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A NEW COMPOUND, $Lu_2V_2O_7$

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A new compound, $Lu_2V_2O_7$, which belongs to pyrochlore-type, has been successfully synthesized under a low oxygen partial pressure at 1200°C and its formation conditions in oxygen partial pressure, crystal parameters including lattice constant, unit cell volume, density, spacing, and relative intensities were determined.

Up to date, in the lanthanoid-V-O system, many studies on $LnVO_3$ and $LnVO_4$ have been reported.[1,2,3,4] Pyrochlore-type compounds containing double oxides of trivalent and tetravalent have been presented by Roth.[5] But in previous reports, the presence of a compound, $Lu_2V_2O_7$, has not yet been reported.

Through the present study of the phase equilibria in the Lu_2O_3-V_2O_3-V_2O_5 system, the new compound, $Lu_2V_2O_7$, was synthesized and we determined a cell constant, unit cell volume, density, spacing, and relative intensities.

The general experimental procedures and apparatus adopted in the present experiment were the same as those described in a previous paper.[6] As starting materials, Lu_2O_3(99.9%) and V_2O_5, which was made from the guaranteed reagent grade of NH_4VO_3 by heating at 500°C in air for 24 hours, have been employed. The calculated weights of each Lu_2O_3 and V_2O_5 (one in mole ratio) were fully mixed in an agate mortar under ethyl alcohol. The mixed sample was heated at 600°C at $Po_2 = 10^{-10.0}$ atm to reduct V_2O_5 to V_2O_3. After 24 hours, the temperature of furnace was increased to 1200°C in the same Po_2. Then the sample was heated for 6 hours and quenched.

The thermogravimetric results were shown in Fig. 1 in the relationship between the oxygen partial pressures and weight changes of the sample, where Wo_2 means the weight change of the sample and W_T is an oxygen increase from $LuVO_3$ to $LuVO_4$. Lu_2O_3 is not affected in the present experimental conditions. In the range of Po_2 of $10^{-8.50}$ to $10^{-8.05}$ atm, the new phase is appeared as shown in Fig. 1.

The new phase seems to have slight composition changes with oxygen partial pressure. The compound is not stoichiometric and has a composition of $Lu_2V_2O_{6.93}$ by means of the thermogravimetry.

Sample used for X-ray powder diffraction was made by the quenching method by hunging for 5 days at log Po_2 = -8.30 atm. The assignment of indices was done with the aid of previous data of $Yb_2Ti_2O_7$.[7] The indices thus obtained fit the data of $Yb_2Ti_2O_7$ quite well as shown in Table 1. The lattice constant was determined by the powder X-ray diffraction method with Ni-filtered $CuK\alpha_1$ radiation and with a slow scanning speed of 0.5° per minute. Instrumental errors were calibrated by

Table 1. Spacing and Relative Intensities

h	k	l	d_{obs}	d_{cal}	I_{obs}	h	k	l	d_{obs}	d_{cal}	I_{obs}
1	1	1	5.737	5.735	39	8	0	0	1.2419	1.2417	9
3	1	1	3.005	2.995	31	7	3	3	1.2136	1.2136	3
2	2	2	2.865	2.868	100	7	5	1	1.1470	1.1470	5
4	0	0	2.4832	2.4834	46	6	6	2	1.1395	1.1395	19
3	3	1	2.2787	2.2789	35	8	4	0	1.1108	1.1106	16
5	1	1	1.9111	1.9117	16	9	1	1	1.0902	1.0904	5
4	4	0	1.7557	1.7560	57	8	4	4	1.0138	1.0139	14
5	3	1	1.6792	1.6791	16	6	6	6	0.9557	0.9559	14
5	3	3	1.5147	1.5149	4	8	8	0	0.8780	0.8780	6
6	2	2	1.4975	1.4976	51	9	5	5	0.8679	0.8679	4
4	4	4	1.4339	1.4338	15	10	6	2	0.8395	0.8396	16
7	1	1	1.3909	1.3910	6	8	4	4	0.8278	0.8278	14
7	3	1	1.2933	1.2933	5						

measuring the diffraction angles of a standard specimen of silicon. The new phase has a cubic system and lattice constant is 9.934±0.001 A, unit cell volume 980.3±0.1 A^3. In Table 1, spacing and relative intensities are given. From the systematic absence of h $\bar{k}$ l, even of h + k, k + l, and l + h in h k l, and even of h + l in h h l, the space group was determined to be Fd3m as well as $Yb_2Ti_2O_7$. Density was also determined to be 7.64 g/cm^3 by the usual powder method. This value is in good agreement with the value, 7.62, which was calculated from the obtained unit cell volume, formula weight, and Z = 8. Details of the phase equilibria in the Lu_2O_3-V_2O_3-V_2O_5 system at 1200°C will be published in the near future.

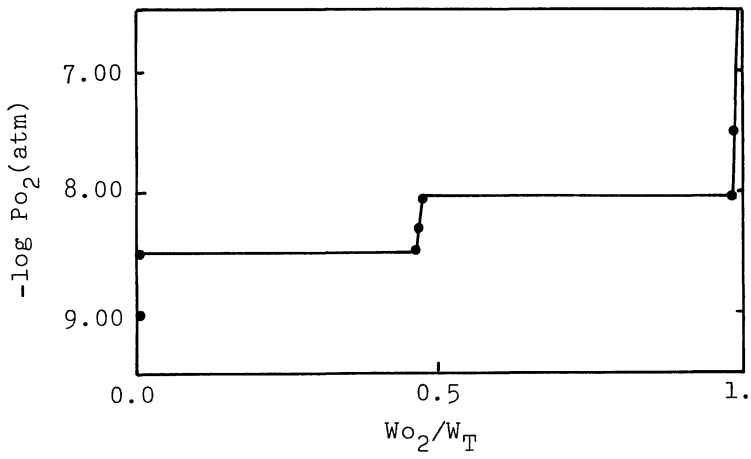

Fig. 1. The relationship between oxygen partial pressures and weight changes of sample, Lu_2O_3/V_2O_5 = 1.

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