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## A Structural Study of Cadmium Yttrium Molybdate $\text{CdY}_4\text{Mo}_3\text{O}_{16}$

BY JEAN BERNARD BOURDET,\* RAYMOND CHEVALIER, JEAN PAUL FOURNIER,  
ROBERT KOHLMULLER AND JEAN OMALY

*UER Sciences Exactes et Naturelles, BP No. 45, 63170 Aubière, France*

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### Abstract

$\text{CdY}_4\text{Mo}_3\text{O}_{16}$  crystallizes in the cubic space group  $Pn\bar{3}n$  with  $a = 10.688(2) \text{ \AA}$ ,  $Z = 4$ ,  $d_c = 4.83$ ,  $d_m = 4.87 \text{ Mg m}^{-3}$ . The final  $R$  value is 0.04 for 173 independent reflexions.  $\text{Mo}^{6+}$  ions are in 12( $d$ ) sites;  $\text{Y}^{3+}$  is partly in pure 12( $e$ ) sites and the remainder is statistically distributed with  $\text{Cd}^{2+}$  in 8( $c$ ) sites. The  $\text{O}^{2-}$  ions are in 48( $i$ ) and 16( $f$ ) sites.

### Introduction

The study of  $\text{Ln}_2\text{MoO}_6\text{--CdMoO}_4$  systems has revealed that by heating to a temperature of between 1173 and 1623 K,  $\text{CdLn}_4\text{Mo}_3\text{O}_{16}$  phases are obtained for  $66\% < \text{Ln}_2\text{MoO}_6 < 68\%$ . The study of these phases by crystal luminescence, IR spectroscopy and powder X-ray crystallography has shown that their structure is derived from a fluorite structure and that  $\text{CdTm}_4\text{Mo}_3\text{O}_{16}$  in particular can be described in space group  $Pn\bar{3}n$ , with an  $R$  value of 0.03 in the case of a powder sample (Faurie & Kohlmuller, 1971). Significant results, which are still being studied, relate to a double doping of the  $\text{CdY}_4\text{Mo}_3\text{O}_{16}$  phase and its properties, and these have led us to produce  $\text{CdY}_4\text{Mo}_3\text{O}_{16}$  single crystals in order to determine their structure.

\* Present address: Université des Sciences et de la Technologie Houari Boumediene Bab Ezzouar, BP No. 9, Dar El Beida, Algeria.

### Experimental

#### (a) Crystal preparation

The synthesis of  $\text{CdLn}_4\text{Mo}_3\text{O}_{16}$ -phase single crystals is difficult because decomposition occurs at about 1473 K. Furthermore, in the case of  $\text{CdY}_4\text{Mo}_3\text{O}_{16}$ , differential thermal analysis has revealed the existence of a completely reversible thermal decomposition at 1315 K which is probably of structural origin.

These results led us to adopt a maximum preparation temperature of 1273 K. In order to prepare doped crystals, the melt should contain the smallest possible number of extraneous elements.

After experimentation, this led us to select a  $4\text{CdO--}8\text{CdCl}_2$  sublimable flux for 1 mol of  $\text{CdY}_4\text{Mo}_3\text{O}_{16}$ . This sublimable flux did not, however, permit formation of the molybdate without the presence of a secondary reaction. In an open tube, evaporation is too rapid to allow the formation of single crystals.

In a vacuum-sealed gold tube, slowly cooled from 1173 to 923 K ( $3 \text{ K h}^{-1}$ ) no precipitation was observed from the flux. Only under the following conditions was it possible to obtain single crystals. The mix was placed in a gold crucible, enclosed in a sealed low-vacuum quartz tube. The cadmium oxide and chloride vapour reacts with the upper part of the tube, forming friable cadmium chlorosilicate, which cracks the tube, causing elimination of the excess melt. The crucible remains, containing only crystals, which are several tenths of a millimeter in size. They show two crystallographic forms, one cubic, the other of a more complex

morphology. Our study concentrated initially on the cubic crystals.

### (b) X-ray data

The crystallographic study was carried out on the {100} face of a crystal of edge 0.104 mm; the linear absorption coefficient  $\mu = 230 \text{ cm}^{-1}$ .

Examination by means of Laue and precession methods showed that the crystal was of the  $m\bar{3}m$  Laue group. The conditions limiting possible reflections were  $hhl$ ,  $l = 2n$  and  $0kl$ ,  $k + l = 2n$ . Such conditions are only compatible with the space group  $Pn\bar{3}n$ .

### (c) Structure determination and refinement

1046 reflexions were recorded on a Nonius CAD-4 diffractometer up to  $\theta = 45^\circ$ . Only 173 of these had non-zero readings; this low proportion can be explained by the presence of a fluorite-type sublattice one-eighth the size of the true lattice. This results from an order between cations and oxygen displacements from the ideal fluorite positions.

The measured intensities were corrected for Lorentz, polarization and absorption factors (Ahmed, 1974). The scattering factors used were those of *International Tables for X-ray Crystallography* (1968). Dispersion corrections for the atomic scattering factors of Cd, Y and Mo were introduced at the beginning of the refinement. The value  $Z = 4$  led us to start with 4 Cd, 16 Y, 12 Mo and 64 O in the cell. This being close to the fluorite structure, we placed Mo in site 12(*d*) and tested a number of hypotheses concerned with the distribution of the Y and Cd atoms between sites 12(*e*) and 8(*c*). We put the 64 O atoms in sites 48(*i*) and 16(*f*). The refinements for the distribution of the Cd and Y atoms in sites 12(*e*) and 8(*c*) were carried out with average scattering factors which were calculated for each of the hypothetical distributions. The lowest factor,  $R = 0.051$ , was obtained when  $Y^{3+}$  was postulated to be in site 12(*e*) and also in site 8(*c*) associated with four  $Cd^{2+}$ .

A final refinement was carried out by introducing anisotropic thermal factors in accordance with the symmetry rules of Peterse & Palm (1966) for the Cd, Y and Mo atoms. A reliability factor of 0.04\* was obtained for the atomic positional coordinates and the thermal vibration factors shown in Table 1.

The similarity of the  $R$  values obtained for different distributions of the  $Y^{3+}$  and  $Cd^{2+}$  ions in sites 12(*e*) and 8(*c*) suggested that a careful examination of the distances observed in this structure was justified. Thus,

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36898 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

we calculated the average valencies of the ions in the different sites based on the observed distances, using the work of Brown & Wu (1976).

Table 2 shows the various  $M-O$  distances found in the hypothetical distribution. In addition, their average size is compared with those calculated using the ionic-radius tables of Shannon & Prewitt (1969).

Table 3 summarizes the average valencies found in each site of the structure. These were calculated using

Table 1. Atomic coordinates ( $\times 10^4$ ) and isotropic or [for Mo, Y, (Cd, Y)] equivalent isotropic thermal parameters

Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> or <i>B</i> <sub>eq</sub> ( $\text{\AA}^2$ )	
O(1)	48( <i>i</i> )	3280 (15)	874 (15)	8645 (13)	0.5 (2)
O(2)	16( <i>f</i> )	1196 (12)	1196 (12)	1196 (12)	0.3 (2)
Mo	12( <i>d</i> )	0	$\frac{1}{2}$	$\frac{1}{2}$	0.5 (1)
Y	12( <i>e</i> )	139 (3)	$\frac{1}{2}$	$\frac{1}{2}$	0.6 (1)
(Cd, Y)	8( <i>c</i> )	0	0	0	0.5 (1)

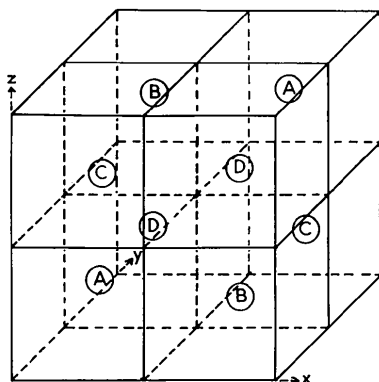
Table 2. Observed ( $d_{\text{obs}}$ ), mean ( $d_m$ ) and calculated ( $d_{\text{cal}}$ )  $M-O$  interatomic distances ( $\text{\AA}$ )

	$d_{\text{obs}}$	$d_m$	$d_{\text{cal}}$
Mo—O(1 <sup>i</sup> )	1.75 (3)	1.75 (3)	1.78
Mo—O(1 <sup>ii</sup> , I)			
Mo—O(1 <sup>iii</sup> , II)			
Mo—O(1 <sup>iv</sup> , III)			
Y—O(2 <sup>v</sup> )	2.27 (2)	2.38 (2)	2.38
Y—O(2 <sup>vi</sup> )			
Y—O(2 <sup>vii</sup> )			
Y—O(2 <sup>viii</sup> )			
Y—O(1 <sup>ix</sup> , IV)	2.50 (2)	2.44 (3)	2.41
Y—O(1 <sup>x</sup> , IV)			
Y—O(1 <sup>xi</sup> , IV)			
Y—O(1 <sup>xii</sup> , IV)	2.22 (2)	2.44 (3)	2.41
(Cd, Y)—O(2 <sup>x</sup> )			
(Cd, Y)—O(2 <sup>xiii</sup> )			
(Cd, Y)—O(1 <sup>xiv</sup> , V)			
(Cd, Y)—O(1 <sup>xv</sup> , VI)	2.52 (3)	2.44 (3)	2.41
(Cd, Y)—O(1 <sup>xvi</sup> , VII)			
(Cd, Y)—O(1 <sup>xvii</sup> , VIII)			
(Cd, Y)—O(1 <sup>xviii</sup> , IX)			
(Cd, Y)—O(1 <sup>xix</sup> , IX)	2.52 (3)	2.44 (3)	2.41
(Cd, Y)—O(1 <sup>xx</sup> , IV)			

#### Symmetry code

(i)	$y, z, x$	(x)	$z, \frac{1}{2} - x, \frac{1}{2} - y$
(ii)	$y, 1 - z, 1 - x$	(xi)	$z, \frac{1}{2} - y, x$
(iii)	$y, \frac{1}{2} + x, z$	(xii)	$z, y, \frac{1}{2} - x$
(iv)	$y, x, \frac{1}{2} + z$	(xiii)	$\bar{x}, \bar{y}, \bar{z}$
(v)	$x, y, z$	(xiv)	$\frac{1}{2} + x, \bar{z}, \bar{y}$
(vi)	$x, \frac{1}{2} - y, \frac{1}{2} - z$	(xv)	$\bar{z}, \bar{y}, \frac{1}{2} + x$
(vii)	$x, \frac{1}{2} - z, y$	(xvi)	$\frac{1}{2} - x, z, y$
(viii)	$x, z, \frac{1}{2} - y$	(xvii)	$y, \frac{1}{2} - x, z$
(ix)	$z, x, y$		

(I)	$x, y + 1, z$	(VI)	$x, y - 1, z + 1$
(II)	$x, y, z + 1$	(VII)	$x + 1, y, z - 1$
(III)	$x, y + 1, z - 1$	(VIII)	$x, y - 1, z$
(IV)	$x - 1, y, z$	(IX)	$x, y, z - 1$
(V)	$x - 1, y + 1, z$		


 Fig. 1. The eight sublattices of edge  $a/2$ .

the formulae  $S_i = (R_i/R_1)^{-N}$  and  $V_i = \sum S_i$ , where  $S_i$  is the bond valency,  $R_i$  the bond length,  $R_1$  the length for a valency of 1, and  $N$  the average atom-dependence coefficient.

The  $R_1$  and  $N$  values used were those proposed by Brown & Wu (1976). These are given in Table 3.

From an examination of Tables 2 and 3 we conclude that the ion distribution indicated in Table 1, corresponding to the lowest  $R$  value, is appropriate.

On the other hand, we could evaluate the sum of the cation valencies in the structure as  $V_i = 130$  instead of 128 for the 64 O atoms, which would seem a good approximation. Furthermore, this evaluation would give a valency of 2.1 for the O atoms in site 16(*f*) and a valency of 2 for those in site 48(*i*).

#### (d) Description and discussion of the structure

The structure of  $\text{CdY}_4\text{Mo}_3\text{O}_{16}$  can thus be represented as a cube formed by eight sublattices with an

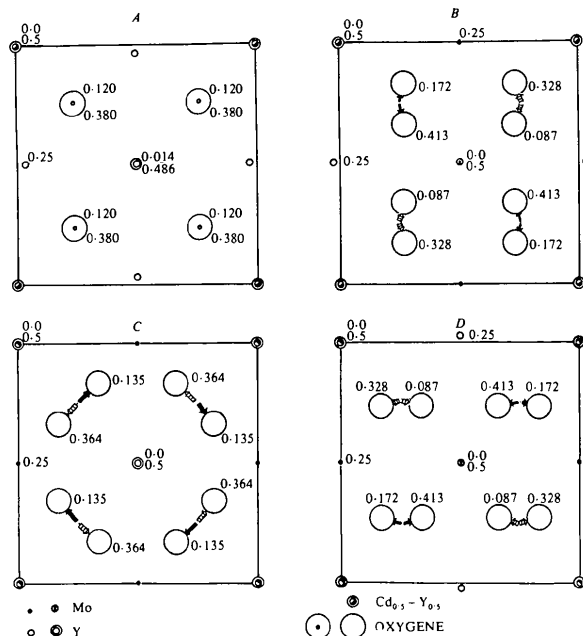


Fig. 2. Projection on the  $xOy$  plane of the four sublattices with an edge of  $a/2$ . Coordinates are expressed relative to the real cell. The arrows indicate the oxygen displacement *versus* the ideal positions of fluorite ( $\blacktriangleright$  displacement  $\Delta z > 0$ ;  $\blacktriangleleft$  displacement  $\Delta z < 0$ ).

edge of  $a/2$  (Fig. 1). Each sublattice is shown in Fig. 2(A, B, C, D). The oxygen displacement is shown in relation to the ideal fluorite positions. This displacement is such that the O atoms approach the  $\text{Mo}^{6+}$  ion, leading to a tetrahedral environment. This tetrahedron is almost regular, with the four Mo—O distances equal and the angles very close to  $109^\circ$ .

The O atoms in site 16(*f*) occupy a position near those of an ideal fluorite structure; but it would appear

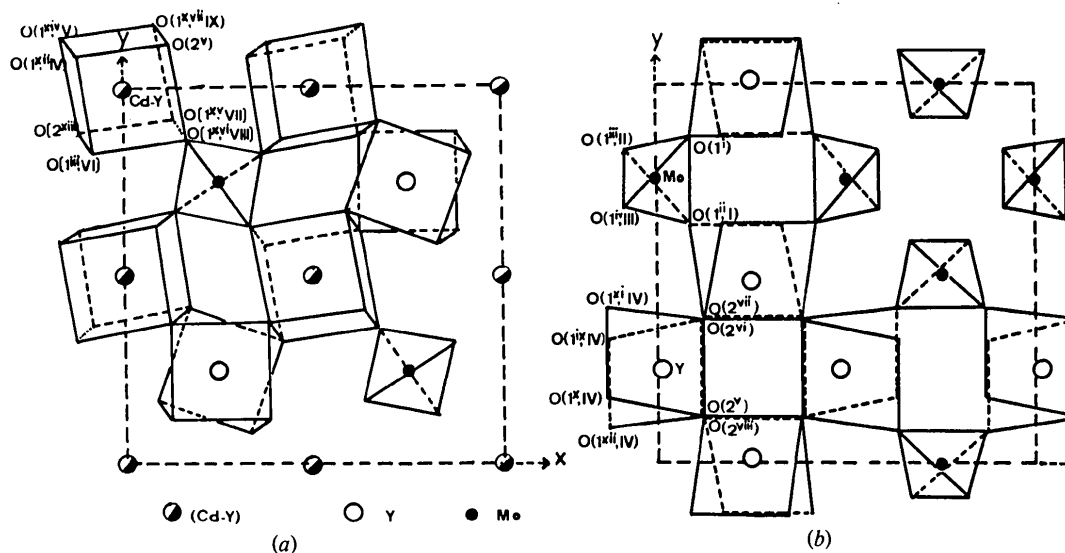


Fig. 3. (a) Oxygen polyhedra for cations at  $z = 0$ : (Cd, Y) and Mo; and  $z = 0.014$ : Y. (b) Oxygen polyhedra for cations at  $z = 0.25$ .

Table 3. *Calculated ion valencies in the different sites*

	Site	Bond number	$R_i$ (Å)	$R_i$ (Å)	$N$	$S_i$	$V_i$
Mo	12(d)	4	1.75 (2)	1.88	6.0	1.53	6.1 (3)
Y	12(e)	{4	2.27 (2)	2.07	7.0	0.52	3.1 (2)
		4	2.50 (2)	2.07	7.0	0.27	
(Cd,Y)	Y	8(c)	2	2.22 (2)	2.07	7.0	0.61
			6	2.52 (3)	2.07	7.0	0.25
	Cd	8(c)	2	2.22 (2)	1.99	7.4	0.44
			6	2.52 (3)	1.99	7.4	0.17

that none participate in the  $\text{Mo}^{6+}$  tetrahedral environment. This is not, however, the case for the site 48(i) O atoms, all of which participate in the  $\text{MoO}_4$  tetrahedra.

The  $\text{Y}^{3+}$  ions are in deformed cubic coordination. The 8(c) site is in cubic coordination deformed by flattening along the 3 axis of the cube.

The oxygen coordination polyhedra are shown for cations at  $z = 0$  (Fig. 3a) and 0.25 (Fig. 3b).

### Conclusion

The structure of  $\text{CdY}_4\text{Mo}_3\text{O}_{16}$  can thus be described as a derivative of a fluorite-type structure, from which a

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## Structure du Tétrathiomonophosphate(V) Heptathiodiphosphate(V) d'Argent

PAR PATRICK TOFFOLI, PARVIZ KHODADAD ET NOËL RODIER

Laboratoire de Chimie Minérale, Faculté des Sciences Pharmaceutiques et Biologiques, rue J.-B. Clément, 92290 Châtenay-Malabry, France

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### Abstract

$\text{Ag}_7(\text{PS}_4, \text{P}_2\text{S}_7)$ , monoclinic, space group  $B2/b$ ,  $a = 23.97$  (1),  $b = 24.88$  (1),  $c = 6.361$  (4) Å,  $\gamma = 110.85$  (5)°,  $Z = 8$ ,  $D_m = 4.43$  (5),  $D_c = 4.50$   $\text{Mg m}^{-3}$ . The crystal structure was solved by direct methods and refined by full-matrix least-squares calculations. The final  $R$  value is 0.066 for 1655 independent reflections [ $I > 3\sigma(I)$ ] measured on an automatic diffractometer;  $R_w = 0.070$ . The structure contains  $\text{PS}_4^{3-}$  and  $\text{P}_2\text{S}_7^{4-}$  groups linked together by  $\text{Ag}^+$  ions. The  $\text{PS}_4^{3-}$  groups form layers which alternate with double layers of  $\text{P}_2\text{S}_7^{4-}$ . The  $\text{Ag}^+$  ions are disordered among interstices in the anion array. Only one metallic site is entirely occupied; seven others have an occupancy ratio of more than 0.70 and the remainder of less than 0.09. Most of the  $\text{Ag}^+$  ions are surrounded by four S atoms [ $d(\text{Ag}-\text{S}) < 3.13$  Å] which form an irregular tetrahedron, but two have five S atoms in their neighbourhood. In some cases, one, two or three  $\text{Ag}-\text{S}$

number of anions are displaced in order to provide a tetrahedral environment for the  $\text{Mo}^{6+}$  cations. The remainder of the anions, which make up the pseudo-cubic  $\text{Y}^{3+}$  and  $(\text{Cd}_{0.5}, \text{Y}_{0.5})^{2.5+}$  coordination polyhedra, remain in positions which are very close to those found in fluorite structures.

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distances are longer than the others. It is probable that  $\text{Ag}_7\text{P}_3\text{S}_{11}$  would reveal ionic conductivity.

### Introduction

L'étude cristallographique de  $\text{Ag}_7\text{P}_3\text{S}_{11}$  a été entreprise dans le cadre des recherches effectuées au Laboratoire sur les thio- et les sélénophosphates. Ce composé peut être obtenu par synthèse directe à partir des éléments. Argent, phosphore et soufre, pris en proportions calculées, sont chauffés vers 823 K pendant trois à quatre semaines dans une ampoule de silice transparente vidée d'air et scellée. Il se forme des cristaux allongés, transparents, de couleur jaune, stables dans les conditions habituelles.

La formule du produit étudié a été établie en faisant l'analyse d'un monocristal à l'aide d'une microsonde électronique.