Short Communication

Neutron Powder Diffraction Profile Refinement Studies on $Ca_{11.3}Al_{14}O_{32.3}$ and $CaClO(D_{0.88}H_{0.12})$

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Structure of $Ca_{12-x}Al_{14}O_{33-x}$. The crystal structure of $Ca_{12}Al_{14}O_{33}$ was determined by Bartl and Scheller[1] from X-ray single crystal diffraction data and refined to $R = 7.5\%$. The space group is $I\bar{4}3d$ and the content of the unit cell is $Ca_{24}Al_{28}O_{66}$. The coordinates of the atoms are listed in Table 1. The oxygen atoms O(1) and O(2) account for 64 of the oxygens in the unit cell. The remaining two oxygens, O(3), are placed in site 24(*d*) with one-twelfth occupancy, giving a total of 66 oxygen atoms. The structure is thus disordered to a certain extent. The degree of disorder would vary with a non-stoichiometry of the compound if the chemical formula was of the type $Ca_{12-x}Al_{14}O_{33-x}$. The existence of such a non-stoichiometry has now been established by neu-

tron powder diffraction profile refinement of the structure of the compound.

The sample of $Ca_{12}Al_{14}O_{33}$ was prepared from a mixture of CaO and Al_2O_3 by zone melting, as reported previously.[2] The zone-melted material was crushed in a boron carbide mortar and the powder that could pass a 150-mesh sieve (~ 0.112 mm) was used.

A neutron powder diffraction pattern was recorded in the 2θ range 6–110°, using 1.226 Å neutrons, on the diffractometer at channel 3T2 of the ORPHEE reactor at the *Laboratoire Léon Brillouin,* Saclay. In the profile refinement calculations the scattering lengths used (in 10^{-12} cm units) were: Ca: 0.3449, Al: 0.490 and O: 0.577.[3]

The experimental profile is fitted to Gaussian

Table 1. Atomic coordinates of $Ca_{12}Al_{14}O_{33}$. Coordinates with standard deviations are for $Ca_{11.3}Al_{14}O_{32.3}$. $a = 11.981(2)$ Å.

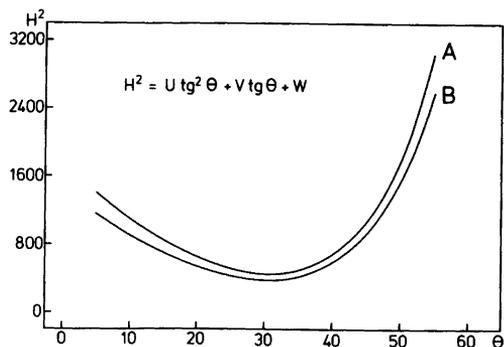| Atom	Site	x	y	z	$B/Å^2$
Ca(1)	24(*d*)	0.1397	0	1/4	
		0.1414(4)	0	1/4	1.22(7)
Al(1)	16(*c*)	0.0187	0.0187	0.0187	
		0.0181(3)	0.0181(3)	0.0181(3)	0.80(12)
Al(2)	12(*b*)	7/8	0	1/4	
		7/8	0	1/4	0.57(3)
O(1)	48(*e*)	0.151	−0.037	0.057	
		0.1509(2)	−0.0368(2)	0.0583(2)	0.82(3)
O(2)	16(*e*)	−0.0641	−0.0641	−0.0641	
		−0.0646(2)	−0.00646(2)	−0.0646(2)	0.84(7)
O(3)	24(*d*)	0.337	0	1/4	
		0.351(5)	0	1/4	0.85

Fig. 1. The θ-dependence of the half-width parameter for two compounds, obtained by least-squares fit to the experimental profiles.
A: $Ca_3Al_2(OD)_{12}$, $H^2 = 3713\ tan^2θ–4429\ tanθ + 1959$.
B: $Ca_{11.3}Al_{14}O_{32.3}$, $H^2 = 3114\ tan^2θ–3668\ tanθ + 1648$ (θ in degrees and H in 0.01 degrees).

Fig. 2. Isotropic temperature factor parameter $B(Å^2)$ for Ca(1) vs. x for $Ca_{12-x}Al_{14}O_{33-x}$, together with the R-value (profile) vs. x.

profile shape functions in the profile refinement.[4,5] The full width in 2θ at half maximum H of the shape function has the θ-dependence

$$H^2 = U\tan^2θ + V\tanθ + W$$

The three profile parameters U, V and W are mainly instrument-dependent, but they also have a sample dependence and must thus be treated as parameters in the profile refinement. Fig. 1 shows the θ-dependence of H^2 for two compounds measured on the diffractometer with the same collimation of the neutron beam. The compound $Ca_3Al_2(OD)_{12}$ was prepared by hydrothermal hydrolysis of $Ca_{12}Al_{14}O_{33}$ and has smaller grains, resulting in broader lines in the powder neutron diffraction patterns.

During the refinement it became clear that the occupancy of O(3) was less than one-twelfth. The calcium atom Ca(1) had, in addition, an isotropic temperature factor parameter which was approximately 50 % greater than those for the other atoms. This indicated a non-stoichiometry of the compound of the type $Ca_{12-x}Al_{14}O_{33-x}$, with $x = 2$ as the limiting value. Profile refinements were then carried out for different values of x (see Fig. 2), and the composition yielding the lowest R-value was $Ca_{11.3}Al_{14}O_{32.3}$. For this composition, the temperature factor parameter for the Ca(1) atom was still significantly greater than those for the other atoms. The sample investigated thus
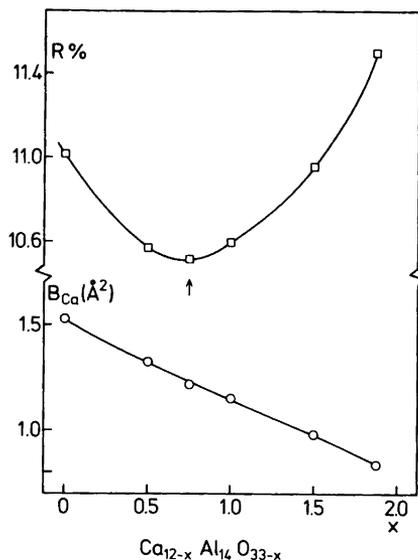
shows, in addition to the statistical distribution of the O(3) atom, a non-stoichiometry.

The atomic coordinates arrived at with the R-value of 10.53 % are listed in Table 1. They do not deviate significantly from the coordinates reported previously.[2] Fig. 3 shows observed and calculated profiles together with a difference plot.

Structure of CaClOD. The compound CaClOH has the CdClOH structure,[6] space group $P6_3mc$, and the structure was recently confirmed by Westman et al.[7] by analysis of an X-ray powder diffraction pattern. A neutron powder diffraction profile refinement has now been made in order to determine the position of the deuterium atom in the structure of CaClOD.

The compound was prepared from a mixture of CaO (obtained from $CaCO_3$, Merck analytical grade), $CaCl_2$ (Merck technical grade) and D_2O (95 % nominal purity). The CaClOD reaction product contained an unidentified impurity and the neutron diffraction investigation (see below) indicated the composition $CaClO(D_{0.88}H_{0.12})$.

The neutron powder diffraction pattern was recorded using 1.226 Å neutrons in the 2θ range 6–105° on the diffractometer described above. The
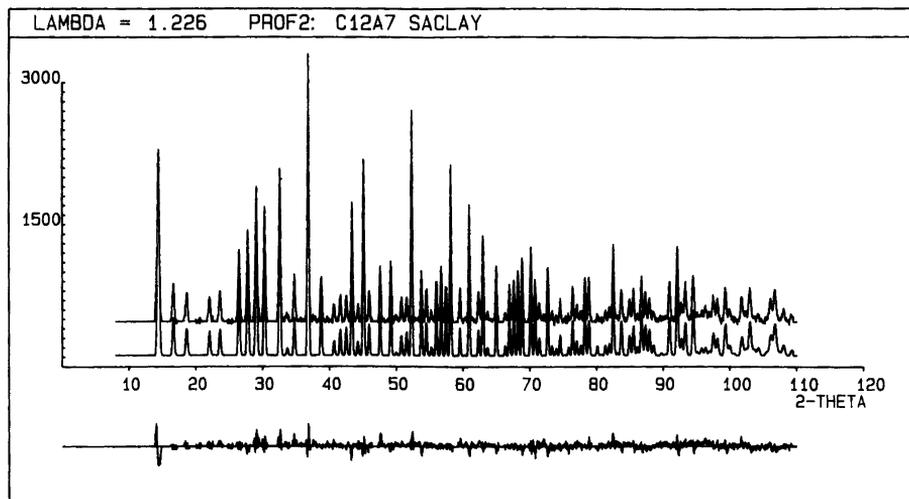
Fig. 3. Observed (upper) and calculated (lower) neutron powder diffraction pattern and difference pattern for $Ca_{12.3}Al_{14}O_{32.3}$. The abscissa is in degrees and the ordinate is counts in arbitrary units.

Table 2. Atomic coordinates and interatomic distances for $CaClO(D_{0.88}H_{0.12})$. $a = 3.868(2)$ Å, $c = 9.901(4)$ Å. Distances: Ca–Cl 2.95(5), Ca–O 2.35(5) and O–D 0.98(5) Å.

Atom	Site	x	y	z	$B/Å^2$
Ca	2(*b*)	1/3	2/3	0.0	1.5(3)
Cl	2(*b*)	1/3	2/3	0.3048(17)	0.6(1)
O	2(*a*)	0	0	0.0737(28)	1.1(2)
D	2(*a*)	0	0	0.1733(26)	2.1(3)

scattering lengths used in the profile refinements (in 10^{-12} cm units) were: Ca: 0.49, Cl: 0.99, O: 0.577 and D: 0.65. The starting parameters were the coordinates from Ref. 6 with the deuterium atom in site 2(*a*) at a distance of 1 Å from the oxygen atom. Owing to the presence of the impurity the profile refinement yielded the rather high *R*-value of 19.6%. The coordinates obtained are listed in Table 2. The interatomic distances are in acceptable agreement with those found by Westman *et al.*[7]. The O–D distance is 0.98(5) Å.

References

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