December, 1980] © 1980 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 53, 3563—3566 (1980) 3563

Studies on High-pressure Reaction of Er_2O_3 or Yb_2O_3 with VO_2

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(Received April 22, 1980)

The reaction of erbium sesquioxide (Er_2O_3) or ytterbium sesquioxide (Yb_2O_3) with vanadium dioxide (VO_2) at 1400 °C and 50 kbar and 30 kbar pressures was studied. Quadrivalent vanadium ions were reduced to the trivalent state, erbium vanadite ($ErVO_3$) or ytterbium vanadite ($YbVO_3$) being obtained. The crystal structure of $ErVO_3$ obtained at 50 kbar pressure was vaterite-type isostructural with $ErBO_3$ belonging to a hexagonal system, and that obtained at 30 kbar calcite-type belonging to a rhombohedral (pseudo-hexagonal) system. In the reaction of Yb_2O_3 with VO_2 at high pressure, a perovskite-type crystal was obtained. The electrical and magnetic properties of the vaterite- and the calcite-type $ErVO_3$ were studied.

Success in the synthesis of a diamond has encouraged studies on high-pressure syntheses for the development of new functional materials. In general, increase in pressure tends to stabilize dense phase and lower valence state.[1] It is considered that the most dense ABO_3 phase has cubic-perovskite structure. Rare-earth vanadites ($LnVO_3$) obtained by the reaction of rare-earth sesquioxides (Ln_2O_3) and divanadium trioxide (V_2O_3) at atmospheric pressure are perovskite-type compounds isostructural with orthorhombic $GdFeO_3$.[2] When the reactions were carried out at high pressures, the products were perovskites isomorphous with those obtained by synthesis at atmospheric pressure, their density not depending on pressure.[3]

Pyrochlore-type ytterbium vanadite ($Yb_2V_2O_7$) was obtained by the reaction of ytterbium sesquioxide (Yb_2O_3) and vanadium dioxide (VO_2) at 1400 °C in a vacuum. However, a mixture of perovskite-type $ErVO_3$ and zircon-type $ErVO_4$ was obtained under the same conditions by the reaction between erbium sesquioxide (Er_2O_3) and vanadium dioxide.[4] When the reaction of Er_2O_3 or Yb_2O_3 with VO_2 is carried out at high pressure, the quadrivalent vanadium ions are expected to be reduced to form a type of erbium or ytterbium vanadite ($ErVO_3$ or $YbVO_3$) differing from that of perovskite compounds.

Experimental

Materials. Erbium and ytterbium sesquioxides (Er_2O_3 and Yb_2O_3) (minimum purity 99.9%, Shin-etsu Kagaku Co. Ltd.) were ignited at 1200 °C in order to remove volatile constituents. Divanadium trioxide (V_2O_3) and divanadium pentaoxide (V_2O_5) of special reagent grade were used without further purification. Vanadium dioxide (VO_2) was prepared by heating V_2O_3–V_2O_5 1 : 1 mixture at 1000 °C in a vacuum furnace for 4 h.[5]

Procedure. Er_2O_3 or Yb_2O_3 and VO_2 in 1 : 2 mixtures were weighed and ground with an aluminum mortar and then placed in a cell (Fig. 1). The reactions were carried out at 1400 °C and 50 and 30 kbar pressures with a 15 mm diam. cubic anvil-type apparatus.[6] The samples were subjected to pressure before the temperature was raised. After being kept at 1400 °C for a certain time, the samples were cooled under pressure. The pressure was then released and the products were subjected to X-ray powder-diffraction analysis.

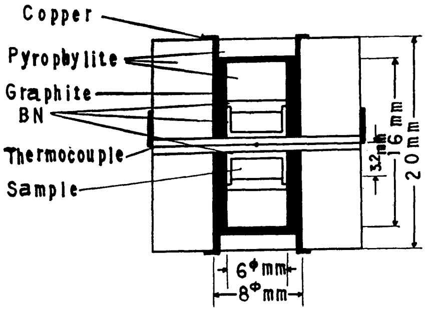

Fig. 1. Cell assemblage for a cubic anvil type high pressure apparatus.

Analysis. The analysis was carried out with a Rigaku Denki Geiger-Flex D-6C diffractometer, using Ni-filtered Cu-K_α radiation ($\lambda = 1.5418$ Å) at a scanning rate of 0.25° (2θ)/min. The diffractometer was calibrated with high-purity silicon.

The atomic ratio of rare-earth to vanadium in the products was determined by fluorescent X-ray analysis with a Rigaku Denki Fluorescent X-ray Analysis Unit.

The valence states of vanadium in the products were inferred from oxygen analysis, which was carried out by igniting the samples in an oxygen stream in order to oxidize all the vanadium ions in the products completely to V^{5+} and calculating their oxygen contents from the weight gain.

Measurements of the Physical Properties. The electrical conductivity measurements were carried out at room temperature (18±1 °C) using polycrystalline pellets, diam. *ca.* 4 mm and thickness 1 mm, by a d.c. two-probe method.

The magnetic suceptibility was measured with a Shimadzu magnetic balance MB-11 equipped with a low temperature apparatus built by members of the Shiokawa Laboratory in the temperature range 4—300 K.

Results and Discussion

The Reaction Products of Er_2O_3 or Yb_2O_3 with VO_2 at High Pressures. Er_2O_3 or Yb_2O_3–VO_2 1 : 2 mixtures were heated at 1400 °C and 50 or 30 kbar pressure. The atomic ratio of erbium or ytterbium to vanadium in the products was determined to be 1.0 by fluorescent X-ray analysis. The valence states of vanadium in the products were inferred from oxygen analysis. The results of oxygen analysis, valence states of vanadium ions and formulas of products obtained by high-pressure

TABLE 1. RESULTS OF OXYGEN ANALYSIS

Starting materials	Reaction conditions	Weight gain %	Valence state of V	Formula
$Er_2O_3+2VO_2$	1400 °C 50 kbar 30 min	5.93	3.0	$ErVO_{3.0}$
$Er_2O_3+2VO_2$	1400 °C 30 kbar 30 min	5.88	3.0	$ErVO_{3.0}$
$Yb_2O_3+2VO_2$	1400 °C 50 kbar 30 min	4.71	3.4	$YbVO_{3.2}$
$Yb_2O_3+2VO_2$	1400 °C 30 kbar 30 min	4.34	3.5	$YbVO_{3.3}$
$Yb_2O_3+2VO_2$	1400 °C 50 kbar 60 min	5.86	3.0	$YbVO_{3.0}$
$Yb_2O_3+2VO_2$	1400 °C 30 kbar 60 min	5.45	3.1	$YbVO_{3.1}$

synthesis are given in Table 1. We see that quadrivalent vanadium ions are reduced gradually to the trivalent states, formulas of the products being eventually $ErVO_3$ or $YbVO_3$.

X-Ray Diffraction Results. X-Ray diffraction data for vaterite (μ-$CaCO_3$)-type $ErBO_3$[7] and the reaction product of 1 : 2 mixtures of Er_2O_3 and VO_2 at 50 kbar are given in Table 2. The fact that the X-ray diffraction pattern for $ErVO_3$ is similar to that of the vaterite-type compound suggests that the compound crystallizes in the hexagonal space group $P6_3/mmc$, $a_0=3.762$ Å and $c_0=8.790$ Å.

X-Ray diffraction data for calcite-type $LuBO_3$[7] and $ErVO_3$ at 30 kbar are given in Table 3. Since the X-ray diffraction pattern for $ErVO_3$ is similar to that of calcite-type $LuBO_3$, the compound seems to crystallize in the rhombohedral (pseudo-hexagonal) space group $R\bar{3}c$-D_{3d}^6, $a_0=4.929$ Å and $c_0=16.429$ Å.

The density of $ErVO_3$ calculated from X-ray diffraction data was 7.99 g/cm³ for the perovskite-type,[8] 7.68 g/cm³ for the calcite-type and 8.25 g/cm³ for the vaterite-type structure. It is the first time that $ErVO_3$ with

TABLE 2. X-RAY DIFFRACTION DATA DOR VATERITE-TYPE $ErBO_3$ AND $ErVO_3$

	$ErBO_3$[7] Vaterite-type hexagonal $a_0=3.761$ Å $c_0=8.790$ Å		$ErVO_3$ $a_0=3.762$ Å $c_0=8.790$ Å		
hkl	*d*	*I*	d_{obsd}	d_{calcd}	*I*
002	4.38	30	4.39	4.40	90
100	3.25	100	3.25	3.26	100
101	3.05	12	3.05	3.05	5
102	2.62	75	2.62	2.62	70
004	2.20	8	2.20	2.20	20
103	2.18	2	—		—
110	1.880	40	1.880	1.881	42
104	1.821	30	1.820	1.821	30
112	1.729	30	1.728	1.729	20
200	1.629	14	1.629	1.629	15
202	1.527	18	1.527	1.527	12
006	1.462	2	1.465	1.465	5
114	1.429	8	1.429	1.429	7
106	1.335	6	1.335	1.336	11
204	1.309	8	1.308	1.309	4
210	1.231	8	1.232	1.231	5
212	1.186	12	1.186	1.186	8
116	1.155	4	1.156	1.156	2
008	—	—	1.099	1.099	6
300	1.086	6	1.087	1.086	7
214	1.074	6	1.073	1.074	5
302	1.055	4	1.055	1.054	3

TABLE 3. X-RAY DIFFRACTION DATA FOR CALCITE-TYPE $LuBO_3$ AND $ErVO_3$

	$LuBO_3$[7] Calcite-type pseudo-hexagonal $a_0=4.913$ Å $c_0=16.214$ Å		$ErVO_3$ $a_0=4.929$ Å $c_0=16.429$ Å		
hkl	*d*	*I*	d_{obsd}	d_{calcd}	*I*
012	3.76	95	3.78	3.79	80
104	2.933	100	2.96	2.96	100
006	2.699	10	2.73	2.74	10
110	2.453	55	2.47	2.47	30
113	2.235	8	2.25	2.25	7
022	2.057	45	2.07	2.07	32
024	1.883	25	1.890	1.894	15
018	1.828	30	1.850	1.851	20
116	1.817	55	1.833	1.832	30
122	1.577	25	1.585	1.583	10
$10\underline{10}$	1.515	10	1.534	1.533	8
214	1.495	25	1.504	1.502	10
208	1.468	12	—		—
300	1.418	14	1.425	1.423	5
$00\underline{12}$	1.351	4	—		—
$02\underline{10}$	1.290	6	1.302	1.302	4
128	1.260	10	1.269	1.269	4
306	1.256	12	1.262	1.263	5
220	1.228	6	1.232	1.232	2
$11\underline{12}$	1.184	8	1.197	1.197	8
312	1.168	8	—		—
$21\underline{10}$	1.142	8	1.153	1.151	4
134	1.133	8	1.139	1.138	5

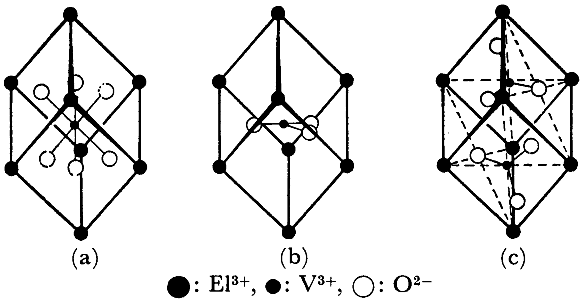

Fig. 2. Comparison of the three structure types of $ErVO_3$.
(a) : Perovskite, (b) : calcite, (c) vaterite.

density greater than that of perovskite has been obtained. The coordination of atoms in these three structure types is given in Fig. 2. In the vaterite-type structure (Fig. 2(c)), two vanadium ions and two of six oxygen ions are at the center of the faces, two of the oxygen ions in the unit cell, the remainder being out of the cell of the hexahedron consisting of eight erbium ions. $ErVO_3$ having calcite-type or vaterite-type structure, is a salt of Er^{3+} with $VO_3{}^{3-}$, rather than a mixed oxide of Er_2O_3 with V_2O_3 as in the perovskite-type $ErVO_3$.

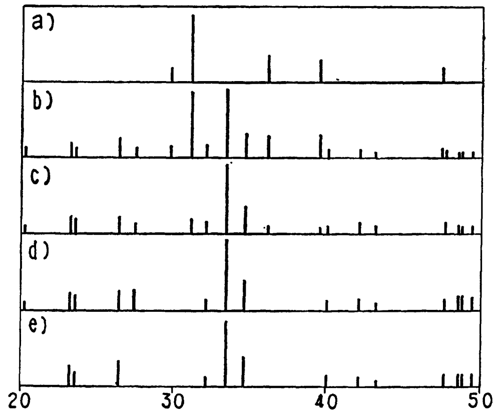

Fig. 3. X-Ray diffraction patterns.
a): Pyrochlore-type $Yb_2V_2O_7$, b): product obtained at 50 kbar for 30 min, c): product obtained at 50 kbar for 60 min, d): product obtained by reheating of c) at 1400 °C in a vacuum for 3 h, e): perovskite-type $YbVO_3$.

The X-ray diffraction patterns of the products obtained by the reaction of Yb_2O_3–VO_2 1 : 2 mixtures along with that of the pyrochlore-type $Yb_2V_2O_7$ and the perovskite-type $YbVO_3$ are shown in Fig. 3. When the reaction was carried out at 1400 °C and 50 kbar pressure for 30 min, a mixture of pyrochlore-type $Yb_2V_2O_7$ and perovskite-type $YbVO_3$ was obtained (Fig. 3(b)). It can be seen that the longer reaction time results in a decrease in $Yb_2V_2O_7$ and an increase in $YbVO_3$. In the reaction of Yb_2O_3 with VO_2, pyrochlore-type $Yb_2V_2O_7$ would be formed first and then transformed into a perovskite-type crystal gradually evolving its oxygen.

Crystal-structures Consideration. Rare-earth vanadites obtained from the reaction of rare-earth sesquioxides and divanadium trioxide at atmospheric or high pressure are perovskite-type compounds isomorphous with orthorhombic $GdFeO_3$. In the case of the reaction of Yb_2O_3 with VO_2 at high pressure, a pyrochlore-type compound $Yb_2V_2O_6O'$ (Fig. 4) is formed first. In this structure, V^{4+} ions occupy corner-shared octahedra and Yb^{3+} ions occupy an eightfold, hexagonal-bipyramid interstice. Two types of tetrahedrally coordinated anions can be distinguished: O^{2-} anions having two Yb^{3+} and two V^{4+} ions as near-neighbors; and O'^{2-} anions having four Yb^{3+} as near-neighbours. The O'^{2-} anions are located at the top and bottom of the apex-shared hexagonal bipyramids. The unique O'^{2-} anion might disappear at high pressure.

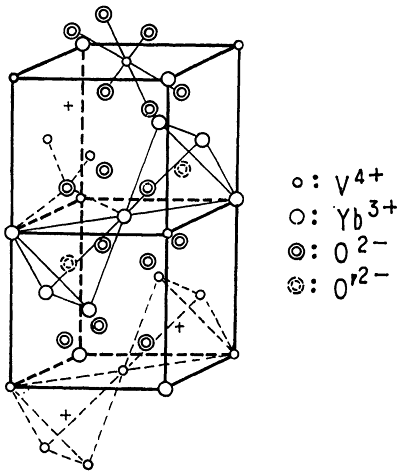

Fig. 4. Idealized crystal structure of a pyrochlore-type $Yb_2V_2O_6O'$ derived from a fluorite-type structure.

The defect pyrochlore $Yb_2V_2O_6$, in which a large electrostatic repulsion between Yb^{3+} cations facing each other across the anion vacancy is introduced, would be transformed easily into a perovskite-type $YbVO_3$ as the tolerance factor of the former was within the limit of perovskite-forming. The reaction product between Yb_2O_3 with VO_2 was a pyrochlore at atmospheric pressure and a perovskite at high pressure. However, in the case of the erbium sesquioxide, the radius ratio, r_{Er}/r_V is so great that no pyrochlore-type structure is formed.[4] It seems that the intermediate phase in the reaction of Er_2O_3 with VO_2 contains no octahedral-site vanadium as in the pyrochlore structure but V_2O_7 clusters of corner-shared tetrahedra or chains of paired trigonal bipyramidal sites sharing corners along a chain and between pairs. Elimination of shared O^{2-} ions would produce $VO_3{}^{3-}$ clusters, leading to a calcite or vaterite structure.

Physical Properties of $ErVO_3$. The electrical conductivity at 18 °C was 1×10^{-3}, 2×10^{-7} and 1×10^{-7} $\Omega^{-1}\,cm^{-1}$ for perovskite-, calcite- and vaterite-type $ErVO_3$, respectively. The conductivity for calcite- or vaterite-type $ErVO_3$ was much lower than that for perovskite-type $ErVO_3$. This can be interpreted as follows: for perovskite-type $ErVO_3$ electrons are conducted by small polarons produced by anion defects,[8] while calcite- and vaterite-type $ErVO_3$ are salts of Er^{3+} with $VO_3{}^{3-}$.

Magnetic susceptibility measurements were carried out in the temperature range 4—300 K. Data for perovskite-type $ErVO_3$ and products obtained by high-pressure synthesis are summarized in Table 4. The

TABLE 4. SUMMARY OF MAGNETIC PROPERTIES

	Magnetic moment (μ_B)		T_N (K)
Perovskite-type $ErVO_3$	10.0	$T>110$ K	109
	9.3	$T<50$ K	
Calcite-type $ErVO_3$	8.9	$T>70$ K	65
	9.3	$T<50$ K	
Vaterite-type $ErVO_3$	8.8	$T>65$ K	65
	9.3	$T<50$ K	

fact that all the observed values of the magnetic moment for $ErVO_3$ at low temperatures are close to that for Er^{3+} ($\mu_{\mathrm{Er}^{3+}}=9.4\ \mu_{\mathrm{B}}$) shows that V^{3+} ions order antiferromagnetically at low temperature, and therefore, the observed transitions are attributable to antiferromagnetic ordering of the V^{3+} ions. The perovskite-type $ErVO_3$ is an antiferromagnet with a weak ferromagnetism because of antisymmetric exchange interaction below the transition temperature.[9] All the compounds were paramagnetic, the magnetic susceptibility following the Curie-Weiss law above the transition temperature.

The observed value of the magnetic moment for the perovskite-type $ErVO_3$ above the transition temperature is in good agreement with the calculated value ($\mu_{\mathrm{cal}}=9.8\ \mu_{\mathrm{B}}$), if we assume that there was no magnetic interaction between Er^{3+} ions and V^{3+} ions. However, the values for the calcite-type and the vaterite-type $ErVO_3$ are smaller than the calculated ones. The value of μ_{cal} was calculated by

$$\mu_{\mathrm{cal}} = \sqrt{\mu^2_{\mathrm{Er}^{3+}} + \mu^2_{\mathrm{V}^{3+}}}$$

where $\mu_{\mathrm{Er}^{3+}}=9.4\ \mu_{\mathrm{B}}$ and $\mu_{\mathrm{V}^{3+}}=2.8\ \mu_{\mathrm{B}}$. The peculiar magnetic property of these compounds would be interpreted by means of the following. There is a magnetic interaction between an Er^{3+} ion and a V^{3+} ion to make their spins align antiparallel in a unit of $ErVO_3$ (Fig. 5). The net magnetic moment takes the value shown by dotted lines in the figure. The value calculated by $\mu_{\mathrm{cal}}=\sqrt{\mu^2_{\mathrm{Er}^{3+}}-\mu^2_{\mathrm{V}^{3+}}}$ is 8.9 μ_{B}, being in good agreement with the observed one for the calcite- and vaterite-type $ErVO_3$.

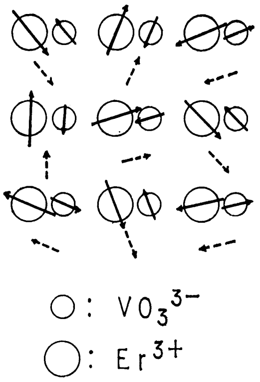

Fig. 5. Proposed orientation of the magnetic moment for the vaterite- or the calcite-type $ErVO_3$ above the transition temperature.

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