Cell Dimensions of the Molybdates $La_2(MoO_4)_3$, $Ce_2(MoO_4)_3$, $Pr_2(MoO_4)_3$, and $Nd_2(MoO_4)_3$

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Single crystals of $La_2(MoO_4)_3$ have been grown by the Czochralski technique. The space group of $La_2(MoO_4)_3$ has been found to be Cc or $C2/c$ from single-crystal X-ray photographs, and the refined cell dimensions are: $a = 17.006 \pm .004$ Å, $b = 11.952 \pm .003$ Å, $c = 16.093 \pm .004$ Å, and $\beta = 108.44 \pm .01°$. Accurate cell dimensions have also been determined for isostructural $R_2(MoO_4)_3$ molybdates where R is Ce, Pr, or Nd. $Ce_2(MoO_4)_3$ was checked for second harmonic generation and found to give no signal. This indicates a high probability of the existence of centrosymmetry and therefore would indicate $C2/c$ as the most likely correct space group.

Introduction

The rare earth molybdates $R_2(MoO_4)_3$ are of interest since some of the members (Pr through Ho) are ferroelectric (*1*). The phase relationships for most of the compounds have been discussed by Nassau (*2*), but no structure was given for $Ce_2(MoO_4)_3$ and the high-temperature form of $La_2(MoO_4)_3$ was somewhat questionable. The low-temperature form, originally termed "N" and designated as α in this paper, was discussed recently by Jamieson et al. (*3*) for $Nd_2(MoO_4)_3$ only.

Experimental

The four molybdates, $La_2(MoO_4)_3$, $Ce_2(MoO_4)_3$, $Pr_2(MoO_4)_3$, and $Nd_2(MoO_4)_3$ (subsequently designated as LMO, CMO, PMO, and NMO), were first prepared by solid-state reaction between the rare earth oxide (Kerr–McGee 99.99% purity) and MoO_3 (obtained by decomposition of Climax Molybdenum Co. $(NH_4)_6Mo_7O_{24}·4H_2O$). La_2O_3 was prefired in air, as it readily absorbs water and CO_2. Ce_2O_3 was prepared by hydrogen reduction of CeO_2 at 1100°C. Since Ce_2O_3 rapidly reoxidizes even at room temperature, all weighing and mixing operations were carried out under argon in a

dry box, and the firing was done in a sealed, evacuated quartz tube. To prepare PMO, black Pr_6O_{11} was the starting oxide; it readily loses excess oxygen above 1000°C and forms the intensely green molybdate. NMO was prepared by treating the appropriate mixture at 600°C for 14 hr, grinding and refiring at 800 and 900°C for 2 hr each. Single crystals of LMO were grown by the Czochralski technique, employing pulling speeds of .5 to .8 cm/hr. If the crystals are kept above the transition temperature of 848°C, they remain glass clear. Slow cooling through this transition appears to be disruptive and causes the boule to disintegrate into a polycrystalline mass. Crystals large enough for X-ray work could be separated from the bulk. If the clear boule is rapidly quenched from above 848°C, it still fractures, but large single-crystalline portions of the frozen-in, high-temperature form can be salvaged.

Crystals of $La_2(MoO_4)_3$ were examined under a polarizing microscope. Although most crystals were twinned, an apparently single crystal was found. Precession photographs further indicated that this crystal was single. Guinier powder photographs were taken at 25°C with a Hägg camera using $CuK\alpha_1$ radiation and an internal standard of high purity KCl ($a = 6.2931$ Å at 25°C). Cell dimensions were refined by least squares using the Guinier data.

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TABLE I

CELL DIMENSIONS AND TRANSITION TEMPERATURES FOR THE α-RMO COMPOUNDS

R	Color	Trans. temp., °C	M.p., °C	a, Å[a]	b, Å	c, Å	β, °	V	"IR"-VI
La[b]	colorless	848 to $I4_1/a$	1024	17.006	11.952	16.093	108.44	3102.8	1.045
Ce	yellow	none observed	1035	16.902	11.842	15.984	108.58	3032.7	1.010
Pr	green	987 to $P\bar{4}2m$	1045	16.849	11.778	15.914	108.50	2994.9	0.997
Nd	blue	959 to $P\bar{4}2m$	1081	16.788	11.719	15.849	108.54	2956.3	0.983

[a] Cell constants can be considered accurate to ± 4 for a, ± 2 for b and ± 3 for c.

[b] The calculated X-ray density of 4.83 g ml^{-1} for this compound is in good agreement with the pycnometrically determined number of 4.75 g ml^{-1}.

Results

The space group of α-LMO was found to be either $C2/c$ or Cc from single-crystal X-ray data. The relationship to the scheelite subcell indicates that there are 12 formula units per unit cell. The powder patterns of α-CMO, PMO, and NMO were readily indexed by analogy to α-LMO. The refined cell dimensions are given in Table I, and Fig. 1 shows a plot of cell volume vs. r^3 of the rare earth ion. The agreement between observed and calculated d values was very good in all cases, and an indexed pattern of NMO is presented in Table II. The agreement between our pattern and that reported by Nassau et al. (2) for NMO is also good. However, a pattern calculated on the basis of the cell given by Jamieson et al. (3) does not account well for our powder pattern or the powder pattern given by Nassau et al. (2). Furthermore, we were un-

successful in obtaining better agreement by refining the NMO cell dimensions given by Jamieson et al. (3).

Melting and transition temperatures are also given in Table I. α-LMO transforms to β-LMO at 848°C. β-LMO has an undistorted tetragonal scheelite structure with $a = 5.365$ Å and $c = 11.945$ Å. This transition is therefore an order–disorder transition where La and vacancies are disordered in β-LMO and ordered in α-LMO.

CMO maintains the α-LMO structure all the way to the melting point whereas PMO and NMO transform to the tetragonal ($P\bar{4}2_1/m$) structure (2). We therefore used this prototype composition to see if it would generate a second harmonic of the 1.06 μ Nd^{3+} laser light. The test was negative and therefore strongly indicates that we are dealing with a centrosymmetric structure. This would establish $C2/c$ as the more probable of the two possible space groups.
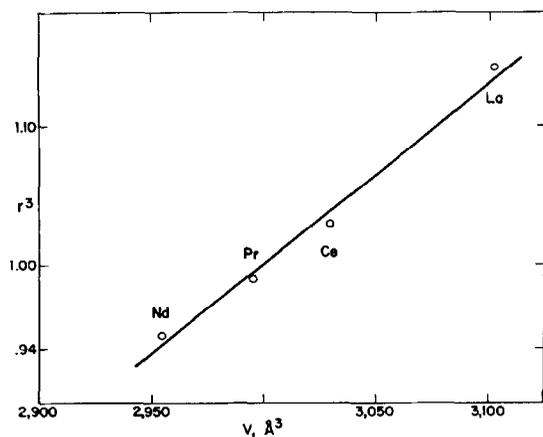
Discussion

In an earlier paper (4) we have shown a change in structure on going from α-SMO to α-NMO. While we could demonstrate that the α-R$_2$ (MoO$_4$)$_3$ compounds, R = Sm through Dy, have the Eu$_2$(WO$_4$)$_3$ structure (5), we were unable to index our powder data for R = La through Nd. However, it was obvious from the powder patterns that all these molybdates have scheelite-related structures.

Although Jamieson et al. (3) reported a space group and cell dimensions for NMO, a full structural refinement was not presented. Their refinement of positional parameters was based on the scheelite subcell, completely ignoring the

FIG. 1.

TABLE II

POWDER DIFFRACTION DATA FOR α-NMO

I_0	$h\,k\,l$	d_0	d_C	d_{NLL}	I_{NLL}	d_{JAB}	$h\,k\,l$	I_0	$h\,k\,l$	d_0	d_C	d_{NLL}	I_{NLL}	d_{JAB}	$h\,k\,l$
mw	−1 1 1	8.767	8.771			13.031	2 0 0	vw	−1 3 4	2.777	2.777			4.648	2 2 1
mw	0 0 2	7.504	7.513			11.430	0 0 1	vvw	3 3 2	2.725	2.724			4.471	−6 0 1
m	−1 1 2	6.498	6.506	6.50	vvw	10.678	1 1 0	s	6 0 0	2.652	2.653			4.354	4 2 0
ms	0 2 1	5.454	5.459	5.45	vw	10.000	−2 0 1	s	−2 0 6	2.641	2.641	2.64	m	4.344	6 0 0
mw	−3 1 1	5.044	5.047			8.261	−1 1 1	vw	−5 1 5	2.582	2.580			4.331	−4 2 1
mw	3 1 0	4.828	4.833			7.650	2 0 1	vw	−6 2 1	2.502	2.502			4.188	−5 1 2
mw	−1 1 3	4.812	4.816	4.80	vvw	7.413	1 1 1	vw	2 4 2	2.495	2.495			4.130	−2 2 2
m	2 0 2	4.757	4.760			6.976	3 1 0	vw	−4 4 2	2.383	2.383			4.089	0 2 2
w	2 2 1	4.274	4.277	4.28	vw	6.610	−3 1 1	vw	−2 4 4	2.345	2.345			4.062	5 1 1
m	3 1 1	4.252	4.256			6.516	4 0 0	vw	−7 1 3	2.326	2.327			4.023	3 1 2
mw	−4 0 2	4.094	4.096			6.438	−4 0 1	w	5 1 3	2.321	2.321			4.005	−6 0 2
vw	−2 0 4	3.926	3.911			5.853	0 2 0	w	−1 5 1	2.308	2.308			3.948	−2 0 3
m	−1 1 4	3.739	3.741	3.75	vw	5.830	−2 0 2	vw	6 0 2	2.284	2.284			3.859	1 3 0
vvw	3 1 2	3.632	3.616			5.715	0 0 2	w	−4 4 4	2.192	2.193			3.849	4 2 1
w	−1 3 2	3.494	3.495			5.462	3 1 1	w	−2 2 7	2.110	2.110	2.11	vw	3.825	4 0 2
w	−4 0 4	3.307	3.306	3.31	vw	5.339	2 2 0	w	5 1 4	2.085	2.085			3.810	0 0 3
w	4 2 0	3.293	3.292			5.282	−1 1 2	w	−7 3 2	2.044	2.044			3.802	−4 2 2
w	−5 1 1	3.207	3.209	3.20	vw	5.209	0 2 1	w	1 1 7	2.014	2.013	2.02	vw	3.748	−4 0 3
vs	2 2 3	3.153	3.151	3.16	s	5.110	4 0 1	vw	4 2 5	1.976	1.976			3.746	6 0 1
vw	−3 3 2	3.116	3.119			5.051	−2 2 1	s	6 4 0	1.966	1.966			3.718	−1 1 3
w	4 2 1	3.056	3.052			5.000	−4 0 2	s	−2 4 6	1.962	1.962	1.96	ms	3.707	2 2 2
vw	3 3 1	2.968	2.969			4.967	−3 1 2	vw	0 6 0	1.954	1.953			3.700	−1 3 1
s	0 4 0	2.930	2.930	2.93	ms	4.828	5 1 1	vw	0 6 1	1.936	1.937	1.90	w	3.689	−3 1 3
vvw	−5 1 4	2.844	2.844			4.790	2 0 2	ms	−8 0 6	1.875	1.875			3.659	−7 1 1
w	−2 2 5	2.783	2.784			4.762	5 1 0	ms	4 0 6	1.869	1.869	1.87	m	3.613	1 3 1

superstructure. Such parameters are of questionable significance. A scheme of ordering Nd and vacancies was postulated to rationalize the superstructure, but this scheme was not proved.

We attempted unsuccessfully to use the cell dimensions given by Jamieson et al. (3) for α-NMO to index our α-NMO Guinier data as well as the α-NMO data given by Nassau et al. (2). It would appear that the crystal used by Jamieson et al. (3) either was not single or was not representative of α-NMO.

Contrary to the findings of Nassau et al. (2) we find that α-CMO is isostructural with α-LMO, PMO, and NMO. Since they do not mention precautions to prevent the presence of Ce^{4+}, it appears that their cerium molybdate contained Ce^{4+} instead of Ce^{3+}. This is further supported by the fact that their reported melting point for CMO of 970°C is anomalous compared to that of other Ln molybdates. We find that Ce_2-($MoO_4)_3$ does not melt congruently in air and the melting point of CMO determined under argon is 1035°C which is not anomalous.

Acknowledgment

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