

## Lattice Parameters and Space Group of $\text{Ce}(\text{MoO}_4)_2$

L. H. BRIXNER, J. F. WHITNEY, AND M. S. LICIS KAY

*Central Research Department,\* E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898*

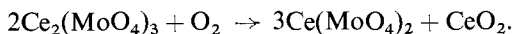
Received February 28, 1972

The title compound has been prepared in single crystal form by the Czochralski technique. Precession X-ray work indicated triclinic symmetry with either 1 or  $\bar{1}$  as space group. A second harmonic generation test was negative and therefore strongly suggests  $\bar{1}$  as the proper space group for  $\text{Ce}(\text{MoO}_4)_2$ . The refined cell dimensions were found to be:  $a = 10.150 \pm 2 \text{ \AA}$ ,  $b = 18.422 \pm 3 \text{ \AA}$ ,  $c = 9.559 \pm 2 \text{ \AA}$ ,  $\alpha = 96.76 \pm 1^\circ$ ,  $\beta = 101.91 \pm 1^\circ$ , and  $\gamma = 103.96 \pm 1^\circ$ .

### Introduction

In compounds, cerium is known to exist in both the trivalent and the tetravalent state. Although the latter configuration is more stable in covalent compounds, very few ternary compounds with  $\text{Ce}^{4+}$  have been well characterized.  $\text{Ce}(\text{SO}_4)_2$  (1), for instance, exists but its structure is not known.  $\text{CeGeO}_4$  (2) crystallizing in a scheelite structure is one of the few structurally characterized cerium(IV) oxometallates. Compositions with Ce(III) in the cation site appear more plentiful as, for instance,  $\text{Ce}^{3+}\text{GaO}_3$  (3),  $\text{Ce}_2\text{Zr}_2\text{O}_7$  (4),  $\text{Ce}^{3+}\text{NbO}_4$  (5), and  $\text{Ce}_2(\text{MoO}_4)_3$  (6). It was in conjunction with the latter compound that we started to further investigate  $\text{Ce}(\text{MoO}_4)_2$  which appears as an oxidation product during the decomposition of cerium(III) molybdate in air.

Nassau (6) described  $\text{Ce}_2(\text{MoO}_4)_3$  but left its structural characterization open. In a recent paper (7), we demonstrated that pure  $\text{Ce}_2(\text{MoO}_4)_3$  belongs to an isostructural series with La, Pr, and Nd molybdates. However, when heated in air,  $\text{Ce}_2(\text{MoO}_4)_3$  oxidizes according to

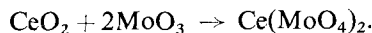


This oxidation reaction was first noticed during an attempted DTA analysis of  $\text{Ce}_2(\text{MoO}_4)_3$  in air. While this reaction explains the abnormally low melting point quoted by previous authors (6), it does not yield pure  $\text{Ce}(\text{MoO}_4)_2$ . We, therefore,

attempted to grow single crystals of  $\text{Ce}(\text{MoO}_4)_2$ , and it is the purpose of this paper to describe the preparation, cell dimensions, and other physical characteristics of this compound.

### Experimental

Polycrystalline  $\text{Ce}(\text{MoO}_4)_2$  has been prepared from the constituent components  $\text{CeO}_2$  (99.9% Kerr-McGee Co.) and  $\text{MoO}_3$  (Molybdenum Climax Co., high purity) according to



Both  $\text{CeO}_2$  and  $\text{MoO}_3$  were pre-fired at  $600^\circ\text{C}$  for 14 hr to eliminate any moisture and other volatile constituents. The reaction was carried out in two steps: a first firing at  $650^\circ\text{C}$  for 10–20 hr followed by careful homogenization through ball milling in an agate mill, and a second firing at  $800^\circ\text{C}$  for 4–8 hr. The intensely yellow composition obtained this way yields an extremely complicated X-ray pattern which is free of any lines from the starting components.

Single crystals were grown via the Czochralski technique. The container was a  $1\frac{1}{2}$  in. high  $\times$   $1\frac{1}{2}$  in. wide Pt–40% Rh crucible which was inductively heated with a 20 KVA Ecco 450 kHz high-frequency generator. Growth was initiated on a Pt wire at pulling speeds of 0.5 to 1.0 cm/hr and a rotation rate of 60 rpm.

For the X-ray studies, powder patterns were obtained at  $25^\circ\text{C} \pm 1^\circ\text{C}$  with a Hagg-Guinier camera using  $\text{Co}_3\text{O}_4$  ( $a = 8.0832 \text{ \AA}$  at  $25^\circ\text{C}$ ) as

\* Contribution No. 1907.

an internal standard and CrK $\alpha_1$  radiation. These data were refined by a least-squares method (10). Single crystal patterns were obtained in a precession camera using MoK $\alpha_1$  radiation.

### Results and Discussion

Precession photography on the intensely yellow single crystals indicated triclinic symmetry, with  $a = 12.428 \text{ \AA}$ ,  $b = 19.700 \text{ \AA}$ ,  $c = 10.138 \text{ \AA}$ ,  $\alpha = 108.87^\circ$ ,  $\beta = 131.07^\circ$ , and  $\gamma = 91.25^\circ$ . This cell was reduced via the program TRACER (9) to give  $a = 10.138 \text{ \AA}$ ,  $b = 18.435 \text{ \AA}$ ,  $c = 9.575 \text{ \AA}$ ,  $\alpha = 97.07^\circ$ ,  $\beta = 101.89^\circ$ , and  $\gamma = 103.81^\circ$ . Both cells yielded calculated  $d$  values in good agreement with the Cr-Guinier data using a powder pattern generator program (10). A least-squares refinement, indexing 66 out of 67 lines,<sup>1</sup> gave the following parameters:

$$a = 10.150 \pm 2 \text{ \AA}$$

$$b = 18.422 \pm 3 \text{ \AA}$$

$$c = 9.559 \pm 2 \text{ \AA}$$

$$\alpha = 96.76 \pm 1^\circ$$

$$\beta = 101.91 \pm 1^\circ$$

$$\gamma = 103.96 \pm 1^\circ$$

$$V = 1670.57 \text{ \AA}^3.$$

The pycnometrically determined density of  $4.518 \text{ g}\cdot\text{ml}^{-1}$  gave a  $Z$  of close to 10. Using this number of molecules per unit cell, the X-ray density is calculated to be 4.572, in good agreement with the experimental value. Typical calculated and observed  $d$  values are summarized in Table I.

The space group for Ce(MoO<sub>4</sub>)<sub>2</sub> is either  $I$  or  $\bar{I}$ . In a first attempt to distinguish between these two possibilities, crystals were examined by the transmission method (8) for their piezoelectric response. This test was negative and therefore pointed toward the centrosymmetric  $\bar{I}$  space group. However, since this test is not completely unambiguous, Ce(MoO<sub>4</sub>)<sub>2</sub> was also checked for second harmonic generation (SHG) of the  $1.06 \mu\text{m}$  Nd laser light. As this test was also negative, we can state that the most likely space group is indeed  $\bar{I}$ .

Although the vapor pressure of MoO<sub>3</sub> is appreciable at the melting point of Ce(MoO<sub>4</sub>)<sub>2</sub>, the compound does melt congruently at  $980^\circ\text{C}$ . There are two endothermic peaks at  $672^\circ$  and  $782^\circ\text{C}$ , suggesting structural transformations. It

<sup>1</sup> The unindexed line was of extremely low intensity.

TABLE I  
OBSERVED AND CALCULATED  
 $d$ -VALUES FOR Ce(MoO<sub>4</sub>)<sub>2</sub>

$l$	$h$	$k$	$l$	$d_{(\text{obsd})}$	$d_{(\text{calcd})}$
20	-1	1	0	9.5575	9.5626
10	1	0	-1	7.6239	7.6223
10	-1	1	1	7.1799	7.1854
10	1	1	-1	6.8170	6.8178
20	-1	1	-1	6.1826	6.1902
20	0	2	1	5.8604	5.8650
60	-1	3	0	5.7485	5.7480
10	1	1	1	5.1966	5.2017
10	-1	3	-1	4.9350	4.9344
20	-1	3	1	4.8215	4.8192
5	2	0	0	4.7729	4.7764
20	0	3	1	4.5973	4.5933
15	-2	2	1	4.5230	4.5262
30	1	3	-1	4.4931	4.4950
40	1	3	0	4.4846	4.4822
20	-1	1	2	4.4099	4.4110
10	2	1	0	4.3228	4.3208
20	0	1	2	4.2714	4.2728
10	-1	4	-1	4.1445	4.1435
20	-2	2	-1	4.0077	4.0074
20	-1	1	-2	3.9282	3.9268
80	2	0	1	3.8723	3.8716
90	2	0	-2	3.8119	3.8111
50	-2	3	-1	3.7880	3.7869
50	0	4	1	3.7215	3.7221
95	1	3	1	3.6856	3.6847
90	-1	3	-2	3.6402	3.6402

was the melting point of  $980^\circ\text{C}$  which is close to Nassau's quoted temperature of  $970^\circ\text{C}$  for Ce<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> which first suggested that he may indeed not have had pure Ce<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub>. Detailed DTA studies with high purity Ce<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> confirmed this, as a run in air gave a broad exothermic peak starting at  $750^\circ\text{C}$  and peaking at  $850^\circ\text{C}$  because of oxidation of Ce<sup>+3</sup> to Ce<sup>+4</sup>. The X-ray pattern of such a frozen melt showed a mixture of CeO<sub>2</sub> + Ce(MoO<sub>4</sub>)<sub>2</sub>.

In summary, we can state that Ce(MoO<sub>4</sub>)<sub>2</sub> now constitutes one of the few well-characterized ternary Ce(IV) oxometallates.

### Acknowledgment

The authors express their gratitude to Professor L. E. Cross of the Pennsylvania State University for running the SHG test.

### References

1. E. G. JONES AND F. G. SOPER, *J. Chem. Soc.* 802 (1935).

2. F. BERTAUT, *C.R.H. Acad. Sci.* **238**, 2173 (1954).
3. A. RUGGIERO AND R. FERRO, *Atti Accad. Naz. Lincei Cl. Sci. Fis. Mat. Nat. Rend.* **17**, 48 (1954).
4. J. J. CASEY, L. KATZ, AND W. C. ORR, *J. Amer. Chem. Soc.* **77**, 2187 (1955).
5. A. N. KOMKOV, *Dokl. Akad. Nauk. SSSR* **126**, 953 (1959).
6. K. NASSAU, H. J. LEVINSTEIN, AND G. M. LOIACONO, *J. Phys. Chem. Solids* **26**, 1805 (1965).
7. L. H. BRIXNER, A. W. SLEIGHT, AND M. S. LICIS KAY, *J. Solid State Chem.*, to be published.
8. R. J. BLUME, *Rev. Sci. Instrum.* **32**, 598 (1961).
9. S. L. LAWTON AND R. A. JACOBSON, "U.S.A.E.C. Research and Development Report IS-1141, Chemistry (UC-4), TID-4500," July 1, 1965.
10. The powder pattern generator and least-squares refinement programs were written by Dr. A. W. Sleight.