

Table 3 (cont.)

<i>h</i>	<i>k</i>	<i>l</i>	<i>F_o</i>	<i>F_c</i>	<i>h</i>	<i>k</i>	<i>l</i>	<i>F_o</i>	<i>F_c</i>
3	2	1	340	345	9	7	2	131	166
5	2	1	-461	-431	6	3	3	-184	-210
7	2	1	219	252	10	3	3	134	171
9	2	1	-226	-213	5	4	3	-85	-52
11	2	1	206	215	6	5	3	-196	-213
4	3	1	146	101	10	5	3	150	199
6	3	1	185	219	7	6	3	-199	-207
10	3	1	-220	-180	9	6	3	164	192
5	4	1	20	17	8	4	4	-65	-41
9	4	1	94	84	7	6	4	68	50
6	5	1	306	302	6	6	4	324	335
10	5	1	-210	-247	8	6	4	308	364

Table 4. Bond lengths (e.s.d. 0.03 Å) and angles (e.s.d. 1°)

Al-O	1.97	O-Al-O	(i)	86°	} Value for regular cube = 73.32°
			(ii)	94	
Ba-O (i)	2.66	O-Ba-O	(i)	61°	
(ii)	2.59	(adjacent oxygen atoms)	(ii)	74	
			(iii) & (iv)	77	

Table 5. Infrared absorption bands (cm⁻¹) for the hydrogarnet group of compounds

	Ca ₃ Al ₂ (OH) ₁₂	Sr ₃ Al ₂ (OH) ₁₂	Ba ₃ Al ₂ (OH) ₁₂
O-H stretching	3658	3655	3660
Al-O-H bending	800	785	780
Al-O ₆ stretching	530	510	490

The chemical analysis indicated a BaO:Al₂O₃ ratio of about 2.5, which is too low. This can probably be attributed to the contamination with hydrous alumina mentioned above; the presence of only 4% by weight would be sufficient to account for the analytical result. However, it is also just possible that there are vacancies in the barium sites, balanced by omission of OH⁻ or substitution of H₂O for OH⁻. We attempted to check this by refinements assuming statistical occupancy of the barium sites, but were unable to reach any definite conclusion: the barium is very much the heaviest atom in the structure and reducing the number of barium atoms in the cell results in little more than a change in the scale factor. Attempts to settle the matter from consideration of the density, refractive index or thermal weight loss curves were also inconclusive. On balance it seems likely that the material does have the ideal formula.

The infrared absorption spectrum of Ba₃Al₂(OH)₁₂ was recorded over the range 4000-400 cm⁻¹ using a Perkin-

Elmer 457 Grating Spectrophotometer. The sample, prepared as a Nujol mull, was held between two KBr discs. The principle bands recorded are given in Table 5, together with those quoted for the Sr and Ca analogues by Tarte (1967). They are in excellent agreement.

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The effects of extinction corrections on the variable position and thermal parameters of Ca₂PO₄Cl and Ca₂CrO₄Cl. By MARTHA GREENBLATT, EPHRAIM BANKS and BEN POST, *Polytechnic Institute of Brooklyn, Brooklyn, New York 11201, U.S.A.*

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The crystal structures of Ca₂PO₄Cl and Ca₂CrO₄Cl which have been described in a recent publication, have been refined further by applying isotropic extinction corrections. The estimated standard errors of thermal and position parameters decreased significantly. The conventional *R* factor decreased from about 8% (for all observed reflections) to 2.5%.

We recently reported the determination of the crystal structures of the isomorphous Ca₂PO₄Cl and Ca₂CrO₄Cl (Greenblatt, Banks & Post, 1967). These were refined by conven-

tional full-matrix least-squares methods. Initial efforts led to values of the conventional *R* index ($\sum |ΔF| / \sum |F|$) of 7.1% for Ca₂CrO₄Cl and 9.6% for Ca₂PO₄Cl.

Table 1. Atomic position coordinates

	Ca ₂ CrO ₄ Cl			Ca ₂ PO ₄ Cl		
	x	y	z	x	y	z
Ca(1)	0.6204 (2)	0.2500	0.0000	0.6334 (1)	0.2500	0.0000
Ca(2)	0.1394 (2)	0.4701 (1)	0.2500	0.1286 (1)	0.4720 (1)	0.2500
Cl	0.4792 (2)	0.1782 (2)	0.2500	0.5184 (2)	0.2175 (1)	0.2500
X*	0.1242 (1)	0.2500	0.0000	0.1377 (1)	0.2500	0.0000
O(1)	0.0416 (5)	0.7353 (3)	0.3766 (2)	0.0102 (3)	0.7278 (2)	0.3855 (2)
O(2)	0.7105 (5)	0.5690 (3)	0.5315 (2)	0.7160 (3)	0.5763 (2)	0.5232 (2)

* X=Cr or P.

Table 2. R.m.s. displacements along principal axes of thermal ellipsoids (in Å)

	Ca ₂ CrO ₄ Cl			Ca ₂ PO ₄ Cl		
	1	2	3	1	2	3
Ca(1)	0.095 (3)	0.107 (5)	0.127 (2)	0.073 (2)	0.074 (2)	0.092 (1)
Ca(2)	0.098 (2)	0.102 (2)	0.125 (3)	0.076 (2)	0.078 (2)	0.104 (1)
Cl	0.113 (4)	0.117 (2)	0.171 (3)	0.085 (2)	0.091 (2)	0.168 (1)
X*	0.089 (2)	0.095 (2)	0.102 (4)	0.060 (3)	0.062 (2)	0.073 (2)
O(1)	0.104 (6)	0.112 (6)	0.133 (5)	0.073 (4)	0.086 (3)	0.105 (3)
O(2)	0.102 (5)	0.118 (7)	0.130 (6)	0.069 (4)	0.098 (3)	0.111 (3)

* X=Cr or P.

At this stage it was evident that a large number of reflections in both structures were significantly affected by extinction effects. Values of F_{calc} for strong reflections were systematically larger than the corresponding F_{obs} . When the most seriously affected reflections (twelve in Ca₂CrO₄Cl and nineteen in Ca₂PO₄Cl) were omitted from the least-squares refinement, the value of R decreased to 4.1% for the chromate and 4.3% for the phosphate.

We have recently 're-refined' both of these structures, applying isotropic extinction corrections in the form suggested by Zachariasen (1963) and modified for computer calculations by Coppens & Hamilton (1969). We believe the results will be of interest to crystallographers who have not yet used these corrections. In the new calculations we included all reflections which had previously been omitted because of extinction effects. After three cycles the residual R was 2.5% for the phosphate (760 reflections) and 2.4% for the chromate (367 reflections). The corresponding values of the weighted R factors were 3.7 and 3.6%. The new parameters are listed in Tables 1, 2 and 3. A comparison of these values with those obtained previously indicates that: none of the changes in bond distances and angles exceeded one standard deviation; the calculated standard errors of the atomic position parameters decreased by 25 to 50%; all the anisotropic atomic temperature factors increased by about 10%; scale factors also increased by 10% (the scale factor was applied to F_{calc}).

Table 3. Interatomic distances and bond angles

	Ca ₂ CrO ₄ Cl	Ca ₂ PO ₄ Cl
Ca(1)—O(1)	2.514 (3) Å	2.532 (2) Å
Ca(1)—O(2)	2.464 (3)	2.491 (2)
Ca(2)—O(1)	2.425 (3)	2.424 (2)
Ca(2)—O(2)	2.593 (3)	2.655 (2)
Cl—Cl	3.5707 (2)	3.499 (1)

Table 3 (cont.)

	Ca ₂ CrO ₄ Cl	Ca ₂ PO ₄ Cl
Cl—O(1)	3.331 (3)	3.263 (2)
Cl—O(2)	3.227 (3)	3.192 (2)
X*—O(1)	1.710 (3)	1.547 (2)
X—O(2)	1.689 (3)	1.533 (2)
O(1)—O(2')	2.694 (4)	2.481 (2)
O(1')—O(2')	2.931 (4)	2.578 (2)
O(2)—O(2')	2.670 (5)	2.477 (3)
O(1)—O(1')	2.719 (5)	2.494 (3)
O(1)—X—O(2')	104.8 °(1)	107.3 °(1)
O(1')—X—O(2)	104.8 (1)	107.3 (1)
O(2)—X—O(2')	104.4 (2)	107.7 (1)
O(1)—X—O(1')	105.3 (2)	107.5 (1)
O(1)—X—O(2)	119.2 (1)	113.6 (1)
O(1')—X—O(2')	119.2 (1)	113.6 (1)

X*=Cr or P

Similar and even more striking results have been obtained in the course of the refinement of the recently prepared Ca₂VO₄Cl. Crystals of this compound exhibited extinction and multiple reflection effects even greater than did the phosphate and chromate. In one cycle of refinement in which an isotropic extinction correction was applied, the R factor decreased from 8 to 2.3% and reached a final value of 2.1% in one more cycle. The final weighted R value was 3.2%.

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