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A Product of the Thermal Decomposition of Mixed Hydroxides of Calcium and Titanium

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Re-examination of the X-ray powder diffraction data obtained from a compound in the $CaO–TiO_2$ system, reported to be $Ca_2Ti_5O_{12}$, suggests that the compound is a hitherto unknown defect pyrochlore of composition $Ca_2Ti_2O_6$. The lattice parameter is 9.953 ± 0.002 Å. © 1986 Academic Press, Inc.

Savenko and Sakharov (*1*) have reported the existence of a metastable compound which they prepared by thermal decomposition of mixed hydroxides of titanium and calcium. They assigned to this compound the composition $Ca_2Ti_5O_{12}$, and they indexed its X-ray diffraction pattern on the basis of a primitive cubic unit cell with lattice parameter 8.62 Å. This note points out that alternative interpretations of the X-ray data are possible. One of these, in our opinion, is more likely to be correct. Our interpretation, however, is not consistent with the composition deduced by Savenko and Sakharov.

The indices assigned by Savenko and Sakharov to six lines in the X-ray powder diffraction pattern are shown in Table I, together with values of $N = h^2 + k^2 + l^2$. Note that there is a factor of 3 common to all values of N. Dividing by 3 gives the values 3, 4, 7, 8, 11, and 12. There is no set of indices for which $N = 7$, but if the values of N are doubled to 6, 8, 14, 16, 22, and 24, the data can be indexed on the basis of a body-centered unit cell with lattice parameter 7.04 Å. The calculated interplanar spacings are the same as before. However, there is no obvious reason why other lines allowed with a body-centered structure, e.g., those for which $N = 2, 4, 10, 12$, etc., should not appear in the pattern. The indices assigned by Savenko and Sakharov are, of course, equally if not more peculiar.

With the exception of line 3, which appears at $2\theta = 48.30°$ when using Cu$K\alpha$ radiation, the numbers obtained by dividing the N values of Savenko and Sakharov by 3 are exactly the numbers expected with a face-centered cubic structure. This made us wonder whether, perhaps, line 3 was due to some other compound. Fortunately, Savenko and Sakharov published three diffractograms and in none of them is there a trace of a line at 48.30°. However, all show lines at approximately 47.6°, attributed to perovskite, and at 76.6°, attributed to $Ca_2Ti_5O_{12}$. This line is not included in their table, but occurs at the angle expected for the next line ($N = 16$) if the structure is

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TABLE I

INDICES ASSIGNED BY SAVENKO AND SAKHAROV (*1*) TO LINES IN THE X-RAY POWDER DIFFRACTION PATTERN FROM A COMPOUND THOUGHT TO BE $Ca_2Ti_5O_{12}$

	Line					
	1	2	3	4	5	6
h k l	221 (300)	222	421	422	441 (522)	600 (442)
$h^2 + k^2 + l^2$	9	12	21	24	33	36

face-centered cubic. The lattice parameter corresponding to this interpretation is 4.98 Å.

If we speculate about the structure, it immediately becomes apparent that it will be impossible to fit a formula unit of $Ca_2Ti_5O_{12}$ into a unit cell of size 4.98 Å. Apart from the shortage of special sites with sufficiently low numbers of equivalent positions in any cubic space group, let alone one with face-centered symmetry, there is the problem that the density would be 6.88 Mg/m^3, which is excessively large for a calcium titanate. A possible explanation is that the 4.98 Å cell is not the true unit cell but a subcell, with the true unit cell being of size 9.96 Å or even larger. However, it is also possible that the composition is not $Ca_2Ti_5O_{12}$.

The evidence on which the composition $Ca_2Ti_5O_{12}$ was based is far from strong. If we discount it and speculate on what composition might fit into a face-centered unit cell of size 4.98 Å or a multiple thereof, the pyrochlore structure comes to mind. Pyrochlore, of composition $A_2B_2X_6Y$, where *A* and *B* are metals and *X* and *Y* (which occupy crystallographically distinct sites), are O, OH, or F, has a face-centered cubic structure with a lattice parameter of about 10 Å. Defect pyrochlore structures of composition $A_2B_2X_6$ are also formed. Furthermore, both structures are based on a subcell of size ~5 Å in which the combined pattern of *A* and *B* sites is face-centered. If *A* and *B* are Ca and Ti, of roughly equal scattering power, non-fcc reflections of the subcell will occur but they will be much weaker than fcc reflections. We therefore calculated the diffraction patterns to be expected from $Ca_2Ti_2O_6$ and $Ca_2Ti_2(O,OH)_7$, ignoring the difference in scattering power between O^{2-} and OH^-. In both cases the *x* parameter of the *X* site, which is the only atomic positional variable in the structure, was taken as the value that would give regular TiO_6 octahedra. The results of this calculation are shown in Table II, together with the intensities observed by Savenko and Sakharov. In this table all lines of intensity greater than two percent of that of the strongest line and for which $d > 1.2$ Å have been included.

The agreement between the observed and calculated intensities for a defect pyrochlore structure is very good, but there are some discrepancies that we cannot explain. Line 111 may not have been observed due to starting the diffractometer trace at too great an angle, and line (333, 511), for

TABLE II

CALCULATED INTENSITIES FOR LINES IN THE POWDER DIFFRACTION PATTERNS OF $Ca_2Ti_2(O,OH)_7$ AND $Ca_2Ti_2O_6$ (IDEAL AND DEFECT PYROCHLORES, RESPECTIVELY), TOGETHER WITH INTENSITIES OBSERVED BY SAVENKO AND SAKHAROV (*1*)

Line	*h k l*	I_1[a]	I_2[b]	I_{obs}
1	1 1 1	2.3	10.6	
2	2 2 2	100.0	100.0	100
3	4 0 0	13.9	19.1	20
4	3 3 1	11.6	6.9	
5	4 2 2	2.5	6.1	
6	3 3 3, 5 1 1	6.0	7.0	
7	4 4 0	46.2	40.2	40
8	6 2 0	2.2	0.9	
9	6 2 2	31.3	31.3	25
10	4 4 4	7.3	8.6	5
11	8 0 0	5.4	4.8	5

[a] Calculated intensities for $Ca_2Ti_2(O,OH)_7$.
[b] Calculated intensities for $Ca_2Ti_2O_6$.

which d = 1.915 Å, would have been obscured by the strong perovskite line with d = 1.911 Å, but lines 331 and 422 should have been observed. We have tried the effect of varying the oxygen x parameter, without success. Nevertheless, the close agreement between the observed and calculated intensities for a defect pyrochlore structure leaves little doubt that this interpretation is basically correct, and that the material examined is $Ca_2Ti_2O_6$. The best value for the lattice parameter is 9.953 ± 0.002 Å.

We conclude that $Ca_2Ti_5O_{12}$ was not synthesized by Savenko and Sakharov and that a metastable defect pyrochlore of composition $Ca_2Ti_2O_6$ is formed by thermal decomposition of mixed hydroxides of titanium and calcium.

Acknowledgment

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Reference

1. V. G. Savenko and V. V. Sakharov, *Russ. J. Inorg. Chem.* **24,** 770 (1979).

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