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A New Compound, $Nb_5Co_2O_{14}$

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A new compound, $Nb_5Co_2O_{14}$, has been successfully synthesized under low oxygen partial pressure at 1200 °C. The relationship between the composition of the compound and the oxygen partial pressure was determined together with crystal parameters and density.

In the Nb-Co-O system there are three ternary compounds, Nb_2CoO_6, $Nb_2Co_4O_9$, and $Nb_4Co_3O_{14}$[1] and their crystallographic and physical properties have been studied.[2,3] But the precise phase equilibrium of the system has not been reported.

Through the study of the phase eqilibrium in the Nb-Co-O system, the new compound, $Nb_5Co_2O_{14}$, was found and synthesized at 1200 °C.

The general experimental procedures and apparatus adopted in the present experiment were the same as those described in a previous paper.[4] Starting materials, Nb_2O_5(99.9%) and CoO(99.9%) have been employed. The calculated weights of each Nb_2O_5 and CoO in mole ratio were fully mixed in an agate mortar. The mixture thus obtained was heated to about 1200 °C several times with intermittent mixings and was used in the thermogravimetry. The sample used for X-ray powder diffraction was made by the quenching method by heating for 15 h at log (Po_2/atm) = -12.50. The assignment of indices was carried out with the aid of previous data of TiO_2.[5] Lattice constants were determined by the X-ray powder diffraction method with Mn-filtered FeKα_1 radiation and with a slow scanning speed of 0.5° 2θ/min. The instrumental error of 2θ was calibrated by a standard specimen of silicon.

Thermogravimetric result for a sample, Nb_2O_5/CoO = 56/44, was shown in Fig. 1 in the relationship between the oxygen partial pressure, -log (Po_2/atm), and the weight change, Wo_2/W_T. Here, Wo_2 means the weight decrease of the sample from the referential weight at 1 atm O_2 and W_T is the total oxygen-weight decrease calculated from the sample weight at 1 atm O_2 according to reactions, CoO = Co + 1/2 O_2 and Nb_2O_5 = 2 NbO_2 +

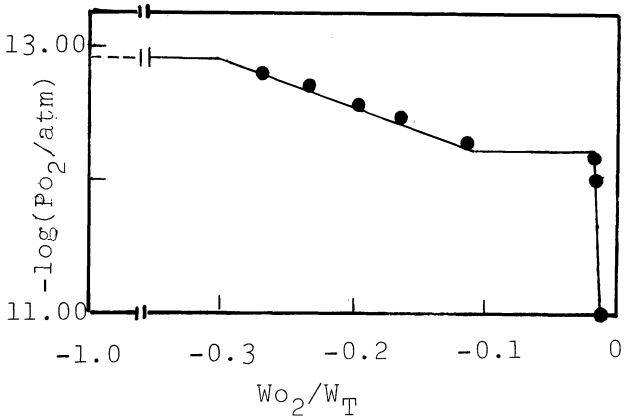

Fig. 1. The oxygen partial pressure and the weight change.

Table 1. Spacings and Intensities

h	k	l	d_{obs}	d_{cal}	I/I_o
1	1	0	3.3649	3.3657	1.00
1	0	1	2.5685	2.5691	.84
2	0	0	2.3801	2.3799	.23
1	1	1	2.2606	2.2608	.16
2	1	1	1.7459	1.7459	.72
2	2	0	1.6828	1.6828	.25
0	0	2	1.5260	1.5260	.14
3	1	0	1.5051	1.5052	.17
3	0	1	1.4078	1.4077	.27
1	1	2	1.3897	1.3898	.19

1/2 O_2.

The new phase, $Nb_5Co_2O_{14}$, appears as shown in Fig. 1. The phase changes the composition from $Nb_5Co_2O_{14.30}$ at -12.20 to $Nb_5Co_2O_{13.36}$ at -12.90 in log (Po_2/atm), and the composition can be represented by an equation, $N_O/N_{Nb_5Co_2O_{14}} = 1.343 \log Po_2 + 16.68$, where N_O and $N_{Nb_5Co_2O_{14}}$ are the mole fraction of the substance denoted by the subscript.

The d-spacings obtained are fit well with those calculated as shown in Table 1. The new phase is black and the structure is tetragonal with a = 4.7598(3) Å, c = 3.0519(2) Å, and V = 69.147(7) Å^3. The X-ray powder diffraction pattern did not exhibit superstructure reflections. The density was determined to be 6.5(1) g/cm^3 by the pycnometric method. Using the obtained cell volume, density, and formular weight, Z was calculated to be 0.33 (= 1/3).

Details of the phase equilibrium in the Nb-Co-O system at 1200 °C will be published in the near future.

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