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The scheelite-type europium molybdate $Eu_{0.96}MoO_4$

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$Eu_{0.96}MoO_4$ crystallizes with the scheelite-type structure in the space group $I4_1/a$. The Eu and Mo atoms are in $4b$ and $4a$ positions with $\overline{4}$ symmetry, and the O atoms are in general $16f$ positions.

Comment

The Eu_xMO_4 (M = Mo, W; $0.67 \leq x \leq 1.00$) series of compounds was studied three decades ago (Houlihan *et al.*, 1973; Greedan *et al.*, 1976) for their magnetic properties because of the mixed valence of the Eu atoms. However, we can find no report of a corresponding determination of the crystal structure of the molybdates, and only lattice parameters for the Eu_xMoO_4 compounds have been published (Banks & Nemiroff, 1974).

Fig. 1 shows the crystal structure of $Eu_{0.96}MoO_4$. As in other scheelite-type compounds, the Eu atoms are in an eightfold coordination environment, with 4 O atoms at 2.5714 (11) Å and the others at 2.5992 (12) Å. The Mo atoms are in a tetrahedral environment, with four equal Mo—O bond lengths of 1.7746 (11) Å. This value is similar to those observed in the scheelite-type alkaline-earth molybdates $MMoO_4$ (M = Ca, Sr and Ba) (Hazen *et al.*, 1985; Guermen *et al.*, 1971; Nassif *et al.*, 1999), in which they are 1.771 (3), 1.767 (4) and 1.765 (3) Å, respectively. As shown previously by Greedan *et al.* (1976) from magnetic measurements, the deficiency in europium implies the presence of Eu^{2+} and Eu^{3+} on the same site. On the other hand, Greenwood *et al.* (1976) rule out the presence of Mo^{5+} in the series Eu_xMO_4 from Mössbauer measurements. Consequently, if we assume that, in the title compound, all Mo atoms are in an oxidation state of +6, the percentage of Eu^{3+} is 8.3%.

Experimental

Single crystals of $Eu_{0.96}MoO_4$ were prepared from a mixture of Eu_2O_3 (Rhone Poulenc, 99.99%), MoO_3 (Cerac, 99.95%) and Mo (Plansee, 99.9999%) with the nominal composition $EuMoO_4$. Before use, Mo powder was reduced under flowing H_2 gas at 1273 K for 10 h in order to eliminate any trace of oxygen. The initial mixture (*ca* 5 g) was cold pressed and loaded into a molybdenum crucible, which was sealed under a low Ar pressure using an arc-welding system. The charge was heated at 300 K h^{-1} to 1923 K, held at that temperature for 48 h, cooled at a rate of 100 K h^{-1} to 1373 K and finally cooled to room temperature by switching off the furnace. The final product was multiphasic, with $Eu_{0.96}MoO_4$ and Eu_3MoO_7 (Prévost-Czeskleba, 1987) as the predominant phases. The crystals obtained were irregular blocks with no well defined faces. Five crystals resulting from the above reaction were measured and showed no significant variation of the unit-cell volume.

Crystal data

$Eu_{0.96}MoO_4$
$M_r = 305.82$
Tetragonal, $I4_1/a$
$a = 5.3875\ (2)$ Å
$c = 11.9811\ (4)$ Å
$V = 347.75\ (2)$ Å^3
$Z = 4$

$D_x = 5.841$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 20.61$ mm^{-1}
$T = 293\ (2)$ K
Irregular block, black
$0.06 \times 0.05 \times 0.04$ mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: analytical (de Meulenaar & Tompa, 1965)
$\quad T_{min} = 0.378,\ T_{max} = 0.528$

6132 measured reflections
686 independent reflections
506 reflections with $I > 2\sigma(I)$
$R_{int} = 0.031$
$\theta_{max} = 44.0°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.016$
$wR(F^2) = 0.031$
$S = 1.06$
686 reflections
16 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0087P)^2 + 0.6855P]$
$\quad$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.72$ e Å^{-3}
$\Delta\rho_{min} = -0.83$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 1997)
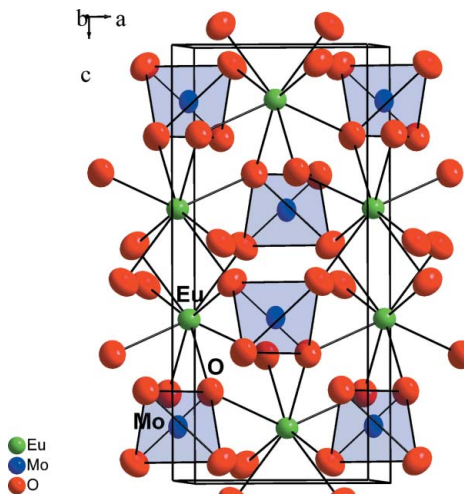Extinction coefficient: 0.0073 (3)

Figure 1
A view of the structure of $Eu_{0.96}MoO_4$. The unit cell is outlined and displacement ellipsoids are drawn at the 97% probability level.

Separate refinements of the site-occupation factors for Eu, Mo and O yield 0.960 (2), 1.000 (2) and 0.980 (6), respectively, leading to the formula $Eu_{0.96}MoO_{3.92}$. However, such a formula implies the presence of Mo^{5+}, which was ruled out by Greenwood *et al.* (1976). Consequently, the site-occupation factor for O was reset to full occupancy for the final cycles of the refinement. Since most scheelite-type structures are described with origin choice 2 of space group $I4_1/a$, we have also used this setting.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *COLLECT*; data reduction: *EVALCCD* (Duisenberg *et al.*, 2003); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2001); software used to prepare material for publication: *SHELXL97*.

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