ESRF	**Experiment title: Thermal decomposition of chromium(VI) oxide; high resolution in-situ powder diffraction studies of mixed valence chromium oxides.**	**Experiment number**: 01-01-263
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Shifts: 15	**Local contact(s)**: Hermann Emerich	*Received at ESRF:*

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Report:

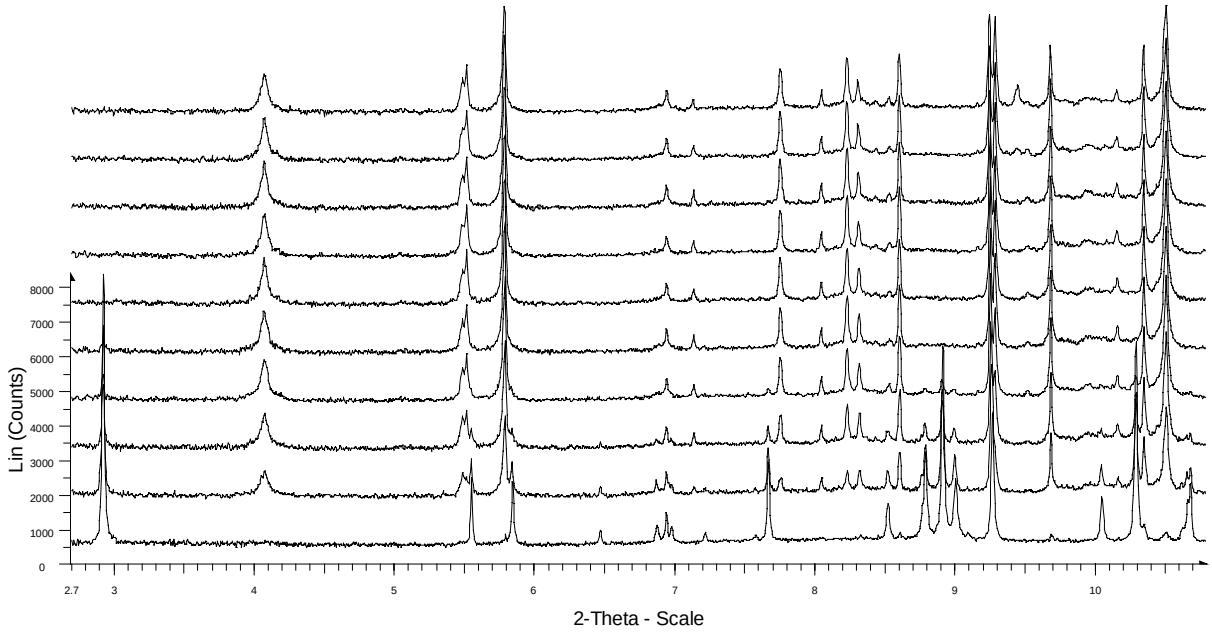
CrO_3, chromium(VI) oxide, has a 1-dimensional crystal structure formed by infinite single chains of corner linked CrO_4-tetrahedra. When heated, CrO_3 will decompose through several steps to chromium(III) oxide, Cr_2O_3. The thermal decomposition of CrO_3 has been the topic of many studies, but the decomposition sequence and the structures and stoichiometry of the intermediate mixed valence chromium oxides are still not fuly understood. The decomposition is strongly dependent on e.g. pressure, oxygen partial pressure and traces of moisture. Several mixed-valence compounds have been identified in the decomposition sequence. A compound known as Cr_3O_8 was shown by structure determination(1) to have the true composition Cr_8O_{21}. It is triclinic, a = 5.433, b = 6.557, c = 12.117Å, α = 106.36, β = 95.73 and γ = 77.96º and contains chromium(III), chromate- and tetrachromate groups, and the composition can be given as $Cr(III)(Cr(VI)O_4)_2(Cr(VI)_4O_{13})$. The existence of one or more phases with composition $Cr_2O_5(Cr_6O_{15})$ has been reported, but no structural information is available. Cr_5O_{12} was syntesized at high pressure, and the structure has been determined. In Cr_5O_{12} chromium(III) is connected by chromate groups, and the composition can be given as: $Cr(III)_2(Cr(VI)O_4)$. Thus the transformation sequence observed is:

$$CrO_3 \rightarrow Cr_8O_{21} \rightarrow Cr_6O_{15}(Cr_2O_5) \rightarrow (Cr_5O_{12}) \rightarrow Cr_2O_3.$$

When taking into account the appropriate oxidation states of chromium, the compounds are:

$$Cr(VI)O_3 \rightarrow Cr(III)_2Cr(VI)_6O_{21} \rightarrow Cr(III)_2Cr(VI)_4O_{15} \rightarrow Cr(III)_2Cr(VI)_3O_{12} \rightarrow Cr(III)_2O_3.$$

A systematic change in stoichiometry is observed. A couple of interesting missing stoichiometries are: Cr_7O_{18} ($Cr(III)_2Cr(VI)_5O_{18}$) and Cr_4O_8 ($Cr(III)_2Cr(VI)_2O_8$). Cr_7O_{18} has so far not been observed, but it could exist as a chromium chromate trichromate, $Cr(III)(Cr(VI)O_4)_2(Cr(VI)_3O_{10})$. Cr_4O_8 does exist (CrO_2); not as a mixed valence compound, but as a chromium(IV) oxide.
High resolution powder diffraction was used to follow the thermal decomposition of CrO_3 and Cr_8O_{21} under various reaction conditions, such as different oxygen partial pressures. The aim was to identify new phases in the decomposition sequence, and to resolve the issue concerning the structure of $Cr_6O_{15}(Cr_2O_5)$.



The Figure shows an example of a series of powder diffraction patterns collected during heating of Cr_8O_{21}. The formation of an intermediate phase is clearly visible. During the experiments several different, but closely related, phases with assumed composition close to $Cr_2O_5(Cr_6O_{15})$ were obtained. One of the phases has been indexed based on a triclinic unit cell, a = 6.561, b = 8.401, c = 8.951Å, α = 99.95, β = 73.16 and γ = 89.06°. The structure determination is not yet completed.

1. P. Norby, A. Nørlund Christensen, H. Fjellvåg and M. Nielsen
"The crystal structure of Cr_8O_{21} determined from powder diffraction data. Thermal transformation and magnetic properties of a chromium-chromate-tetrachromate."
J. Solid St. Chem. **94** (1991) 281.