Ln₂MoO₆-Type Rare Earth Molybdates—Preparation and Lattice Parameters

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The title compounds have been prepared for Ln = rare earth elements 58 (Ce) through 71 (Lu) as well as Y and La. They fall into three structural categories: the tetragonal $I\bar{4}2m$ space group for the large ions up to and including Sm_2MoO_6, which can also crystallize in the $C2/c$ symmetry found for the small rare earths; and an $Fm3m$ related structure for Ce_2MoO_6, which constitutes an exception in the series. Cell parameters are also given for Gd_2WO_6 and a series of $Gd_{2-x}Bi_xMoO_6$ solid solutions.

Introduction

In conjunction with the ferroelectric $Ln_2(MoO_4)_3$-type rare earth molybdates (1), Gd_2MoO_6 has been of interest as an impurity component in single crystals of $Gd_2(MoO_4)_3$. Together with all other rare earth compositions of the same type (except Ce_2MoO_6) as well as the Y and La compounds, Gd_2MoO_6 has been discussed by Blasse (2). The structure of La_2MoO_6 has been determined by Sillen (3). Blasse (2) postulated a structure for the small rare earth molybdates based on a monoclinic distortion of the $I\bar{4}2m$ symmetry of La_2MoO_6. While this appeared to be a reasonable approach, it was not unambiguous, lacking single-crystal data for these monoclinic compositions. We were also unable to index our Guinier patterns using Blasse's (2) parameters. One of the difficulties with the Ln_2MoO_6 type rare earth molybdates is the fact that they are highly refractory with melting points in the vicinity of 1600–2000°C. Such melts are usually dark colored, because of at least a partial loss of oxygen, and would not be suitable for direct crystal growth via the Bridgeman or Czochralski technique. We therefore followed an alternative approach by substituting Bi for Gd in Gd_2MoO_6, thereby lowering the melting point. Although the range of existence for the monoclinic structure of these

solid solutions is rather limited, single crystals of this structure could be obtained by sintering at 1400°C. Precession work with such single crystals indicated $C2/c$ or $C2$ symmetry, and we were able to accurately index and refine all monoclinic patterns based on these findings.

It is the purpose of this paper to establish the range of the two principal structures, to present precision cell parameters based on least-squares refinement, and to describe Ce_2MoO_6 as a new composition. The system $Gd_{2-x}Bi_xMoO_6$ will also be discussed over a limited range of x.

Experimental

All compounds described in this paper were prepared by standard solid-state techniques from Kerr–McGee 99.9% pure rare earth oxides and Molybdenum Company high purity MoO_3. Homogenized and pressed pellets were sintered finally in sealed Pt capsules between 1400 and 1600°C. Ce_2MoO_6 was prepared via:

$$6CeO_2 + Mo + 2MoO_3 \rightarrow 3Ce_2MoO_6$$

in sealed evacuated quartz ampoules. The starting oxide for Pr_2MoO_6 was black Pr_6O_{11} which readily loses its excess oxygen at 1200°C as does Tb_4O_7, which was used to prepare Tb_2MoO_6. All other rare earth oxides are in the true sesquioxide state and were only prefired prior to use.

* Contribution No. 1878.

Small crystals of Gd$_{1.70}$Bi$_{0.30}$MoO$_6$ were obtained by sintering polycrystalline material of this composition in sealed platinum capsules, fluctuating the temperature between 1400 and 1500°C. Such crystals were examined by X-ray diffraction using a precession camera with Mo radiation. Powder patterns were obtained with a Hägg Guinier camera using CuKα radiation and an internal standard of KCl ($a_0 = 6.2931$ Å at 25°C).

Results and Discussion

Although crystals of Gd$_{1.70}$Bi$_{.30}$MoO$_6$ were twinned, the space group appeared unambiguous as either Cc or $C2/c$ with $a = 16.62$ Å, $b = 11.23$ Å, $c = 5.45$ Å, and $\beta = 108.6°$. This cell satisfactorily indexed the Guinier pattern, and similar cells could be used to index all the monoclinic Ln$_2$MoO$_6$ phases. The refined cell dimensions are given in Table I.

A body-centered monoclinic cell can also be used to describe this structure. This cell appears to be related to the tetragonal cell found for Ln$_2$MoO$_6$ phases where Ln is large. Consequently, the dimensions of the body-centered cell are also given in Table I. Its apparent relationship to the tetragonal cell is:

$$a_M \sim \sqrt{2} \times a_T$$
$$b_M \sim 2\sqrt{2} \times a_T$$
$$c_M \sim c_T.$$

The most likely relationship of our body-centered cell with Blasse's interpretation is the following:

$$a_M \sim b_B$$
$$b_M \sim 2/3 \times c_B$$
$$c_M \sim 3 \times a_B$$
$$\beta_M \sim 180 - \gamma_B.$$

The tetragonal $I\bar{4}2m$ structure extends from La$_2$MoO$_6$ to Sm$_2$MoO$_6$, and the refined cell dimensions of these phases are also given in Table I. Only Sm$_2$MoO$_6$ has been prepared in both tetragonal and monoclinic modifications. When prepared at 1400°C, Sm$_2$MoO$_6$ has the tetragonal structure, and when prepared at 900°C, the monoclinic structure is found. The transition from tetragonal to monoclinic is not merely a distortion because the tetragonal form is readily obtained at room temperature by air quenching. Thus, the transition is slow and

TABLE I

Refined Cell Dimensions,[a] Space Groups, and Colors of the Ln$_2$MoO$_6$-Type Rare Earth Molybdates

Ln	Space group	a, Å	b, Å	c, Å	β, °	V, Å^3	c', Å	β', °	Color
La	$I\bar{4}2m$	4.093		16.017		268.33			White
Ce	$Fm3m$	5.578[b]				173.55			Black
Pr	$I\bar{4}2m$	4.030		15.852		257.48			Green
Nd		4.005		15.813		253.65			Blue
Sm		3.963		15.686		246.36			Orange
Sm	$C2/c$	5.470	11.272	15.791	90.92	973.5	16.628	108.28	
Eu		5.439	11.218	15.735	91.01	960.0	16.558	108.16	White
Gd		5.425	11.185	15.678	90.85	951.1	16.514	108.33	White
Tb		5.396	11.119	15.626	90.78	937.5	16.462	108.35	White
Dy		5.371	11.071	15.573	90.78	925.9	16.542	109.72	Yellow
Ho		5.349	11.028	15.516	90.65	915.2	16.469	109.60	Brown
Er		5.328	10.985	15.479	90.59	905.3	16.412	109.53	Pink
Tm		5.310	10.933	15.419	90.48	895.1	16.266	108.57	White
Yb		5.290	10.895	15.387	90.35	886.8	16.240	108.66	White
Lu		5.274	10.875	15.346	90.19	880.2	16.211	108.80	White
Y		5.351	11.022	15.510	90.67	914.7	16.466	109.63	White

[a] The unprimed values refer to the body-centered cell, and the primed values to the C-centered cell where $c' = a$ and $b' = b$. The 4–5 Å edges are accurate to ±.001 Å, the 10–11 Å edges to ±.002 Å, and the 15–16 Å to ±.003 Å.

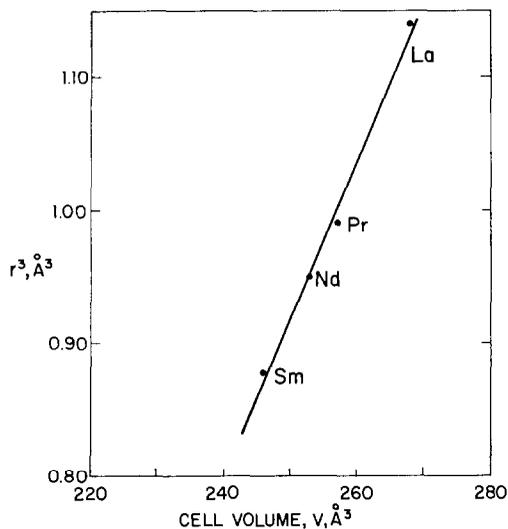[b] This cell edge and space group only represents a subcell.

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FIG. 1. Cell volume vs. r^3 for the tetragonal Ln_2MoO_6 compounds.

involves some rearrangement of atoms. Attempts to convert Nd_2MoO_6 to a monoclinic form by annealing for 60 hr at 600°C were unsuccessful. Likewise, attempts to convert Eu_2MoO_6 to a tetragonal form by quenching from 1600°C were unsuccessful. A sample of Gd_2MoO_6 was melted (~2000°C) with a torch flame and quenched. Its X-ray pattern appeared to be of the CaF_2 type with $a = 5.40$ Å; however, the composition of this phase may differ slightly from Gd_2MoO_6.

Since the monoclinic modifications are more dense than the tetragonal modifications, we attempted to transform the tetragonal phases by quenching from 65 kbar and 1000°C. The powder patterns of the products resembled the monoclinic type much more than the tetragonal type, but good indexings were not obtained.

The relationship between the cube of the ionic radii (4) and the cell volumes is given in Fig. 1
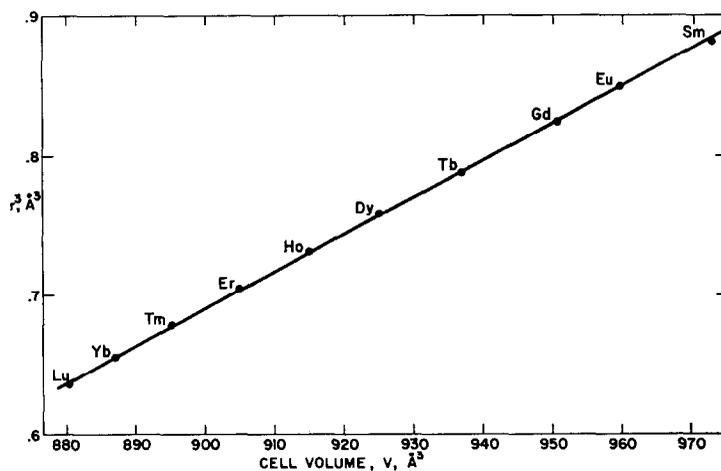

FIG. 2. Cell volume vs. r^3 for the monoclinic Ln_2MoO_6 compounds.

TABLE II

LATTICE PARAMETERS FOR THE $Gd_{2-x}Bi_xMoO_6$ SYSTEM

X	Composition	Space group	a, Å	b, Å	c, Å	β, °	V
0.1	$Gd_{1.9}Bi_{0.1}MoO_6$	$C2/c$	16.559	11.206	5.438	108.40	957.46
0.2	$Gd_{1.8}Bi_{0.2}MoO_6$		16.599	11.218	5.447	108.523	961.72
0.3	$Gd_{1.7}Bi_{0.3}MoO_6$		16.624	11.227	5.452	108.61	964.33
0.4	$Gd_{1.6}Bi_{0.4}MoO_6$	$I\bar{4}2m$	3.941	—	15.690	—	243.67
0.5	$Gd_{1.5}Bi_{0.5}MoO_6$		3.946	—	15.719	—	244.73
0.6	$Gd_{1.6}Bi_{0.4}MoO_6$		3.948	—	15.738	—	245.32

compounds.

TABLE III

OBSERVED AND CALCULATED d VALUES FOR Gd_2MoO_6

I	$h k l$	d (obs)	d (calc)
10	1 1 0	9.068	9.104
10	2 0 0	7.813	7.837
10	3 1 0	4.723	4.734
5	1 1 1	4.160	4.167
15	−3 1 1	4.114	4.118
10	1 3 0	3.623	3.627
100	2 2 1	3.137	3.138
100	−4 2 1	3.105	3.106
10	3 3 0	3.033	3.034
5	5 1 0	3.018	3.018
20	−3 3 1	2.851	2.852
70	0 4 0	2.794	2.796
65	−2 0 2	2.710	2.712
60	6 0 0	2.612	2.612
5	4 2 1	2.453	2.454
10	3 3 1	2.427	2.427
2	5 3 0	2.403	2.399
5	0 2 2	2.339	2.338
5	5 1 1	2.314	2.316
5	2 4 1	2.249	2.250
2	−4 4 1	2.239	·2.238
15	1 5 0	2.214	2.214
10	−3 3 2	2.168	2.168
10	3 5 0	2.056	2.056
2	3 1 2	2.031	2.031
20	−7 1 2	2.003	2.003
10	−7 3 1	1.982	1.982
5	8 0 0	1.957	1.959
80	−2 4 2	1.946	1.946
75	6 4 0	1.909	1.909
60	4 0 2	1.895	1.895
40	−8 0 2	1.868	1.867
15	−5 5 1	1.824	1.824
5	−7 3 2	1.787	1.787
10	−1 1 3	1.745	1.745
10	−5 1 3	1.734	1.734
15	−1 5 2	1.717	1.717
5	−4 2 3	1.707	1.707
50	2 6 1	1.672	1.672
45	−4 6 1	1.668	1.668
15	−9 3 1	1.646	1.645
50	0 2 3	1.641	1.640
36	−6 2 3	1.627	1.627
2	−7 1 3	1.614	1.615
45	−1 3 3	1.596	1.597
15	−5 3 3	1.588	1.588
40	−10 2 1	1.584	1.583
40	4 4 2	1.569	1.569
10	−9 3 2	1.557	1.557
25	−8 4 2	1.553	1.553
10	0 6 2	1.510	1.509
10	−7 5 2	1.505	1.505
10	−3 7 1	1.503	1.503

To attempt to distinguish between the possible centrosymmetric $C2/c$ and the noncentrosymmetric $C2$ space groups, we examined some $Gd_{1.8}Bi_{0.2}MoO_6$ crystals for their piezoelectric response by the transmission method (5). As this test was negative, it tended to support the $C2/c$ space group. A more unambiguous distinction between the two possibilities was made by a second harmonic generation (SHG) test with the same compound. Since this test was also negative, we assume that $C2/c$ is the correct space group.

Many Ln_2WO_6 tungstates have the same structure found for the monoclinic Ln_2MoO_6 phases. For example, we find the refined body-centered cell dimensions of Gd_2WO_6 to be $a = 5.425$ Å, $b = 11.172$ Å, $c = 15.624$ Å, $\beta = 91.60°$, and $V = 946.7$ Å^3. This series constitutes one of the rare cases where the cell volumes of the tungstates are actually smaller than those of the corresponding isostructural molybdates. Precision cell edges of the remaining Ln_2WO_6 compounds will be the subject of a forthcoming
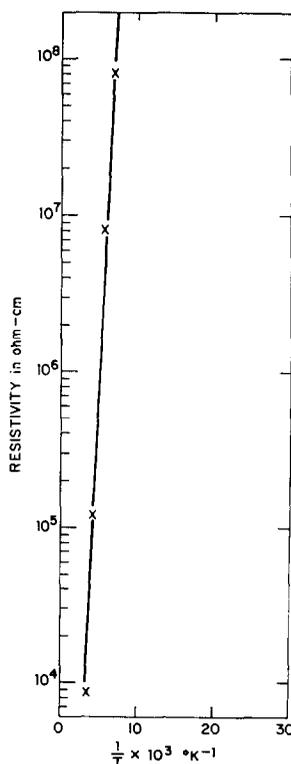

FIG. 3. Log resistivity vs. inverse temperature for Ce_2MoO_6.

publication. The cell dimensions and space group for the $Gd_{2-x}Bi_xMoO_6$ system over a limited region of x are summarized in Table II. Table III gives the observed and calculated d spacings for Gd_2MoO_6 using the C-centered cell.

While there appears to be no question as to the valence state of the rare earths in most of these compositions, it is not quite clear in Ce_2MoO_6. Since the compound is black and a semiconductor, we are assuming at this point that a variable valence distribution such as $Ce^{3+}Ce^{4+}Mo^{5+}O_6$ is responsible for this behavior. It is also probable that this different distribution of valence states is responsible for the different structure observed for this compound. It is interesting to note that Ce^{3+} and Mo^{6+} are apparently compatible in a $1:1.5$ ratio in a compound such as $Ce_2^{3-}(Mo^{6+}O_4)_3$ (which is transparent, yellow, and an insulator) while the $2:1$ ratio in Ce_2MoO_6 did cause a reduction of Mo^{6+} to Mo^{5+}. A typical resistivity vs. tempera-ture plot is given in Fig. 3. The calculated activation energy is .21 eV.

Acknowledgment

References

1. L. H. BRIXNER, P. E. BIERSTEDT, A. W. SLEIGHT, AND M. S. LICIS, 5th Mater. Res. Symp. Solid State Chem., Washington, D.C., October 1971.
2. G. BLASSE, J. Inorg. Nucl. Chem. 28, 1488 (1966).
3. L. G. SILLEN AND K. LUNDBORG, Z. Anorg. Allg. Chem. 252, 2 (1943).
4. R. D. SHANNON AND C. T. PREWITT, Acta Crystallogr. B25, 925 (1969).
5. R. J. BLUME, Rev. Sci. Instrum. 32, 598 (1961).