

Preparation and structure of some Ln_2MoO_5 oxides

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Abstract. Ln_2MoO_5 oxides where $\text{Ln}=\text{La, Pr, Nd, Sm, Gd, Tb, Dy, Ho}$ and Y have been prepared by hydrogen-reduction of the corresponding Ln_2MoO_6 at 800–900°C. The lighter Ln_2MoO_5 oxides ($\text{Ln}=\text{La, Pr}$ and Nd) crystallize in a monoclinic Yb_2ReO_5 structure, while the heavier ones along with the yttrium compound are formed in an anion-deficient fluorite type structure. The latter on annealing at 1200°C in vacuum also transform to the Yb_2ReO_5 structure type.

Keywords. Ln_2MoO_5 oxides; preparation and structure.

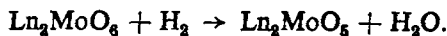
1. Introduction

There is considerable interest in recent years in the study of ternary oxides of Ln_2O_3 – MoO_3 system. Hubert (1974, 1975) has studied pyrochlore type $\text{Ln}_2\text{Mo}_2\text{O}_7$ oxides and elucidated their crystal structures. Recently, compounds of the general formula Ln_2MoO_5 with $\text{Ln}=\text{Dy, Ho, Er, Yb}$ and Y have been prepared by Czeskleba and Tourne (1976). All of them were found to have monoclinic structure isotypic with Yb_2ReO_5 (Muller and Roy 1969). Attempts to prepare similar Ln_2MoO_5 oxides with lighter lanthanides such as Sm, Gd and Tb by solid state reaction between Ln_2O_3 and MoO_3 were unsuccessful (Czeskleba and Tourne 1976). In the present work, several Ln_2MoO_5 oxides with lighter as well as heavier lanthanides ($\text{Ln}=\text{La, Pr, Nd, Sm, Gd, Tb, Dy}$ and Ho) and Y have been prepared by a different method, viz hydrogen-reduction of the corresponding Ln_2MoO_6 oxides and their structure characterized. Among the nine compounds prepared, the first six are reported for the first time.

2. Experimental

Lanthanide oxides (Indian Rare Earths Ltd., purity > 99.9%) and MoO_3 (obtained by decomposition at 500°C of ammonium molybdate, Baker Analyzed Reagent) were ground together in required mole proportions, reacted first at 500°C for 8 hr and later at increasingly higher temperatures upto 1000°C for 2 days with three intermittent grindings to obtain Ln_2MoO_6 oxides (Blasse 1966; Brixner *et al* 1972).

Ln_2MoO_6 oxides were prepared by selective hydrogen-reduction of Ln_2MoO_6 oxides between 800–900°C.

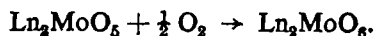


The reduction was carried out in a tubular furnace in flowing hydrogen atmosphere (50 ml/min) for about 60–100 hr at selected temperatures. Completion of the reduction was monitored by weight loss, chemical analysis and x-ray powder diffraction. In certain cases, the products were annealed at a slightly lower temperature than the reduction temperature in hydrogen atmosphere over 7 to 20 days in order to get well-defined x-ray powder diffraction patterns. As we go from La to Ho, reduction of Ln_2MoO_6 to Ln_2MoO_5 occurs at progressively lower temperatures. This is perhaps related to decreasing basicity with decreasing ionic size along the lanthanide series. The pelletised samples of the reduction products as obtained above were sealed in evacuated silica capsules and heated at 1200°C for 24 hr.

A titrimetric analysis was carried out to determine the oxidation state of molybdenum in the samples. For this, a known amount of the reduction product was treated with a known excess of an oxidizing agent ($\text{K}_2\text{Cr}_2\text{O}_7$); after the reaction,



the excess oxidizing agent was determined by titration against Fe^{2+} . The analytical results as well as the reduction temperatures are given in table 1. The oxidation state of molybdenum was also determined by thermogravimetric analysis from the weight gain due to the reaction,



The reduction products as well as the vacuum annealed products were characterized by x-ray powder diffraction with a Phillips Generator PW 1140 using CuK_α radiation. In some cases, x-ray powder diffraction patterns were recorded with Guinier camera and gold powder as internal standard.

Table 1. Preparative temperatures and chemical analyses of Ln_2MoO_6 oxides

Compound	Preparative temperature°C	Analysis of Mo^{4+}	
		Calcd. %	Found %
La_2MoO_6	900	21.14	21.20
Pr_2MoO_6	885	20.96	20.85
Nd_2MoO_6	875	20.66	20.30
Sm_2MoO_6	850	20.13	20.00
Gd_2MoO_6	840	19.56	19.30
Tb_2MoO_6	830	19.43	19.20
Dy_2MoO_6	810	19.15	18.90
Ho_2MoO_6	800	18.97	18.80
Y_2MoO_6	800	27.12	27.00

Table 2. Powder diffraction patterns of La_2MoO_6 , Sm_2MoO_6 and Dy_2MoO_6 (Yb_2ReO_6 type)

<i>hkl</i>	Inten- sity 1	La_2MoO_6		Sm_2MoO_6		Dy_2MoO_6	
		d_{obs} (Å) 2	d_{calc}^a (Å) 3	d_{obs} (Å) 4	d_{calc}^b (Å) 5	d_{obs} (Å) 6	d_{calc}^c (Å) 7
$\bar{2}02, 200$	(w)	3·803	3·798	3·660	3·658	3·575	3·580
013	(vs)	3·382	3·380	3·286	3·283	3·222	3·223
$\bar{2}11$	(vs)	3·314	3·314	3·208	3·206	3·144	3·145
004	(w)	3·082	3·082	2·985	2·984	2·921	2·922
020	(w)	2·975	2·972	2·907	2·907	2·868	2·868
$\bar{2}13, 211$	(w)	2·921	2·919	2·824	2·824	2·768	2·769
$\bar{2}04, \bar{2}02$	(s)	2·863	2·863	2·763	2·764	2·705	2·706
$120, \bar{1}21$	(w)	2·768	2·768	2·702	2·701	2·663	2·662
022	(w)	2·680	2·677	2·613	2·613	2·573	2·574
$\bar{2}22, 220$	(w)	2·341	2·341	2·276	2·276	2·238	2·238
015	(w)	2·276	2·277	2·208	2·208	2·165	2·165
$\bar{2}15, 213$	(vw)	2·256	2·257	2·185	2·184	2·140	2·141
$222, \bar{2}24$	(m)	2·062	2·062	2·003	2·003	1·967	1·968
006	(m)	2·055	2·055	1·990	1·989	1·948	1·948
402	(m)	1·993	1·996	1·921	1·921	1·880	1·880
$\bar{3}23, 320$	(vw)	1·926	1·927	1·868	1·868	n.o.	1·834
033	(vw)	1·784	1·785	1·741	1·742	1·716	1·716
$\bar{2}31$	(w)	1·774	1·775	1·730	1·730	1·705	1·704
$\bar{2}17, 215$	(w)	1·745	1·746	1·690	1·690	1·656	1·656
$\bar{2}26, 224$	(m)	1·715	1·714	1·661	1·663	1·633	1·632
$\bar{4}15, 411$			1·719		1·658		
$\bar{4}06, 402$	(vw)	1·674	1·675	1·617	1·615	1·583	1·581
422	(vw)	1·656	1·657	1·602	1·603	1·572	1·573
$\bar{2}08, 206$	(w)	1·609	1·611	1·559	1·559	1·526	1·526
$\bar{4}24, 420$	(vw)	1·599	1·600	1·547	1·548	1·519	1·518
035	(vw)	1·545	1·545	1·504	1·505	1·479	1·480
$\bar{4}17, 413$	(vw)	1·499	1·501	1·453	1·449	1·416	1·420
315, $\bar{3}18$			1·495				
040	(w)	1·486	1·486	1·453	1·453	1·434	1·434
$\bar{4}08, 404$	(w)	1·432	1·432	1·382	1·382	1·353	1·353
$\bar{5}22$	(vw)	1·404	1·404		1·357		1·330
$\bar{4}33, \bar{4}31$	(vw)	1·395	1·397	1·354	1·356	1·328	1·332
$\bar{2}19, 217$			1·397		1·353		1·325
$\bar{2}37, 235$	(vw)	1·342	1·343	1·306	1·306	n.o.	1·283
044			1·339		1·307		
$\bar{2}44, 242$	(w)	1·319	1·319	1·287	1·286	1·267	1·267

vs = very strong; s = strong; m = medium; w = weak; vw = very weak; n.o. = not observed

$${}^a a_0 = 7.983; \quad b_0 = 5.945; \quad c_0 = 12.958 \text{ \AA}; \quad \beta = 107.94^\circ$$

$${}^b a_0 = 7.685; \quad b_0 = 5.814; \quad c_0 = 12.539 \text{ \AA}; \quad \beta = 107.85^\circ$$

$${}^c a_0 = 7.522; \quad b_0 = 5.735; \quad c_0 = 12.277 \text{ \AA}; \quad \beta = 107.84^\circ$$

3. Results and discussion

X-ray diffraction data (tables 2 and 3) of Ln_2MoO_5 oxides prepared by hydrogen-reduction at 800–900°C reveal that they crystallize in two different crystal structures: (a) monoclinic Yb_2ReO_5 structure for La, Pr and Nd compounds and (b) cubic, fluorite type structure for Gd, Tb, Dy, Ho and Y compounds. The samarium compound shows lines characteristic of both type of structures indicating that it is borderline case.

The diffraction patterns of La_2MoO_5 , Pr_2MoO_5 and Nd_2MoO_5 have been indexed on a monoclinic unit cell by comparison with Yb_2MoO_5 and Yb_2ReO_5 (table 2). The heavier Ln_2MoO_5 ($\text{Ln}=\text{Gd, Tb, Dy, Ho}$ and Y) oxides crystallizing in cubic, fluorite structure did not show any superstructure lines even after prolonged heating at the reduction temperatures in hydrogen atmosphere, indicating that the anion

Table 3. Powder diffraction patterns of Dy_2MoO_5 and Y_2MoO_5 (fluorite type)

<i>hkl</i>	Intensity	Dy_2MoO_5		Y_2MoO_5	
		d_{obs} (Å)	d_{calc}^a (Å)	d_{obs} (Å)	d_{calc}^b (Å)
111	(s)	3.020	3.019	3.005	3.004
200	(m)	2.615	2.614	2.603	2.601
220	(s)	1.849	1.849	1.840	1.840
311	(s)	1.577	1.577	1.569	1.569
222	(w)	1.510	1.509	1.502	1.502
400	(w)	1.307	1.307	1.301	1.301
331	(w)	1.199	1.200	1.193	1.194

$a_0 = 5.229$ Å; $b_0 = 5.203$ Å; s = strong; m = medium; w = weak

Table 4. Unit cell dimensions of Ln_2MoO_5 oxides

Compound	Monoclinic, Yb_2ReO_5 type structure					Cubic, fluorite type structure	
	a_0 (Å)	b_0 (Å)	c_0 (Å)	β°	cell volume V (Å ³)	a_0 (Å)	cell volume V (Å ³)
La_2MoO_5	7.983	5.945	12.958	107.94	585	—	—
Pr_2MoO_5	7.839	5.893	12.753	107.90	561	—	—
Nd_2MoO_5	7.764	5.860	12.672	107.84	549	—	—
Sm_2MoO_5	7.685	5.814	12.539	107.85	533	5.322	150.8
Gd_2MoO_5	7.598	5.781	12.396	107.85	518	5.270	146.4
Tb_2MoO_5	7.558	5.761	12.332	107.85	511	5.245	144.3
Dy_2MoO_5	7.522	5.735	12.277	107.84	504	5.229	143.0
Ho_2MoO_5	7.489	5.725	12.221	107.84	499	5.213	141.7
Y_2MoO_5	7.473	5.719	12.202	107.83	496	5.203	140.9

vacancies in the fluorite lattice are not ordered under the preparative conditions. The indexed powder x-ray data for the fluorite type phases are given in table 3. However, annealing the fluorite type phases at 1200°C in vacuum for 24 hr results in a smooth transformation to the Yb_2ReO_5 structure type. This indicates that the fluorite type phases obtained at lower temperatures are metastable in which the anion vacancies are not ordered. At higher temperatures ($\sim 1200^\circ\text{C}$), ordering of anion vacancies occurs perhaps because of greater mobility resulting in a structural transformation to the more stable Yb_2ReO_5 type. The powder x-ray patterns of all the high temperature phases have been indexed on a monoclinic unit cell (table 2) and the cell dimensions are given in table 4 along with the cell dimensions for cubic, fluorite-type phases. It is of interest to note that La_2MoO_5 , Pr_2MoO_5 and Nd_2MoO_5 obtained

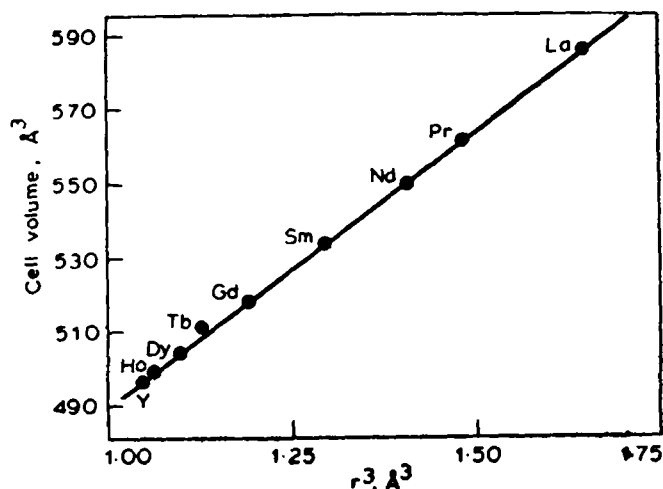


Figure 1. Cell volume vs r^3 for the monoclinic Ln_2MoO_5 compounds (Yb_2ReO_5 type)

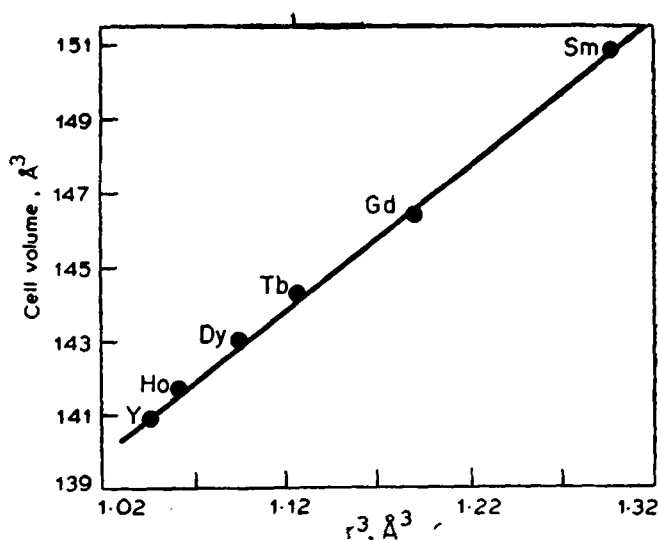


Figure 2. Cell volume vs r^3 for the cubic Ln_2MoO_5 compounds (fluorite type).

in vacancy-ordered Yb_2ReO_5 structure under hydrogen-reduction at $\sim 875\text{--}900^\circ\text{C}$ do not undergo any structural transformation on annealing at $\sim 1200^\circ\text{C}$ in vacuum.

The plot of unit cell volumes for both structure types as a function of r^3 (CN VIII) of lanthanide ions (Shannon and Prewitt 1969) (figures 1 and 2) is linear. Similar linear plots have been obtained for Ln_2MoO_6 (Brixner *et al* 1972) and other ternary lanthanide oxides. Such linear plots of cell volumes vs r^3 indicate that all members of the series are isotypic structurally.

The metastable anion-deficient fluorite type Ln_2MoO_5 phases may be regarded as hypostoichiometric fluorite phases MO_{2-x} (α -phase and $x=0.33$) discussed recently by Eyring and Tai (1976). Such fluorite phases with variable oxygen deficiency are known in the binary oxides of Ce, Pr, Pu, Am, Cm, Bk, etc. and in a number of pseudo-binary systems: $\text{Ln}_2\text{O}_3\text{-ZrO}_2$ (Perez y Jorba *et al* 1961; Collongues *et al* 1965), $\text{Ln}_2\text{O}_3\text{-TiO}_2$ (Collongues *et al* 1965), $\text{Ln}_2\text{O}_3\text{-ReO}_2$ (Ln_4ReO_8 type phases) (Muller and Roy 1969), CaO-ZrO_2 (the phase CaZr_4O_9) (Ray and Stubican 1977) and $\text{Y}_2\text{O}_3\text{-ZrO}_2$ (the phase $\text{Y}_4\text{Zr}_3\text{O}_{12}$) (Ray and Stubican 1977). In all these pseudobinary systems, the fluorite phases have been obtained at high temperatures ($> 1400^\circ\text{C}$) and the anion vacancy-ordered phases at low temperatures ($\sim 1100^\circ\text{C}$). In the present study, the fluorite phases are formed at low temperatures ($< 850^\circ\text{C}$) and the anion vacancy-ordered phases at high temperatures (1200°C). At lower temperatures, the mobilities of both anion vacancies and cations would be much less. At relatively high temperatures (1200°C) the increased mobility of the unit cell constituents results in anion vacancy-ordering. These ordered phases may transform again into the fluorite type vacancy-disordered phases at very high temperatures ($\sim 2000^\circ\text{C}$).

There are at least three different structure types known for A_2BO_5 oxides: Ln_2TiO_5 (Bertaut and Guillen 1966; Müller-Buschbaum and Schenuemann 1973), Sr_2UO_5 (Sawyer 1963; Loopstra and Rietveld 1969) and Yb_2ReO_5 (Muller and Roy 1969). A careful comparison of the x-ray powder diffraction data of monoclinic Ln_2MoO_5 phases reported in this study with those for the three structures indicates that the monoclinic Ln_2MoO_5 oxides belong to the Yb_2ReO_5 family reported by Muller. However, a confirmation must await single-crystal structure analysis.

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