by Schofield *et al.*<sup>27</sup> is 0.29 Å for Zn and 0.32 Å for W. Analysing their data we found the correct equivalent displacements in their study to be 0.269(3) and 0.263(3) Å for Zn and W, respectively.

The crystal structure of the other end member,  $\text{CdWO}_4$ , conforms to another single-crystal X-ray study done by Morell *et al.*<sup>11</sup> The  $R$ -value in that study is as high as 0.076 for 696 reflections. In this study the corresponding  $R$ -value is 0.032 with more realistic e.s.d. values. Calculating the displacement of the central metal ions in the octahedra, in the same way as described above for  $\text{ZnWO}_4$ , results in 0.353(9) Å for Cd and 0.244(6) Å for W. Comparison with the values for  $\text{ZnWO}_4$  shows that the displacement of the central atom in the octahedra increases for M and decreases for W, when going from  $\text{ZnWO}_4$  to  $\text{CdWO}_4$ .

The structural changes in  $\text{Zn}_{1-x}\text{Cd}_x\text{WO}_4$  can be compared with the effects of an increased pressure on the wolframite structure, as studied by Macavei *et al.*<sup>18</sup> According to them an increased pressure would eventually give a phase transition into the scheelite structure. In the  $\text{Zn}_{1-x}\text{Cd}_x\text{WO}_4$  system, with increasing  $x$ , the M-W distance projected on  $b$  decreases from 0.764(1) Å in  $\text{ZnWO}_4$  to 0.7288(7) Å in  $\text{CdWO}_4$ . This distance is zero in the scheelite structure. Figure 4 shows the change in the  $y$  coordinate for the W and Zn/Cd ions with increasing  $x$ . M is moving towards the corresponding divalent cation position of the scheelite structure, but the phase transition is counteracted by the W movement. The net result is that  $\text{CdWO}_4$  is more closely related to the scheelite structure than is  $\text{ZnWO}_4$ .

Various criteria have been proposed to describe a distorted octahedron. For an octahedron there are two main types of distortions. Extension or compression along the  $S_6$  axis is called trigonal distortion, and extension or compression along a  $C_4$  axis is called tetragonal distortion. The main difference between these types is that for a trigonal distortion the bond lengths remain equal while the angles deviate from 90°, whereas for a

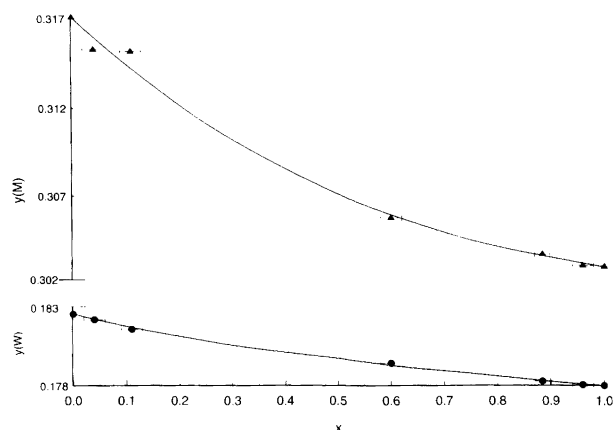


Fig. 4. W and M movements along the  $b$  axis vs.  $x$  in  $\text{Zn}_{1-x}\text{Cd}_x\text{WO}_4$ . Error bars are  $\pm 1$  e.s.d., error bars in the  $y$ -coordinate are within the dots. ●, W; ▲, M.

tetragonal distortion the angles remain at 90° while the bond lengths are unequal. In this work we use the octahedral variance and the mean octahedral elongation<sup>29</sup> to describe the distortion of octahedra. These parameters are defined as

Octahedral angle variance shape:

$$\sigma_{\theta(\text{oct})}^2 = \sum_{i=1}^{12} (\theta_i - 90^\circ)^2/11$$

Mean octahedral elongation:

$$\langle \lambda_{\text{oct}} \rangle = \sum_{i=1}^6 (l_i/l_0)^2/6$$

For a perfect octahedron the mean octahedral elongation is 1 and the octahedral angle variance is 0. From Fig. 5 it can be seen that the octahedral variance and the octahedral elongation increase for both the W and M octahedra with increasing  $x$ . From this one can conclude that the distortion from a perfect octahedron increase when the mean ionic radius of the cation in

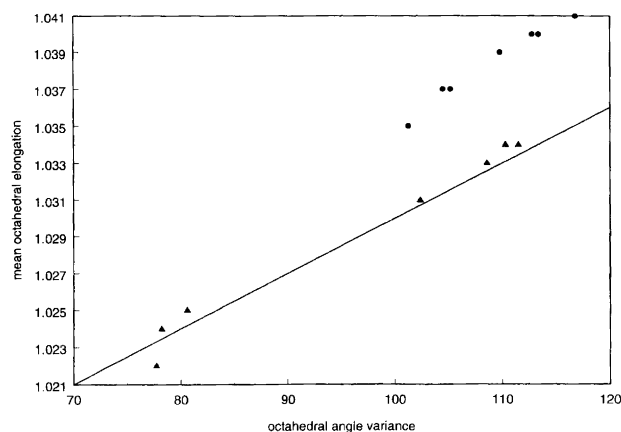


Fig. 5. Mean quadratic elongation vs. octahedral variance for W and M octahedra. The line is calculated from values given by Robinson *et al.*<sup>29</sup> The  $y$ -axis intercept is at one when  $x$  is zero (as for a perfect octahedron). ▲,  $\text{MO}_6$ ; ●,  $\text{WO}_6$ .

$Zn_{1-x}Cd_xWO_4$  increases. The distortion is not trigonal or tetragonal: it involves changes in both bond length and angles. Comparing the results with Robinson *et al.*<sup>29</sup> it is seen that the  $WO_6$  octahedron series deviates substantially from the trendline. The reason for the increased distortion of the  $WO_6$  octahedron is mainly due to the changes in the O–W–O angles for increasing  $x$  values. The W–O distances are almost constant.

*Acknowledgements.* We thank Prof. Jörgen Albertsson for well informed advice. Financial support from the Swedish Technical Science Research Council (TFR) is also gratefully acknowledged.

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Received April 27, 1999.