BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 1878—1880 (1973)

The Synthesis of Some New Europium(II) Vanadites

Tsutomu Shin-ike, Ginya Adachi,* and Jiro Shiokawa*

Department of Chemistry, Osaka Dental Universtiy, Makino-honmachi, Hirakata-shi, Osaka 573

(Received May 12, 1972)

This paper is concerned with the preparation of some new europium (II) double oxides by reactions between europium (II) and vanadium (III) oxides, and with the determination of their crystal structures.

Europium (III) double oxides with vanadium have been prepared previously,[1,2] but no report has appeared regarding the double oxide containing the bivalent europium ion.

We succeeded in synthesizing the double oxides containing the bivalent europium ion. The crystal structures of the double oxides were determined by an X-ray diffraction method.

Experimental

Materials. Europium sesquioxide of a 99.9% purity from the Lindsay Chemical Division, American Potash & Chemicals, vanadium trioxide of a special reagent grade, and graphite of a spectroscopic grade were all used without further purification.

The europium mono-oxide (EuO) was prepared by reducing europium sesquioxide with graphite, as has been described in the literature.[3]

Procedure. The europium mono-oxide was thoroughly mixed with vanadium trioxide by grinding in a mortar, and then pressed at 100 kg/cm^2 to a pellet. The pellet was placed in a graphite crucible and heated in an induction furnace at 1500 °C for a few minutes *in vacuo* ($\sim 10^{-4}$ mmHg).

Analyses. X-Ray diffraction patterns of the products were obtained with a Rigaku Denki Geiger-Flex D-6C diffractometer, using Ni-filtered Cu-Kα radiation at a scanning rate of 1° (2θ)/min.

The atomic ratios of europium to vanadium were determined by means of a Rigaku Denki X-ray fluorescent spectrograph unit with an NaI(Tl) scintillator, a tungsten target X-ray tube, and a lithium fluoride analyzing crystal.

Results and Discussion

The products, the color of which was black, were examined by the X-ray diffraction method. The X-ray diffraction patterns of the samples and the analyzed atomic ratios of europium to vanadium are shown in Fig. 1. The X-ray diffraction pattern, shown in Fig. 1 (a), is similar to that of Eu_2TiO_4,[4] which belongs to a tetragonal system. It seems, therefore, that the crystal structure of this compound is the same as that of Eu_2TiO_4. The arrangement of the ions in this compound may be considered to consist of alternate layers of rocksalt EuO and perovskite $EuVO_3$, as is shown in Fig. 2. Thus, by assuming that the unit cell dimensions of the product are $a_0=3.856$ Å and

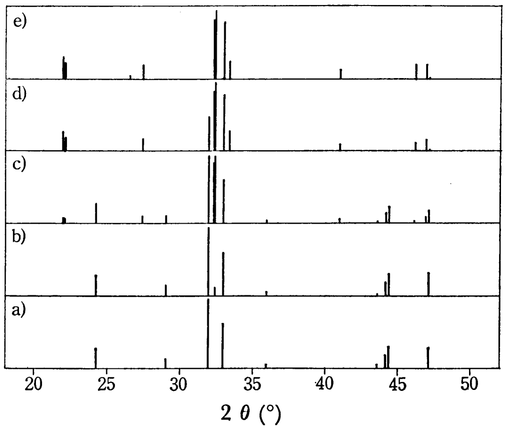

Fig. 1. X-Ray diffraction patterns
Observed Atomic Ratios of Eu: V
a) 1.0: 0.5, b) 1.0: 0.8, c) 1.0: 0.9, d) 1.0: 1.0, e) 1.0: 2.0.

---

* Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadakami, Suita-shi, Osaka.

[1] W. O. Milligan and L. W. Vernon, *J. Phys. Chem.*, **56**, 145 (1952).

[2] A. Wold and R. Ward, *J. Amer. Chem. Soc.*, **76**, 1029 (1954).

[3] M. W. Shafer, *J. Appl. Phys.*, **36**, 1145 (1965).

[4] G. J. McCarthy, W. B. White, and R. Roy, *J. Inorg. Nucl. Chem.*, **31**, 329 (1969).

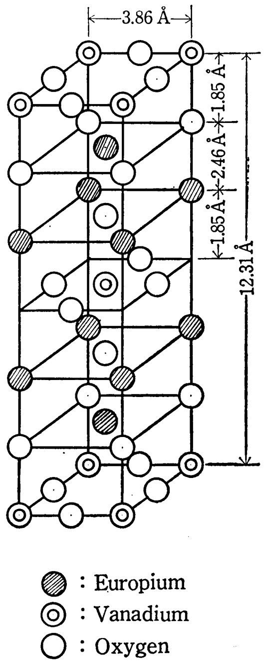

Fig. 2. The proposed structure of Eu_2VO_4

c_0=12.312 Å (in a tetragonal system), the interplanar spacing values (*d*-values) and the relative intensities were calculated. Both the calculated and the observed values are shown in Table 1.

TABLE 1. POWDER DIFFRACTION RESULTS
(Tetragonal system; a_0=3.856Å, c_0=12.312Å)

hkl	*d*(Å) (obsd)	2*θ* (obsd)	*d*(Å) (calcd)	*I*[a] (obsd)	*I*[a] (calcd)
002	—	—	6.155	—	0.4
101	3.681	24.2	3.680	28	28
004	3.079	29.0	3.078	14	14
103	2.809	31.9	2.810	100	100
110	2.722	32.9	2.726	55	62
112	2.493	36.0	2.493	7	6
105	2.076	43.6	2.075	9	3
006	2.049	44.2	2.052	20	12
114	2.041	44.4	2.041	30	31
200	1.928	47.1	1.928	29	31
211	1.709	53.6	1.708	5	5
204	1.636	56.2	1.634	15	9
107	1.600	57.6	1.600	20	10
213	1.590	58.0	1.590	30	36
008	—	—	1.539	—	2
215	1.408	66.4	1.412	15	1
206			1.405		13

a) Relative intensities.

The density of this compound as observed by the conventional pycnometric method was 3.76 g cm^{-3}, very close to the value of 3.79 g cm^{-3} calculated using the unit cell dimensions and supposing the existence of two molecules of Eu_2VO_4 per unit cell.

TABLE 2. X-RAY DIFFRACTION POWDER DATA FOR $Eu_3V_2O_7$
(Tetragonal system; a_0=3.94Å, c_0=19.52Å)

hkl	*d*(Å) (obsd)	2*θ* (obsd)	*d*(Å) (calcd)	I/I_0
101	3.86	23.1	3.86	15
103	3.37	26.5	3.37	5
006	3.25	27.4	3.25	40
110	2.78	32.2	2.78	90
105	2.77	32.3	2.77	100
112	—	—	2.68	—
008	—	—	2.44	—
114	2.42	37.2	2.42	5
107	—	—	2.28	—
116	2.11	42.8	2.11	10
200	1.97	46.1	1.97	50
0010	1.96	46.6	1.95	50
202	1.92	47.1	1.93	20
109	1.90	47.9	1.90	5
204	1.83	50.0	1.83	5

(I/I_0=relative intensities)

When this compound was heated at 1400 °C *in vacuo* for more than 10 min, the peaks in the X-ray pattern assigned to Eu_2VO_4 gradually disappeared, while new peaks appeared. These peaks seemed to be due to another new double oxide, $Eu_3V_2O_7$, in which a rocksalt-type EuO might be located at every two layers of perovskite-type $EuVO_3$. The X-ray diffraction data, given in Table 2, are indexed on a tetragonal cell with a_0=3.94 Å and c_0=19.52 Å. The reason why $Eu_3V_2O_7$ was formed may be that EuO was volatile at high temperatures, if so, the following reactions would occur:

$$2Eu_2VO_4 \longrightarrow Eu_3V_2O_7 + EuO\uparrow \qquad (1)$$

The $Eu_3V_2O_7$ does not seem to be quite stable at such high temperatures, since the X-ray pattern of this compound gradually disappeared during the long period of heating. The final product was $EuVO_3$, which has the same distorted perovskite structure as the lanthanide-vanadites.[5] The $EuVO_3$ must be formed as follows:

$$Eu_3V_2O_7 \longrightarrow 2EuVO_3 + EuO\uparrow \qquad (2)$$

The cell constants of $EuVO_3$ were a_0=3.88 Å, b_0=3.84 Å, c_0=3.88 Å, and β=92.50° in a monoclinic system. Both the calculated and the observed *d*-values are shown in Table 3.

TABLE 3. X-RAY DIFFRACTION POWDER DATA FOR $EuVO_3$
(Monoclinic system; a_0=3.88Å, c_0=3.88Å, b_0=3.84Å, β=92.50°)

hkl	*d*(Å) (obsd)	2*θ* (obsd)	*d*(Å) (calcd)	Intensities
001	3.89	22.9	3.88	m
010	3.84	23.1	3.84	w
011	2.73	32.8	2.73	s
101	2.69	33.3	2.68	m
111	2.20	41.0	2.20	w
002	1.94	46.8	1.94	w
020	1.92	47.5	1.92	w
012	1.73	53.1	1.73	w
021	1.72	53.2	1.72	m
102	1.71	53.6	1.70	w
121	1.561	59.2	1.561	m
112			1.558	
022	1.365	68.8	1.364	w

---

[5] S. Geller, *Acta Crystallogr.*, **10**, 219 (1957).

When the Eu_2VO_4 prepared was heated in air, both $EuVO_4$ and Eu_2O_3 were formed by oxidation. This fact was confirmed by X-ray diffraction analyses. If the following reaction is supposed to occur, the weight gain should be 5.73%:

$$2Eu_2VO_4 + \frac{3}{2}O_2 \longrightarrow 2EuVO_4 + Eu_2O_3 \qquad (3)$$

The observed weight gain, on the contrary, was 7.8% Therefore, it seems that the product was a non-stoichiometric compound, like Eu_2VO_{4-x} $(0.5 \geq x \geq 0)$, in which the oxygen-deficient perovskite-type $EuVO_{3-x}$ was contained, and that the reaction was as follows:

$$4EuO + V_2O_3 \longrightarrow 2Eu_2VO_{3.5} \qquad (4)$$

If excess vanadium trioxide was added, or if the reaction time was prolonged, both Eu_2VO_4 and $Eu_3V_2O_7$ were formed (see Fig. 1 (b)). If much more vanadium trioxide was used, $EuVO_{3-x}$ was formed in addition to Eu_2VO_4 and $Eu_3V_2O_7$ (see Fig. 1 (c) and (d)).

By another procedure, one in which Eu_2O_3, V_2O_3, and graphite were mixed together, in spite of using EuO and V_2O_3, and then heated in an induction furnace at 1400 °C for an hour *in vacuo*, Eu_2VO_{4-x} was also obtained.