

LOW-SPIN \rightarrow HIGH-SPIN STATE TRANSITION IN HIGH PRESSURE COBALT SESQUIOXIDE

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Co_2O_3 with the corundum structure was synthesized under high pressure. A refinement of the structure indicated that Co^{3+} is in the low-spin state. By annealing, this oxide transformed to a corundum structure with a larger volume indicating that the Co^{3+} is in the high spin state. The increase in volume was 6.7 per cent.

ALL TRIVALENT 3d transition metals form a sesquioxide with the corundum structure except cobalt, nickel and manganese. The former two elements are more stable as divalent cations. CoO and NiO with the NaCl structure are the stable oxides. Another cobalt oxide is known, namely Co_3O_4 , which crystallizes with the normal spinel structure. In this oxide 2/3 of the cobalt ions are trivalent while the other third is divalent. It has been shown that the Co^{3+} ions in this compound are in the low spin state. Only a few cobalt compounds are known in which the cobalt ions are all trivalent, LiCoO_2 and CoF_3 are two examples. From the ionic radii of Co^{3+} and Co^{2+} with coordination number 6,¹ one could speculate that the transformation $\text{Co}^{2+} \rightarrow \text{Co}^{3+}$ should be favored by high pressures, especially if the Co^{3+} ions are in the low spin state (see Table 1). This note reports the high pressure synthesis of Co_2O_3 with the corundum structure.

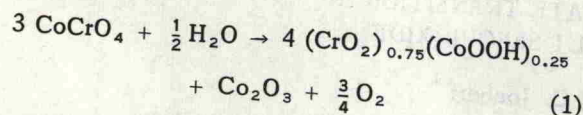
Two different syntheses were performed. In the first the starting material was $\text{Co}^{2+}\text{Cr}^{6+}\text{O}_4$. This double oxide has the orthorhombic

Table 1

Valence	Coord.	Spin	Radius (\AA)
3	6	Low	0.52 _s
2	4	High	0.57
3	6	High	0.61
2	6	Low	0.65
2	6	High	0.74 _s

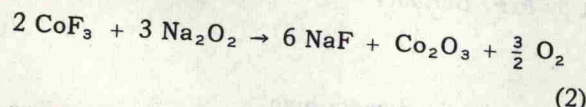
$\text{Cr}^{3+}\text{V}^{5+}\text{O}_4$ structure in which the Co^{2+} ions have octahedral coordination, while the smaller Cr^{6+} ions are tetrahedrally coordinated. The high pressure runs were done in a modified 'belt' apparatus. A platinum cylindrical cell was used as sample container. A standard heater assembly was used. The pressure was calibrated by measuring the resistance of bismuth and thallium wires at room temperature.² The temperature was calibrated by a Pt-Pt/10% Rh thermocouple. By applying a pressure of ≥ 90 kbar and 1000°C in the presence of a small amount of water, CoCrO_4 decomposes into Co_2O_3 with the corundum structure and a solid solution of CoOOH and CrO_2 with the

orthorhombic distortion of the rutile structure, as revealed by X-ray photographs of the quenched materials. The decomposition occurs according to the formula:



Under pressure Co_2O_3 transforms in the presence of water to a high pressure form of CoOOH , therefore different amounts of water affect the composition of the solid solution $(\text{CrO}_2)_x(\text{CoOOH})_{1-x}$.

The second synthesis was based on the following reaction:



The X-ray pattern of the quenched material of a run done at 80 kb and 850°C showed the same hexagonal pattern obtained in syntheses (1). Unfortunately some reduction took place and the quenched material contained some Co_3O_4 .

Table 2. Powder pattern of Co_2O_3 (low spin)

<i>hkl</i>	d_o	d_c	I_o
012	3.476	3.489	25
104	2.546	2.551	100
110	2.389	2.391	66
113	2.088	2.092	16
024	1.743	1.745	33
116	1.601	1.602	90
214	1.408	1.409	43
027	1.379	1.380	50
1010	1.236	1.236	48
119	1.233	1.233	15
220			
217	1.195	1.195	46
306	1.163	1.163	48

Table 2 gives the powder pattern of Co_2O_3 which was indexed on a hexagonal cell, $a = 4.782 \text{ \AA}$, $c = 12.96 \text{ \AA}$, $c/a = 2.710$, $V = 258.5 \text{ \AA}^3$. These values correspond to the material of synthesis (2). The X-ray powder photographs were taken using a Norelco camera of

114.6 mm dia. and filtered $\text{CrK}\alpha$ radiation. In general the synthesis (1) yielded lattice parameters which were slightly larger. A typical run gave $a = 4.790 \text{ \AA}$ and $c = 13.00 \text{ \AA}$. We believe that these larger values are due to a small percentage of substituted Cr. The pattern reported in Table 2 resembles closely that of $\alpha\text{-Al}_2\text{O}_3$ as far as the sequence of the d -spacings is concerned, but the intensities of the reflections are similar to those of V_2O_3 . This indicates that the radius of the Co^{3+} ions is very close to that of the Al^{3+} ions. Therefore the Co^{3+} ions must be in the low spin state. The reported ionic radius for the six coordinated Al^{3+} is 0.53 \AA , while that of the corresponding Co^{3+} in the low spin state is 0.52 \AA . On the other hand the arrangement of the structure of Co_2O_3 should be different from that of Al_2O_3 as the relative intensities indicate.

By annealing Co_2O_3 at 400°C for a half hour in air, this oxide transforms to a corundum structure with a different volume and c/a ratio. The new values are $a = 4.882 \text{ \AA}$, $c = 13.38 \text{ \AA}$, $c/a = 2.742$, $V = 276.2 \text{ \AA}^3$. The X-ray powder pattern is reported in Table 3. Since the unit cell volume and the d -spacings of this Co_2O_3 are nearly the same as those of $\alpha\text{-Fe}_2\text{O}_3$, the Co^{3+} ions must be in the high spin state. The oxide Co_2O_3 with Co^{3+} ions in the low spin state will be referred herein as Co_2O_3 (low spin) whereas that with Co^{3+} ions in the high spin state will be referred as Co_2O_3 (high spin). The transformation Co_2O_3 (low spin) \rightarrow Co_2O_3 (high spin) is accompanied by an increase in volume $\Delta V/V(\text{low spin}) = 6.7$ per cent. These results seem to indicate that Co_2O_3 (high spin) is the cobalt sesquioxide stable at atmospheric pressure whereas Co_2O_3 (low spin) is the high pressure phase. This pressure-induced transformation involves only a change in the spin state of the cations. The coordination of the ions and their packing remain the same. The coordination-number of the cations remains six and for the anions it remains four, while the oxygen packing is nearly h.c.p. in both oxides.

Preliminary refinements of the two structures based on powder intensities gave the positional parameters and the interatomic distances reported in Table 4. The average Co-O distances are 1.90