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Studies on the High-pressure Reaction of Rare-earth Sesquioxides with Vanadium Dioxide

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The reaction of rare-earth sesquioxides (Ln_2O_3) with vanadium dioxide (VO_2) at 1400 °C and 50 kbar** and 30 kbar was studied. Quadrivalent vanadium ions were reduced to the trivalent state, rare-earth vanadates (III) ($LnVO_3$) being obtained. For $LnVO_3$ a typical transformation of the ABO_3-type compounds, one from the aragonite-type to the perovskite-type *via* the vaterite- or calcite-type structure was observed with a decrease in the ionic radius of the rare-earth ions. The magnetic properties of the vaterite-type $LnVO_3$ were studied.

We have previously studied the reaction of erbium sesquioxide (Er_2O_3) with vanadium dioxide (VO_2) at 1400 °C and 50 kbar and 30 kbar, and succeeded to obtain vaterite- and calcite-type $ErVO_3$.¹⁾ Under these conditions quadrivalent vanadium ions are unstable and reduced to the trivalent state. $ErVO_3$ with the crystal structure other than the perovskite-type has been first obtained. In this paper, we report on the high-pressure reaction of the rare-earth sesquioxides (Ln_2O_3) with VO_2.

Experimental

The preparative and analytical methods were similar to those described previously.¹⁾

Results and Discussion

The Reaction Products of Ln_2O_3 with VO_2 at High Pressures. The Ln_2O_3–VO_2 mixtures in 1:2 were heated at 1400 °C and 50 kbar or 30 kbar. The atomic ratio of the rare-earth element to vanadium in the products was determined to be 1.0 by the fluorescent X-ray analysis. The valence states of vanadium in the products were estimated from the result of the oxygen analysis, which revealed that the quadrivalent vanadium ions in the products were reduced to the trivalent state and the formulae of the products were $LnVO_3$ in every case.

Crystal Structures of the Products. X-Ray diffraction data for aragonite-type $LaBO_3$²⁾ and the reaction product of the 1:2 mixture of La_2O_3 and VO_2 heated at 50 kbar for 30 min are given in Table 1. Similarity of the X-ray diffraction pattern of $LaVO_3$ to that of the aragonite-type compound suggests that the compound crystallizes in the orthorhombic system, $a=5.869$ Å, $b=8.261$ Å, and $c=5.103$ Å. The structural feature of $LaVO_3$ obtained at 30 kbar was equal to that of the product obtained at 50 kbar.

The crystal structures of $NdVO_3$ and $SmVO_3$ obtained by heating at 50 kbar and 30 kbar for 30 min belonged to the aragonite-type, same as that of $LaVO_3$. The cell parameters were $a=5.703$ Å, $b=8.032$ Å, and $c=5.011$ Å for the neodymium compound, and $a=$

Table 1. X-Ray diffraction results for aragonite-type $LaBO_3$ and $LaVO_3$

$LaBO_3$²⁾	$LaVO_3$
Orthorhombic	
$a=5.872$ Å	$a=5.869$ Å
$b=8.257$ Å	$b=8.261$ Å
$c=5.107$ Å	$c=5.103$ Å

hkl	*d*/Å	*I*	d_{obsd}/Å	d_{calcd}/Å	*I*
011	4.34	20	4.35	4.34	25
020	4.13	10	4.14	4.13	5
111	3.49	100	3.49	3.49	100
120	3.38	55	3.38	3.38	60
200	2.936	20	2.936	2.935	40
210	2.767	8	2.767	2.765	8
002	2.553	20	2.554	2.552	15
201	2.547	12	2.547	2.544	7
211	2.433	40	2.432	2.431	35
031	2.424	25	2.426	2.423	31
220	2.394	14	2.388	2.392	40
112	2.252	10	2.252	2.251	5
022	2.173	12	2.170	2.170	10
040	2.066	8	2.068	2.065	20
122	2.037	45	2.036	2.036	45
140	1.947	20	1.947	1.948	18
202	1.927	20	1.926	1.926	18
231	1.869	35	1.869	1.869	30
311	1.785	20	1.785	1.784	20
320	1.768	14	1.768	1.768	15
222	1.746	8	1.745	1.745	5
240	1.690	6	1.689	1.689	5
113 241	1.6039	14	1.603	1.603 1.603	12
142	1.5482	12	1.548	1.548	8
151	1.5176	10	1.519	1.518	7
213	1.4497	12	1.447	1.449	8
411	1.3906	8	1.389	1.390	6
233	1.2985	10	1.298	1.298	11
431			1.256	1.255	7
252			1.252	1.254	6
104			1.247	1.247	5
342			1.241	1.241	8
351			1.225	1.225	8

** 1 bar$=10^5$ Pa.

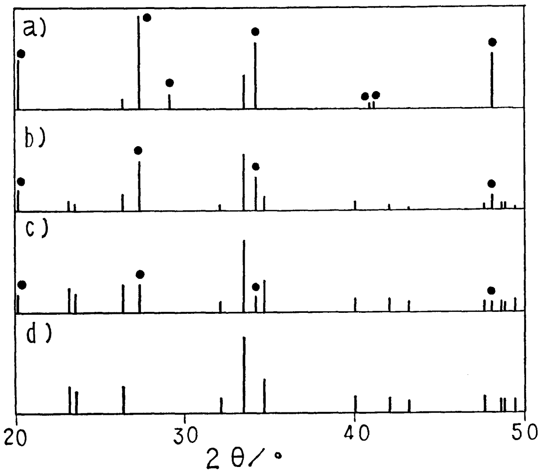

Fig. 1. X-Ray diffraction patterns for Y_2O_3–VO_2 1:2 mixtures at 1400 °C and 50 kbar.
Reaction period; a) 60 min, b) 30 min, c) 10 min, and d) perovskite-type YVO_3.

5.661 Å, b=7.992 Å, and c=5.028 Å for the samarium compound.

The crystal structure of $HoVO_3$ obtained by the reaction of the 1:2 mixture of Ho_2O_3 and VO_2 at 50 kbar for 30 min was isostructural with $HoBO_3$,[2] vaterite-type and belonged to the hexagonal system, while one obtained at 30 kbar was the calcite-type belonging to the rhombohedral (pseudo-hexagonal) system. These results are similar to those of the reaction of Er_2O_3 with VO_2.[1]

The X-ray diffraction patterns of the products obtained by the reaction of Y_2O_3–VO_2 (1:2 mixture) along with that of the perovskite type YVO_3 are shown in Fig. 1. The peaks marked by a dot can be assigned to the vaterite-type crystal. When the reaction was carried out at 1400 °C and 50 kbar for 10 min or 30 min, a mixture of perovskite- and vaterite-type YVO_3 was obtained. A prolonged reaction time (60 min) resulted in a decrease in the perovskite-type and an increase in the vaterite-type compounds.

The reaction product of Dy_2O_3–VO_2 (1:2 mixture) at 50 kbar for 30 min was the perovskite-type crystal including a trace amount of the vaterite-type compound, and those of Y_2O_3–VO_2 and Dy_2O_3–VO_2 (1:2 mixtures) at 30 kbar for 30 min were perovskite-type crystals along with a trace amount of the calcite-type compound. If the reaction time is longer for the Y_2O_3–VO_2 and Dy_2O_3–VO_2 systems, vaterite- or calcite-type crystals will be obtained.

For the reaction products of Eu_2O_3 or Gd_2O_3 with VO_2 their poor crystallinity prevented the determination of their crystal structures.

The reactions between Yb_2O_3, Tm_2O_3, and Lu_2O_3 with VO_2 at high pressures gave perovskite-type oxides.

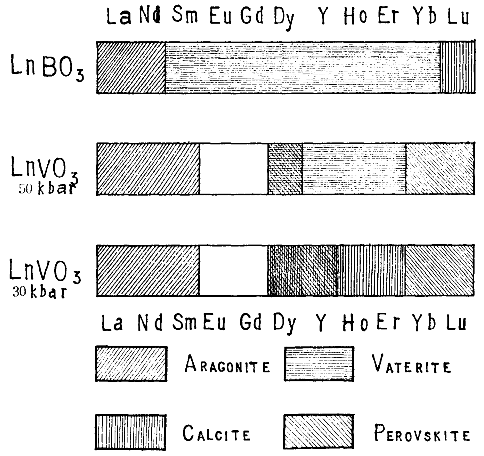

Fig. 2. Crystal structures for $LnVO_3$ and $LnBO_3$.[2]

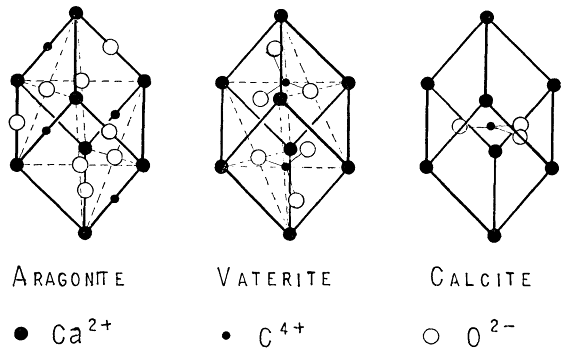

Fig. 3. Comparison of the idealized three structure types of calcium carbonate.

Table 2. Lattice constants and the specific gravity of $LnVO_3$

	Type	a/Å	b/Å	c/Å	S.G.
$LaVO_3$	Aragonite	5.869	8.261	5.103	6.41
	Perovskite	5.548		7.846	6.57
$NdVO_3$	Aragonite	5.703	8.032	5.011	7.07
	Perovskite	5.466	5.569	7.735	6.89
$SmVO_3$	Aragonite	5.661	7.992	5.028	7.31
	Perovskite	5.400	5.591	7.680	7.17
YVO_3	Vaterite	3.779		8.809	5.75
	Perovskite	5.274	5.590	7.579	5.61
$HoVO_3$	Vaterite	3.783		8.792	8.09
	Calcite	4.93		16.47	7.61
	Perovskite	5.281	5.591	7.582	7.86
$ErVO_3$	Vaterite	3.762		8.790	8.24
	Calcite	4.929		16.429	7.70
	Perovskite	5.263	5.585	7.557	7.99

The crystal structures of the high-pressure products as well as those of the rare-earth borates are summarized in Fig. 2. As is well known aragonite, vaterite and calcite are modifications of calcium carbonate (Fig. 3). The rare-earth borate transforms from the aragonite-type to the calcite-type structure *via* the vaterite-type structure with a decrease in ionic radius of the rare-earth ions. For the rare-earth vanadates(III) a typical transformation observed for the ABO_3-type compounds,[3] one from the aragonite-type to the perovskite-type *via* the vaterite- or calcite-type structure was observed with a decrease in ionic radius of the rare-earth ions. That the crystal structure of the rare-earth vanadates(III) depends on the reaction pressure will be due to the difference in the compres-

TABLE 3. MAGNETIC PROPERTIES OF THE VATERITE-TYPE $LnVO_3$

$LnVO_3$	Magnetic moment/μ_B				Transition temp	
	For $LnVO_3$		For Ln^{3+}	Per one vanadium ion at 4.5 K		
	$T>T_N$	$T_N>T>T_C$			T_N/K	T_C/K[a]
YVO_3	1.9	—	—	1.2	30	16
$HoVO_3$	9.8	10.5	10.5	1.7	35	13
$ErVO_3$	8.8	9.3	9.4	1.6	65	12

a) T_C were determined from the plots of σ^3 *vs.* T.

sibilities of the vanadium and rare-earth ions, and at high pressure, the vanadium ions are more compressible than the rare-earth ions.

The cell parameters and the density calculated from X-ray diffraction data of the high-pressure synthesized crystals are summarized in Table 2 along with those of the perovskite-type vanadates(III).[4] In general, the increase in pressure tends to stabilize the denser phase, and the most dense ABO_3 phase is considered to have the cubic-perovskite structure.[5] $LnVO_3$ with the perovskite-type structure are orthorhombically distorted from the ideal cubic perovskite structure, and the distortion increases with decrease in the ionic radius of the rare-earth ions.[4] Since packing of the ions in the perovskite-type crystals is insufficient because of the distortion, aragonite- and vaterite-type $LnVO_3$ crystals except $LaVO_3$ have a larger density than that of perovskite-type $LnVO_3$.

Magnetic Properties of the Vaterite-type $LnVO_3$. The magnetic susceptibility measurements were performed in the temperature range 4.5—300 K. The magnetic properties of the vaterite-type YVO_3, $HoVO_3$, and $ErVO_3$ are summarized in Table 3. As the observed values of the magnetic moment for these crystals are close to those for Ln^{3+}, V^{3+} ions order antiferromagnetically in the temperature range from T_N to T_C, and the observed transformations at high temperature are attributable to their antiferromagnetic ordering. All the compounds with the vaterite-type structure were paramagnetic, the magnetic susceptibility following the Curie-Weiss law above the Neel temperature, T_N. Below the temperature, T_C, they showed ferromagnetic behavior. The value of the magnetic moment at 4.5 K suggests that this transition is attributable to the rearrangement of the antiferromagnetically ordered V^{3+} ions to the ferromagnetic state.

References

1) T. Shin-ike, G. Adachi, J. Shiokawa, M. Shimada, and M. Koizumi, *Bull. Chem. Soc. Jpn.*, **53**, 3563 (1980).

2) E. M. Levin, R. S. Roth, and J. B. Martin, *Am. Mineral.*, **46**, 1030 (1960).

3) R. Kiriyama and H. Kiriyama, "Structural Inorganic Chemistry II," Kyoritsu, Tokyo (1970), p. 8.

4) T. Sakai, G. Adachi, J. Shiokawa, and T. Shin-ike, *Mater. Res. Bull.*, **11**, 1295 (1976).

5) J. B. Goodenough, J. A. Kafalas, and J. M. Longo, "High-Pressure Synthesis," Academic Press, Inc., New York (1972).