CRYSTAL STRUCTURE OF POWELLITE $CaMoO_4$

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Translated from Kristallografiya, Vol. 13, No. 3,
pp. 512-513, May-June, 1968
Original article submitted January 5, 1967

The crystal structures of molybdates and tungstates are of interest in relation to the use of these as laser materials. At the same time, the need for more accurate atom localization has increased. Structures have been determined for new compounds of ABO_4 type, and previous models have been refined [1-7]. In the cases of $NiWO_4$ and $CaWO_4$ [1-3] it has been shown that the earlier work [8-10] gave the structure pattern correctly but that the coordinates of the oxygen atoms were very inaccurate. The cation-oxygen distances calculated from the data of [8-10] agree poorly with the ionic radii [11]. The present structure refinement for $CaMoO_4$ is a continuation of the work of $CdWO_4$ and $CdMoO_4$ [4, 5].

The $CaMoO_4$ crystals were made by hydrothermal recrystallization and were kindly made available by L. N. Dem'yanets (Institute of Crystallography, AN SSSR). Irregular fragments were ground to nearly spherical form (diameter 0.40 ± 0.05 mm). The intensities of the $h0l$ reflections were measured with Mo $K\alpha$ radiation on a URS-50I diffractometer fitted with a MSTR-4 counter. The integral intensities were evaluated from the summed areas of the $K\alpha_1$ and $K\alpha_2$ peaks as recorded by an ÉPP-09 recorder. A correction was applied for counter nonlinearity (determined by foil superposition) for peaks of maximum count rate over 200 sec^{-1}. Reflections of intensity over 1000 sec^{-1} were attenuated with a calibrated attenuator. The F_0^2 were calculated with allowance for absorption ($\mu R = 1.15$).

TABLE 1. Coordinates of the Basis Atoms in $CaMoO_4$, Origin at $\bar{4}$

Atom	x/a	y/b	z/c
Ca	0	0	0
Mo	0	0	0.500
O	0.257	0.145	0.167

The cell parameters and space group of $CaMoO_4$ were as previously found [12]: $a = 5.224$, $c = 11.430$ Å, $Z = 4$, $C_{4h}^6 - I4_1/a$. This group demands that the Ca and Mo lie at the special points on the

TABLE 2. Interatomic Distances and Valence Angles in Mo(W) Polyhedra

ABO_4	Interatomic distance, Å				Valence angles	
	1st coord. sphere		2nd coord. sphere		1st coord sphere	2nd coord. sphere
	B–O	O–O	B–O	O–O	O–B–O	O–B–O
$CaMoO_4$	$B–O_{1-4}$ 1,76	$O_1–O_2$ 2,94 (4) $O_3–O_4$ 2,82 (2)	$B–O_{5-8}$ 2,94	$O_5–O_6$ =4,50 $O_7–O_8$ =4,90	$O_1–B–O_2 = 114°50'$ $O_3–B–O_4 = 107°$	$O_5–B–O_6 = 99°$ $O_7–B–O_8 = 114°55'$
$CaWO_4$	$B–O_{1-4}$ 1,78	$O_1–O_2$ 2,98 (4) $O_3–O_4$ 2,83 (2)	$B–O_{5-8}$ 2,91	$O_5–O_6$ = 4,45 $O_7–O_8$ = 4,87	$O_1–B–O_2 = 113°30'$ $O_3–B–O_4 = 107°25'$	$O_5–B–O_6 = 100°30'$ $O_7–B–O_8 = 114°35'$
$CdMoO_4$	$B–O_{1-4}$ 1,82	$O_1–O_2$ 2,98 (4) $O_3–O_4$ 2,95 (2)	$B–O_{5-8}$ 2,86	$O_5–O_6$ = 4,50 $O_7–O_8$ = 4,80	$O_1–B–O_2 = 110°05'$ $O_3–B–O_4 = 108°35'$	$O_5–B–O_6 = 104°20'$ $O_7–B–O_8 = 114°$
$CdWO_4$	$B–O_{1,2}$ 1,80 $B–O_{3,4}$ 1,87 $B–O_{5,6}$ 2,22	$O_1–O_2$ 2,75 $O_1–O_4$ 2,70 $O_1–O_6$ 2,84 $O_2–O_3$ 2,92 $O_2–O_5$ 2,84 $O_3–O_5$ 2,80 $O_1–O_5$ 2,80 $O_5–O_6$ 3,00	$B–O_{7,8}$ 3,40		$O_1–B–O_2 = 99°40'$ $O_5–B–O_6 = 85°05'$ $O_1–B–O_4 = 91°15'$ $O_2–B–O_3 = 94°20'$ $O_1–B–O_6 = 90°$ $O_2–B–O_5 = 90°$ $O_5–B–O_3 = 91°$ $O_1–B–O_5 = 91°$	

TABLE 3. Interatomic Distances (Å) in the Ca Polyhedron of $CaMoO_4$

Ca – O	O – O
2,45 (4)	3,19 (2)
2,48 (4)	3.75 (4)
	2.78 (4)
	2.96 (4)
	3·05 (4)

$\bar{4}$ axes. The oxygen atoms lie in general positions and were localized from P(xz) and σ(xz) syntheses. Table 1 gives the final values of the coordinates for R = 11% (for all reflections in the range $\sin\theta/\lambda \leq 1.4$ Å^{-1}, B = 0.5 Å^2).

The structure pattern of $CaMoO_4$ is exactly as for scheelite [2, 3], with Ca in a polyhedron with eight vertices characteristic of scheelite [13] and with the Mo in a nearly regular tetrahedron. Tables 2 and 3 give the interatomic distances. $CaMoO_4$ resembles $CdMoO_4$ and $CdWO_4$ in that the Mo(W) atom has four nearest O atoms (1.76-1.82 Å) and four more O atoms (2.86-2.94 Å) forming a second coordination sphere. There is a tendency for the distances in the first sphere to increase (from 1.76 to 1.82 Å) from $CaMoO_4$ to $CdMoO_4$, which is accompanied by reduction of the Mo(W)–O distances in the second sphere (Table 2), which leads on further deformation not only to change in the coordination numbers of both cations but also to the $CdWO_4$ structure type [14, 15].

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