Rietveld refinement of 3CaO.A12O3,6H2O. By Lubomír Srnčok, Institute of Inorganic Chemistry CCHR, Slovak Academy of Sciences, 842 36 Bratislava, Czechoslovakia

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Abstract

The lattice parameter of the title compound was found from X-ray Rietveld refinement to be 12.5755(1) Å; in addition to the diffractometer zero point, the specimen surface displacement was also varied. The estimated atomic positions of O and H atoms obtained from several refinements are in agreement with the values reported previously either from neutron or X-ray data. The degree of serial correlation in residuals was evaluated using the Durbin–Watson d statistic.

Hydration of calcium aluminate ferrites xCaO.y(Al,Fe)2O3 gives rise to Fe-substituted tricalcium aluminate hexahydrate, 3CaO.(Al,Fe)2O3,6H2O which retains the cubic structure of the non-substituted hexahydrate, 3CaO.Al2O3,6H2O (hereafter C3AH6). Attempts to estimate the degree of substitution only from the lattice parameter a may give unreliable results because the composition of a phase under study is usually not very accurately known. Rietveld refinement (Rietveld, 1969) seems to be more promising here because it allows for the simultaneous study of both distribution of intensities and a. To form a picture of the precision and accuracy we could attain in the analysis of this type of compound we have started with the simple case of C3AH6.

Hitherto the structure of C3AH6 has been studied several times using either X-ray or neutron single-crystal or powder data (Büssem & Eitel, 1936; Weiss & Grandjean, 1964; Cohen-Addad & Ducros, 1967; Foreman, 1968; Bartl, 1969, 1986). Hydrogarnet-like structures were recently reviewed.
by Basso (1985), $C_3A H_6$ has space group $Ia3d$ with Ca in 24(c), Al in 16(a) and both O and H in the 96(h) general position.

A well ground powder (particle size $\leq 25 \mu m$) was pressed into a standard aluminium holder and mounted on an HZG4A vertical diffractometer (made in the German Democratic Republic). The pattern was step scanned with $\beta$-filtered Co K$\alpha$ radiation ($\lambda = 1.78892$, $\lambda(2\theta) = 1.79278$ Å) from 13 to 120$°$20, $\Delta 2\theta = 0.05°$, $\tau = 20s$. The largest count was 16 320 and the background varied slowly from ~440 counts at low angles to ~220 counts at high angles. No significant amount of any other phase was noticed and $C_3A H_6$ has no tendency to any preferred orientation.

Calculation using a local version of the DBW2.9 program* (Wiles & Young, 1981) was initiated with the atomic positions given by Foreman (1968); $V$, $W$, the zero point, $a$ and the overall temperature factor were varied. Background was interpolated between 15 points and each of the 83 ($K_2\alpha$) integral intensities was distributed over 3FWHM on either side of a diffraction profile. G, L, ML and IL profile functions (Young & Wiles, 1982) were tested, with the IL giving the best fit, though only marginally better than ML. At the initial stage $a$ refined to 12.5742(2) Å, in contrast to the previously reported 12.5755(9) Å obtained by Nelson–Riley extrapolation of the data from Straumanis cameras (Foreman, 1968), or the 12.5755(4) Å as refined from a Guinier pattern (Kuzel, 1969), internal standards being admixed in both cases. Inclusion of a correction term of the form $-2s(cos \theta)R^{-1}$ into the refinement [where $s$ is the specimen surface displacement and $R$ the diffractometer radius (e.g. Wilson, 1950, 1963; Parrish & Lowitzsch, 1959; Schreiner, Surdukowski & Jenkins, 1982; Schreiner, Surdukowski, Jenkins & Villamizar, 1982)] caused $a$ to remain stable at the value of 12.5755(1) Å. With $R = 250$ mm $s$

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Table 1. Atomic positions ($\times 10^4$), isotropic temperature factors $B$ (Å$^2$), $R$ factors (%) and goodness-of-fit index $S$ with e.s.d.'s in parentheses; $R_E = 6.2\%$

<table>
<thead>
<tr>
<th>X</th>
<th>Y</th>
<th>Z</th>
<th>B</th>
<th>$R_{wp}$</th>
<th>$R_B$</th>
<th>$S$</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>324(1)</td>
<td>514(2)</td>
<td>6407(2)</td>
<td>2.23(6)</td>
<td>15.6</td>
<td>5.4</td>
</tr>
<tr>
<td>H</td>
<td>Not included in refinement</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>281(1)</td>
<td>527(2)</td>
<td>6397(1)</td>
<td>2.50(6)</td>
<td>14.0</td>
<td>3.9</td>
</tr>
<tr>
<td>H</td>
<td>Not refined, atomic positions taken from neutron refinement.*</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>290(2)</td>
<td>527(2)</td>
<td>6401(2)</td>
<td>2.72(6)</td>
<td>13.4</td>
<td>1.8</td>
</tr>
<tr>
<td>H</td>
<td>1719(19)</td>
<td>959(21)</td>
<td>7940(26)</td>
<td>3.65(10)</td>
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<td></td>
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<td>6408(3)</td>
<td>2.74(10)</td>
<td>14.6</td>
<td>3.9</td>
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<tr>
<td>H</td>
<td>1764(31)</td>
<td>991(38)</td>
<td>8406(41)</td>
<td>4.42(186)</td>
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</tr>
</tbody>
</table>

*Full data set: $B$(Ca) = 2.73(5), $B$(Al) = 2.73(7) Å$^2$, $d$ = 2.383, Q(0.1%, 1%, 5%): 1.855, 1.896, 1.932.
†Contracted data set: $B$(Ca) = 2.73(3), $B$(Al) = 3.76(7) Å$^2$, $d$ = 1.927, Q: 1.809, 1.866, 1.917.

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Table 2. Atomic positions ($\times 10^4$) with e.s.d.'s in parentheses; $R_{wp} = 13.4\%$, $R_B = 1.8\%$, $S = 2.1$

<table>
<thead>
<tr>
<th>X</th>
<th>Y</th>
<th>Z</th>
<th>B</th>
<th>$R_{wp}$</th>
<th>$R_B$</th>
<th>$S$</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>-290(2)</td>
<td>527(2)</td>
<td>1401(2)</td>
<td>140(2)</td>
<td>T</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>-282(8)</td>
<td>531(4)</td>
<td>1396(5)</td>
<td>1396(5)</td>
<td>B</td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>-780(19)</td>
<td>440(26)</td>
<td>1540(21)</td>
<td>1540(21)</td>
<td>T</td>
<td></td>
</tr>
<tr>
<td>H</td>
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<td>540(40)</td>
<td>1630(30)</td>
<td>1630(30)</td>
<td>B</td>
<td></td>
</tr>
</tbody>
</table>

T: this work; B: Bartl (1986).

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*Numerical calculations were performed on a Siemens 4004/151 computer of the Computer Centre of Comenius University in Bratislava.

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Fig. 1. Observed, calculated and difference data (full data set). Positions of possible Bragg peaks are marked by vertical bars. The lowermost oscillating line represents the function sign ($Y_c - Y_o$).
Fig. 2. Distribution of residuals (full data set); 1396 entries but only ~95% considered, mean = 1.79, standard deviation = 30.51, median = -3.38, skewness = 0.37, kurtosis = 4.63 (calculated with BMDP-79 (Dixon & Brown, 1979)).

converged to 130(14) μm but was highly correlated with both a and the diffractometer zero point so that all three parameters could not have been refined simultaneously.

The refinement continued with variation of the last FWHM parameter U, an asymmetry parameter, atomic positions and individual isotropic temperature factors. Inasmuch as the Durbin-Watson d statistic (Durbin & Watson, 1950, 1951; Theil & Nagar, 1961; Flack, Vincent & Vincent, 1980; Hill & Madsen, 1986) indicated serial correlation in residuals, one more refinement was carried out with a contracted data set having Δθ = 0.1°. The results are summarized in Tables 1 and 2 and Figs. 1 and 2.*

Table 2 shows that the differences between the most recent X-ray single-crystal refinement and this work are, in the case of the O atom, negligible. Moreover, although the refinement of H atoms from X-ray powder data is less common, the differences again do not exceed acceptable values.

*The numbered intensity of each measured point on the profile in Fig. 1 has been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43851 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Until the paper by Thompson & Wood (1983) appeared, pointing out large discrepancies within otherwise very precise lattice parameters obtained from various X-ray Rietveld refinements, the question of their accuracy had been omitted by many authors. Because the diffractometer zero point is not the most important systematic error in X-ray powder diffractometry, it is recommended that other, non-constant, correction factors also be included in Rietveld refinements. On the other hand, the results presented here may not be applicable in general, and it is therefore desirable that the problem should be studied with some well defined standards.

References