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A New Monoclinic Phase of Cerium Orthovanadate ($CeVO_4$)

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A new monoclinic phase of cerium orthovanadate, $CeVO_4$(H), was found during the course of oxidation of pseudo-perovskite $CeVO_3$ below 400°C. It has been confirmed to crystallize in the huttonite-type structure (C_{2h}^5—$P2_1/n$), that of $LaVO_4$. The lattice parameters were determined to be:

$$a_0 = 6.98\text{Å},\ b_0 = 7.22\ \text{Å},\ c_0 = 6.76\ \text{Å},\ \beta = 105°02',\ V{=}328\ \text{Å}^3 \text{ and } Z = 4.$$

This phase was metastable, and exothermally transformed into a known stable $CeVO_4$ (tetragonal zircon-type, D_{4h}^{19}-$I4_1/amd$) above 400°C, releasing a small amount of oxygen. From magnetic, chemical and thermogravimetric analyses, the valences of cerium ion and vanadium ion in $CeVO_4$(H) seem to be tripositive and pentapositive respectively, but V^{4+} ion is mixed in zircon-type $CeVO_4$; $CeVO_4$(Z).

It has been reported[1–7] that all rare earth (except La) orthovanadates are isostructural with xenotime which has the tetragonal zircon-type structure (D_{4h}^{19}-$I4_1/amd$), while $LaVO_4$ is isostructural with monazite, the monoclinic huttonite-type structure (C_{2h}^5-$P2_1/n$). The polymorphism of $LnMO_4$ (Ln= lanthanide, M=P, As, V, Nb, Ta, *etc.*) was studied in view of crystallographic interest. Stubican and Roy[3] investigated the phase transition of rare earth vanadates and arsenates under high pressure, but gave no description on the polymorphism of $CeVO_4$.

Several researchers[5–7] reported that zircon-type $CeVO_4$, represented as $CeVO_4$(Z), was prepared by the reaction between Ce^{3+} salts or oxide and V_2O_5 in an inert atmosphere taking the instability of Ce^{3+} into consideration. However, this consideration seems unnecessary.

During the course of study on the valence states of ions in cerium vanadium double-oxides, a new monoclinic huttonite-type phase of $CeVO_4$, represented as $CeVO_4$(H), was found as a metastable phase. In this paper, the formation of $CeVO_4$(H) and its characteristic properties are presented in relation to those of $CeVO_4$(Z).

Experimental

Materials are ceria for optical use (CeO_2 contents 99.99%) and a guaranteed grade NH_4VO_3 or V_2O_5 which was obtained by decomposition of NH_4VO_3 at 500°C for 12 hr in air. The reaction processes were traced by the ordinary TGA and DTA methods programmed 5°C/min under various atmospheres. The reaction products were identified by means of powder X-ray diffraction ($CuK\alpha_1$=1.5405 Å).

Samples for X-ray powder diffraction were obtained as follows: $CeVO_4$(H), prepared by oxidation of $CeVO_3$ at 370°C for 8 hr in air. $LaVO_4$ and $CeVO_4$(Z) prepared by heating equimolar mixtures of V_2O_5 and La_2O_3 or CeO_2 at 800°C for 4 hr.

Their magnetic susceptibilities were measured with a torsion-type magnetobalance (Shimadzu MB-II) at temperatures between 77 and 1000°K.

Results and Discussion

Contrary to expectation, the formation of $CeVO_4$ from component salts is represented by the equation,[8]

$$CeO_2 + \tfrac{1}{2}V_2O_5 \longrightarrow CeVO_4 + \tfrac{1}{4}O_2, \qquad (1)$$

[*1] A part of this study was presented at the 21th Annual Meeting of the Chemical Society of Japan, April, 1968. Proceedings II, p. 1340.

1) M. K. Carron, M. E. Mrose and K. J. Murata, *Am. Mineralogist*, **43** (9—10), 985 (1958).

2) H. Schwarz, *Z. anorg. allgem. Chem.*, **323**, 44 (1963).

3) V. S. Stubican and Rustum Roy, *Z. Kristallographie*, **119**, 90 (1963).

4) A. Durif, *Acta Cryst.*, **9**, 471 (1956).

5) ASTM No. 12–757, *Nat. Bur. Standards(U.S.) Mono*, **25**, sect. 1, (1961).

6) V. A. Nautov, *Zhur. Strukt. Khim.*, **3** (5), 608 (1962).

7) L. H. Brixner and E. Abramson, *J. Electrochem. Soc.*, **112**, 70 (1965).

8) T. Sata and M. Yoshimura, Preprints for the 20th Annual Meeting of Chem. Soc. Japan, Tokyo (April, 1967), II, p. 127.

because CeO_2, instead of Ce_2O_3, is obtained by the thermal decomposition of Ce(III) salts under usual conditions.[9] This reaction is different from those of the formation of other lanthanide orthovanadates:

$$\tfrac{1}{2}Ln_2O_3 + \tfrac{1}{2}V_2O_5 \longrightarrow LnVO_4. \qquad (2)$$

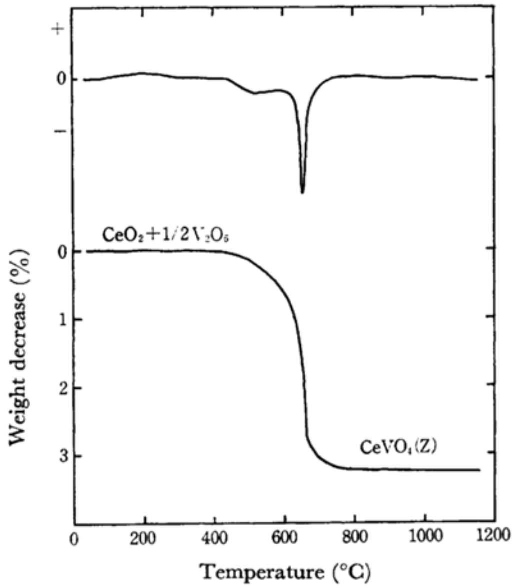

Fig. 1. DTA and TGA curves for the reaction (1).

TGA and DTA curves for the reaction (1) in air are shown in Fig. 1. The same results were also obtained in argon atmosphere. As shown in Fig. 1, the reaction starts above 400°C releasing oxygen, and is completed at about 800°C. The sharp endothermic peak at 655°C near the eutectic temperature[10] of V_2O_5 and YVO_4 suggests that the reaction is accelerated by the formation of liquid phase. The reaction product was dark purplish brown and identified to be the tetragonal zircon-type $CeVO_4$ by means of X-ray analysis. The lattice parameters were calculated to be a_0= 7.400 Å and c_0=6.497 Å. The observed weight decrease (3.230%) was larger than the calculated value (3.041%) according to raection (1). This indicates that the real composition of $CeVO_4$(Z) is not stoichiometric $CeVO_{4.000}$ but $CeVO_{3.968}$. A further discussion on $CeVO_4$(Z) will be presented in a next paper.[11]

$CeVO_4$ was also obtained by the oxidation of $CeVO_3$ which has a pseudo-perovskite structure.[12] This reaction is given by the following equation:

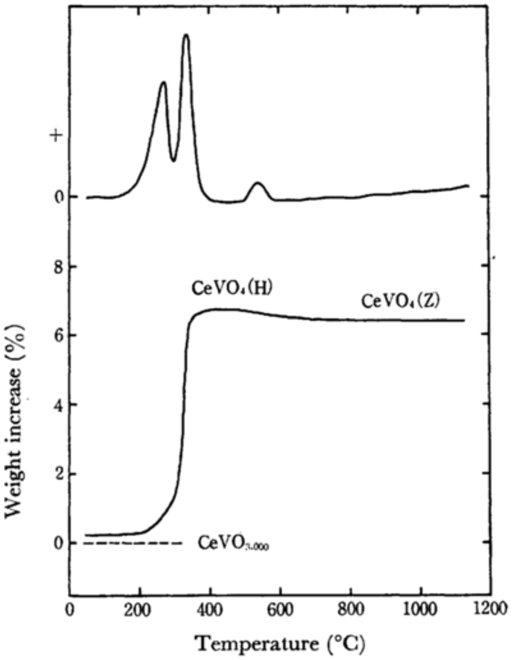

Fig. 2. DTA and TGA curves for the reaction (3). Starting compound, $CeVO_{3.030}$, was prepared by the reaction that equimolar mixture of component oxides was heated at 1200°C for 10 hr in hydrogen atmosphere.

$$CeVO_3 + \tfrac{1}{2}O_2 \longrightarrow CeVO_4. \qquad (3)$$

The TGA and DTA results of this reaction are given in Fig. 2. Two exothermic peaks at 280°C and 330°C seems to be caused by the oxidation of $CeVO_3$. However, no intermediate compound such as $Ce_2V_2O_7$ was found. The same behavior was observed in the case of the oxidation of perovskite $LaVO_3$ into $LaVO_4$. Thus it is reasonable that the valency of cerium ion remained trivalent and only that of vanadium ion changed from trivalent to pentavalent during the course of this reaction. When the oxidation of $CeVO_3$ took place below 400°C, $CeVO_4$(H) was obtained. It was brownish yellow and identified to be isostructural with $LaVO_4$, huttonite-type (C_{2h}^{5}-$P2_1/n$). X-Ray powder data of $CeVO_4$(H) are given in Table 1 in comparison with $LaVO_4$. The difference in the cell volume corresponds to that in ionic radii; Ce^{3+}=1.07 Å, La^{3+}=1.14 Å.

The transition of $CeVO_4$(H) to $CeVO_4$(Z) was exothermic, gradually releasing oxygen gas, as shown in Fig. 3. This gives rise to the increase of lattice symmetry and cell volume. The third peak at about 540°C in Fig. 2 corresponds to this transition.

Magnetic studies on $CeVO_4$ (Fig. 4) demonstrate

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[9] O. K. Srivastava and A. R. Vasudeva Murthy, *J. Sci. Ind. Research (India)*, **20B**, 96 (1961).

[10] E. M. Levin, *J. Am. Ceram. Soc.*, **50**, 381 (1967).

[11] M. Yoshimura and T. Sata, This Bulletin, to be published.

[12] T. Sata and M. Yoshimura, Preprints for the 5th Basic Ceramic Science Symposium, Tokyo (Jan., 1967), pp. 156—159.

TABLE 1. X-RAY POWDER DIFFRACTION DATA FOR $CeVO_4(H)$ AND $LaVO_4$

$CeVO_4(H)$		$LaVO_4$		hkl
d (obsd.)	I/I_0	d (obsd.)	I/I_0	
5.41	10	5.46	10	$\bar{1}01$
4.85	14	4.85	14	110, 011
4.35	20	4.36	18	$\bar{1}11$
—	—	4.19	6	101
3.598	24	3.637	24	111, 020
3.371	60	3.404	60	200
3.181	100	3.210	100	120
3.051	10	3.081	18	210
2.947	72	2.974 2.968	80	$\bar{1}12$ 012
2.711	18	2.727	20	$\bar{2}02$
2.539	18	2.567	30	$\bar{2}12$
—	—	2.518	10	112
—	—	2.336	6	301
2.259	16	2.272	18	031
2.220	20	2.235	20	$\bar{1}03$
2.170	12	2.191	14	221, $\bar{1}31$
1.996	24	2.015	40	212, $\bar{3}12$
—	—	1.973	12	$\bar{2}31$
1.939	24	1.950	40	103, $\bar{1}32$
1.907	22	1.925	22	311, 320
—	—	1.842	22	$\bar{3}22$
1.801	10	1.817	16	231, $\bar{2}22$
1.779	18	1.799	28	132
1.740	10	1.759	16	140, $\bar{3}21$
—	—	1.700	12	400
1.658	8	—	—	$\bar{4}02$
1.642	8	1.656	18	410, $\bar{2}04$
—	—	1.626	8	312
1.593	12	1.603	18	214
$a_0=6.98$ Å		$a_0=7.05$ Å		
$b_0=7.22$ Å		$b_0=7.26$ Å		
$c_0=6.76$ Å		$c_0=6.75$ Å		
$\beta=105°02'$		$\beta=104°56'$		
$V=a_0b_0c_0 \sin\beta=328$ Å^3		$V=334$ Å^3		
$Z=4$		$Z=4$		

that both $CeVO_4(H)$ and $CeVO_4(Z)$ showed paramagnetic behavior following the Curic-Weiss law, $\chi=C/(T+\theta)$, above 100°K, where χ is molar magnetic susceptibility, C, the Curie constant, T, the absolute temperature, and θ, the Weiss constant. The correction of diamagnetism was made using the value given by Selwood.[13)]

Some results of magnetic and chemical analyses for $CeVO_4(H)$ and $CeVO_4(Z)$ are summerized in Table 2. The effective magnetic moment, $2.51\,\mu_B$ for $CeVO_4(H)$, indicates that the valence states are almost tripositive for cerium ion and pentapositive for vanadium ion respectively, since this value is fairly smaller than the theoretical value of $2.54\,\mu_B$ for free Ce^{3+} ion. On the contrary, the value of $2.58\,\mu_B$ would indicate that a small quantity of V^{4+} coexists with V^{5+} in $CeVO_4(Z)$ and the magnetic moment obtained is caused by both Ce^{3+} and V^{4+}. TGA, chemical analysis and color support the results.

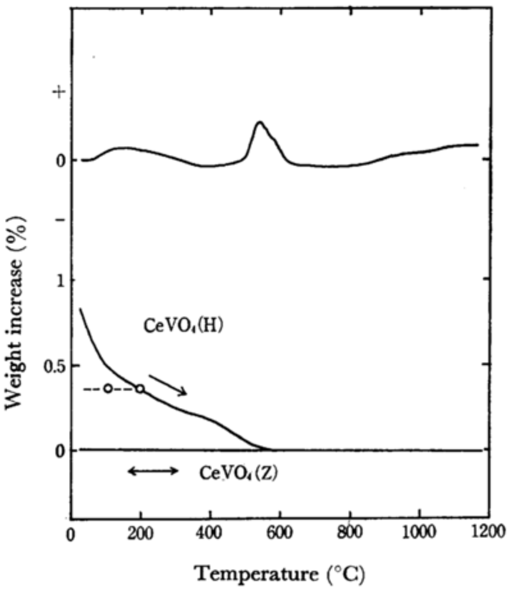

Fig. 3. DTA and TGA curves for the transition from $CeVO_4(H)$ to $CeVO_4(Z)$; $CeVO_4(H)$ was moist. ---○---: after keeping for 2hr at this temp.

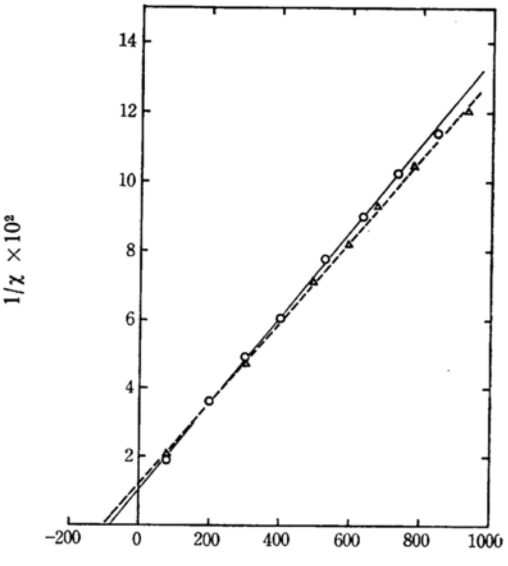

Fig. 4. Reciprocal susceptibility *vs.* temperature of $CeVO_4$. $H=10500$ Oe.
——○—— $CeVO_4(H)$
– –△– – $CeVO_4(Z)$

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13) P. W. Selwood, "Magnetochemistry," Interscience Publishers, New York (1956), 2nd Ed., p. 78.

TABLE 2. MAGNETIC AND CHEMICAL ANALYSES FOR $CeVO_4$(H) AND $CeVO_4$(Z)

	$CeVO_4$(H)	$CeVO_4$(Z)
Composition	$CeVO_{4.024}$	$CeVO_{3.968}$
Curie const. (C)	0.789	0.830
Effective moment	2.51 μ_B	2.58 μ_B
Weiss const. (θ)	−82°K	−103°K
Body color	brownish yellow	dark purplish brown

$CeVO_4$(H) could not be detected during the course of the reaction (1). It was observed that $CeVO_4$(H) transformed into $CeVO_4$(Z) after being kept at 400°C for 20 hr or at 450°C for 8 hr. The reverse transition, $CeVO_4(Z) \rightarrow CeVO_4(H)$, could not be observed. Even treatments under high-pressure oxygen (P_{O_2}=500—1000 atm, temperature 350—500°C, 2—40 hr) gave no change on $CeVO_4$(Z). From these results, it seems that $CeVO_4$(H) is a metastable phase and $CeVO_4$(Z) a stable phase.

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