Two synthetic compounds containing chromium in different valency states.

By W. Johnson, M.A.
The United Steel Companies Limited, Research and Development Dept.,
Swinden Laboratories, Moorgate, Rotherham, Yorkshire.

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Summary. Two compounds, one an apatite and the other a perovskite, have been synthesized by sintering mixtures containing CaO and Cr_2O_3, and CaO, Cr_2O_3, and Fe_2O_3 respectively. The apatite formed by partial oxidation of the Cr_2O_3 and subsequent pick-up of moisture from the atmosphere, to give $Ca_5(CrO_4)_3OH$. The perovskite formed as a non-stoicheiometric compound $Ca_4(Fe,Cr)_4O_{11}$ by partial oxidation of the Cr_2O_3 during firing. Lattice parameters and interplanar spacings are given for the two structures.

It is well known that Al_2O_3 can replace Fe_2O_3 in dicalcium ferrite to form a calcium alumino-ferrite up to a limiting composition of $6{\cdot}37CaO.2{\cdot}28\ Al_2O_3.Fe_2O_3$ (Newkirk and Thwaite, 1958). In the course of work on used chrome-magnesite roof bricks Cockbain and Johnson (1958) found an intergrowth of dicalcium ferrite and calcium silicophosphate (originally liquid) in regions adjacent to the hot face. Hence an investigation into the limits of Cr_2O_3 substitution in dicalcium ferrite or alumino-ferrite was considered necessary in order to assess the composition of the liquid phase in the brick and the mechanism of selective removal of Al_2O_3 and Cr_2O_3 from the chrome spinel grains.

During the course of synthesizing such mixtures two new compounds were discovered both containing tri- and hexavalent chromium. The first was found in mixtures, fired at 1200° C. in air, containing more than about 10 % substitution of Cr_2O_3 for Fe_2O_3 in dicalcium ferrite. This phase became more dominant with increasing substitution till at 40 % it was the only constituent present. X-ray powder data indicated it to be a perovskite-type compound isomorphous with $GdFeO_3$ as reported by Geller (1956) with an orthorhombic unit cell but having *a* 5·415 Å., *b* 5·489 Å., *c* 7·480 Å.

The oxidation of Cr_2O_3 in mixtures of high basicity is well known and our work indicates that only 10 % substitution of Fe_2O_3 by Cr_2O_3 is possible before oxidation begins to occur in air. If complete oxidation of the Cr_2O_3 to CrO_3 occurred then one would expect the $33\frac{1}{3}$ % substitution mixture to give a single phase. This can be expressed clearly by the equation:

$$2CaO.\tfrac{2}{3}Fe_2O_3.\tfrac{1}{3}Cr_2O_3+O \rightarrow 2CaO.\tfrac{2}{3}Fe_2O_3.\tfrac{2}{3}CrO_3 = 3CaO.Fe_2O_3.CrO_3 = 3Ca\mathit{M}O_3,$$

where M is a random mixture of Fe^{3+} and Cr^{6+} in the ratio 2:1, giving a mean valency of 4 and hence the isomorphism with perovskite, $CaTiO_3$.

TABLE I. X-ray powder data, obtained with Co-$K\alpha$ radiation on a Guinier type focusing camera.

Perovskite-type structure. $Ca_4(Fe,Cr)_4O_{11}$.

hkl.	$d_{\text{obs.}}$	*I.*	$d_{\text{calc.}}$	*hkl.*	$d_{\text{obs.}}$	*I.*	$d_{\text{calc.}}$
110	3·863	m	3·858	—	1·916	w	—
*002	3·745	mw	3·740	*004	1·868	ms	1·870
*020	2·740	ms	2·745	221			1·868
*200	2·710	s	2·707	132	1·567	m	1·573
112	2·684	vs	2·684	312	1·561	m	1·559
003	2·495	w	2·493†	024	1·540	mwb	1·545
022	2·217	w	2·212	204			1·539
202	2·193	w	2·192	*040	1·375	w	1·372
—	2·157	vw	—	*400	1·353	wb	1·354
220	1·928	s	1·927	224	1·341	mw	1·342

$d_{\text{calc.}}$ from a 5·415 Å., b 5·489 Å., c 7·480 Å. Probable space-group *Pbnm*.

* Used to calculate a, b, and c.

† 003 not permitted by *Pbnm*, which with the other two unindexed lines perhaps indicates a bigger unit cell or some ordering of the structure.

Chromium analogue of apatite. $Ca_5(CrO_4)_3OH$.

hkl.	$d_{\text{obs.}}$	*I.*	$d_{\text{calc.}}$	*hkl.*	$d_{\text{obs.}}$	*I.*	$d_{\text{calc.}}$
100	8·38	mw	8·38	221	2·287	w	2·286
101	5·37	mw	5·37	311	2·206	w	2·204
110	4·835	w	4·834	222	1·990	ms	1·990
200	4·193	w	4·186	213	1·879	ms	1·880
111	3·978	m	3·981	321	1·850	mw	1·853
201	3·597	vw	3·595	410	1·827	wb	1·827
002	3·504	s	3·505	402	1·798	wb	1·797
102	3·242	w	3·235	004	1·752	wb	1·753
210	3·162	m	3·164	322	1·683	w	1·684
211	2·888	vs	2·884	313	1·645	vw	1·647
112	2·838	ms	2·838	420	1·579	vw	1·582
300	2·791	s	2·791	214	1·542	vw	1·533
202	2·688	ms	2·687	502	1·511	mw	1·511
301	2·595	w	2·593	304	1·482	wb	1·484
310	2·323	mw	2·322	511	1·469	vw	1·470

$d_{\text{calc.}}$ from a 9·67 Å., c 7·01 Å., c/a 0·725. Apatite space-group $P6_3/m$.

Actually, the single-phase region is found near to the 40 % substitution level. This, together with the chemical analysis (CaO 40·5, Fe_2O_3 34·25, Cr_2O_3 12·3, CrO_3 12·4 %, sum 99·45 %), indicates the perovskite to be non-stoicheiometric (oxygen deficient). Its formula is very near to $Ca_4(Fe,Cr)_4O_{11}$, i.e. half-way between dicalcium ferrite $Ca_4Fe_4O_{10}$ and the ideal perovskite $Ca_4M_4O_{12}$. The presence of Cr^{6+} in perovskites has been suggested by Roy (1954), and the recent work of Bertaut, Blum, and Sagnières (1959) on dicalcium ferrite shows clearly the relationship between the two compounds. A comparison of the structures shows the metal atoms and all but two of the oxygen atoms virtually unchanged in position and a shift through about a quarter of a cell of these two oxygen atoms leaves a hole which can accommodate the extra one or two oxygens demanded by the perovskite formula.

The second compound was discovered whilst synthesizing similar mixtures containing only CaO and Cr_2O_3. It is an apatite-type structure with a hexagonal cell having a 9·67 Å. and c 7·01 Å. This phase was formed in mixtures containing CaO and Cr_2O_3 in the molecular ratio of 10:3 when heated in ordinary air at 950° C. It did not form in dry air. Considering the results of Korber and Trömel (1933) on mixtures of $4CaO.P_2O_5$ and $3CaO.P_2O_5$, which gave hydroxyapatite $Ca_5(PO_4)_3OH$ on heating, it seems likely that these chromium-containing mixtures also picked up moisture and formed a hydroxyapatite. Minguzzi (1941) reports small amounts of tri- and hexavalent chromium in solid solution with phosphate apatites and recent work by Glasser and Osborn (1958) has shown that the compound $9CaO.4CrO_3.Cr_2O_3$ is isomorphous with β-$Ca_3(PO_4)_2$. Here the mixture of tri- and hexavalent chromium in the ratio of 1:2 gives a mean valency of 5, thus being equivalent to the pentavalent phosphorus. Hence using this equivalence of phosphorus and chromium in these compounds the formula can be written as $Ca_5(CrO_4)_3OH$ or as $10CaO.4CrO_3.Cr_2O_3.H_2O$ (by analogy with the 9:4:1 compound). This is confirmed by chemical analysis, which gave CaO 49·5, Cr_2O_3 13·25 (by difference), CrO_3 35·6, H_2O 1·65 % (loss at 900° C.), sum 100·00 %.

Experimental details. The first compound was prepared from $CaCO_3$, Cr_2O_3, and ferrous oxalate by mixing in the correct proportions. The sample was initially fired to 1000° C. for 1 hour to decompose the carbonate and oxalate followed by grinding for 20 minutes. It was then rammed into pills and fired for 4 hours at 1200° C. in air. After photographing, each sample was reground, pressed, and refired at 1200° C. for a further 4 hours and then rephotographed.

The second compound was made from $CaCO_3$ and Cr_2O_3 and treated similarly, but heated in pill form for 24 hours at 900° C.

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