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The Unit Cell and Space Group of $4CaO.Al_2O_3.19H_2O$ Polymorphs

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M. H. Roberts (1957) has described the formation of several di- and tetra-calcium aluminate hydrates and their polymorphic forms. The present paper is the first detailed report of X-ray investigations on these preparations and is concerned mainly with the unit-cell determination of the two polytypes of $4CaO.Al_2O_3.19H_2O$, with a discussion on the solid-solution formation between tetra-calcium aluminate hydrate and di-calcium aluminate hydrate. The unit cell of α_1–$4CaO.Al_2O_3.19H_2O$ is hexagonal (possibly rhombohedral) with $a = 5{\cdot}77$, $c = 64{\cdot}08$ Å; the α_2 form of the same composition is hexagonal with $a = 5{\cdot}77$, $c = 21{\cdot}37$ Å. Tables of spacings and indices are omitted but are obtainable on request from Building Research Station (ref. Note A 92).

Introduction

Calcium aluminate hydrates appear as cement hydration products and have been studied at the Building Research Station for some time. In a preliminary account of an investigation of the CaO–Al_2O_3–H_2O system at 25 °C., Roberts (1957) reported a new hydrate, $4CaO.Al_2O_3.19H_2O$ as the only tetra-calcium aluminate hydrate existing in the aqueous system at 25 °C., and 13, 11 and $7H_2O$-hydrates of tetra-calcium aluminate as dehydration products formed on drying under various conditions. In a later work (Jones & Roberts, to be published), two forms of $4CaO.Al_2O_3.19H_2O$, designated as α_1 and α_2, with somewhat different X-ray powder patterns were distinguished, and when formed in aqueous equilibrium, the α_1-modification was found to be unstable with respect to the α_2-modification and to convert into it. In the present paper the X-ray powder patterns of these new $19H_2O$-hydrates are investigated and space group and unit cells determined. Work is continuing on the lower hydrates mentioned, as well as on various di-calcium aluminate hydrates (Aruja, 1960).

Experimental

Specimen

The specimens were made in a glove-box under controlled atmospheric conditions, and exposed to X-rays in a sealed envelope in order to avoid carbonation and dehydration. In earlier experiments a Debye–Scherrer type camera was used, in which the specimen was mounted in a thin-walled quartz capillary of 0·3 mm. diameter, the ends of which were sealed. However, for reasons discussed below, this type of camera was discarded in favour of a Guinier-type focusing camera. Here the powder was placed in a cell consisting of a frame cut out of X-ray film base of about 0·2 mm. thickness, faced on both sides with self-adhesive tape. Several tapes were tried, but 'polythene' and ethyl cellulose were found most satisfactory. 'Polythene' gives one or two broad lines, but these are readily recognized.

Some single-crystal photographs of $4CaO.Al_2O_3.19H_2O$, were also taken, a few flakes being drawn into a quartz capillary together with mother-liquor, after which the ends of the capillary were sealed. With light tapping the flake (or flakes) would settle down. It was difficult, however, to obtain a single flake in the desired orientation, and no significant results have yet been obtained.

Camera

The main requirements for an X-ray camera for this work are the facility to seal the specimen from the outside atmosphere, and high resolution of diffraction lines, especially at lower angles, say up to $\theta = 30°$. A reflection-type focusing camera (on Bragg–Brentano principle) gave the desired resolution but was found unsuitable for two reasons: firstly, the sealing tape affects preferentially the low-angle diffraction lines, and secondly, as the surface layers of the specimen contribute most to the spectrum, any drying or carbonation which may take place in making the specimen, or which may be due to absorption or permeability of the sealing tape, has a disproportionate effect. This observation is applicable also to the usual diffractometer technique.

A Guinier type (transmission) focusing camera of 11·5 cm. diameter was found most suitable. With quartz-crystal-monochromated copper radiation it gives approximately the same line dispersion as an 18 cm. diameter Debye–Scherrer camera with cobalt radiation but, because of much finer lines, its resolution is very much higher. For instance, the 20·2 line of the α_1 phase, at $\theta = 18{\cdot}059°$, could readily be measured between the 20·0 and 20·1 lines of the α_2 phase, at 18·000° and 18·128° respectively.

A drawback of the focusing camera is that the location of the specimen is not readily checked; neither is there the averaging-out process that is obtained by rotating the cylindrical specimen of a Debye camera. The addition of calibrating substances was abandoned because of overlapping. In this paper, therefore, the absolute value of spacings and the unit-cell size is subject to a larger probable error than would be expected from the close agreement between observed and calculated line positions. Preferred orientation of the material in the specimen is almost unavoidable in focusing-camera specimens that require sealing off; it has the effect of reducing the intensities of basal reflections.

Splitting of lines

When the Debye–Scherrer camera was used, the basal reflections, but not other lines nearby, were sometimes split into two reflections. This was rather confusing as the presence of more than one phase in certain specimens produced similar doublets. The components of these split lines appeared sharper than the nearby non-basal lines, and usually showed preferred orientation, the intensity maximum being about 20° to one side of the equator. The specimens were made by repeatedly poking the capillary into the moist powder settled on filter paper; being flaky, the particles align themselves more nearly tangential to the wall of the capillary the nearer they are to this wall. Thus the flakes towards the right- and left-hand sides of the specimen, looking in the direction of the primary beam, are preferentially in the reflection position for basal reflections and the major contribution comes from flakes near the cylinder wall. A similar splitting of lines was observed when the capillary was filled with a slurry of ground mica. Nelson & Riley (1945) met a similar problem with rolled graphite specimens and came to the same general conclusions.

Results

Identification of different phases

There are at least six hydrates or modifications of tetra-calcium aluminate, and the optical identification of some of the phases is uncertain. It has been impossible so far either to prepare or to mount a powder specimen completely free of impurities. The 'impurities' are usually a polymorph or polytype of the same hydrate, or a hydrate of different water content. A classification of the hydrates may be made by their X-ray patterns, especially by spacings greater than 5 Å. So far these have proved to be the basal reflections of type $00{\cdot}l$. But it was found that polymorphic forms exist which have identical basal reflections but show marked variations in some other lines from one specimen to the other. The $19H_2O$-hydrate of tetra-calcium aluminate shows such variation.

Jones & Roberts divided the X-ray patterns of $4CaO.Al_2O_3.19H_2O$ into α_1, α_2, and a mixture of α_1 and α_2, although all had the same basal reflections. It was shown that the α_1 form is precipitated first from solution and then tends to change over to the second, α_2, modification, which is the more stable form. The X-ray pattern of the α_2 modification proved easier to index and is described first, as it helps in the discussion of the following α_1 pattern.

α_2-$4CaO.Al_2O_3.19H_2O$

Several preparations of tetra-calcium aluminate hydrate gave an almost pure α_2 pattern. Even the best of them had about six weak or very weak lines which could not be indexed as α_2, but which coincided with the stronger lines of the α_1 phase or of α-$4CaO.Al_2O_3.13H_2O$.

The unit cell of α_2-$4CaO.Al_2O_3.19H_2O$ is hexagonal $a = 5{\cdot}77 \pm 0{\cdot}01$ Å, $c = 21{\cdot}37 \pm 0{\cdot}03$ Å. Volume of the unit cell, $U = 616{\cdot}1$ Å^3. Density $D_m = 1{\cdot}81$ g.cm.$^{-3}$ (measured in kerosene). With one 'molecule' of $4CaO.Al_2O_3.19H_2O$, (F.W. 668·6) in the unit cell, calculated density $D_x = 1{\cdot}801$ g.cm.$^{-3}$. The agreement between calculated and observed $4\sin^2\theta$ values was very good. Of the 63 observed reflections the difference exceeded 0·0010 only for 15 weak or broad reflections.

Observed reflections

$hk{\cdot}l$ appear in all orders,
$00{\cdot}l$ appear only if $l = 2n$.

The following space groups agree with observed reflections:

$$P6_322\text{-}D_6^6,\ P6_3/m\text{-}C_{6h}^2,\ P6_3\text{-}C_6^6\,,$$

which of these three is the true space group for the α_2 phase cannot be decided from the powder data available.

Two facts may or may not prove significant in the interpretation of powder data. Generally speaking, the differences between calculated and observed $4\sin^2\theta$ values should be randomly distributed, allowing for such systematic camera errors as there may be, and the magnitude of errors would vary with the $\sin^2\theta$ function. There is, however, a marginal tendency for reflections with the same hk to be in closer accord than reflections of differing hk, even if on the film such reflections are close to each other, and therefore the effect of any systematic error should be even.

For instance

$hk{\cdot}l$	$4\sin^2\theta$ differences $\times 10^4$
22·4, 22·6	+8, +6
31·0, 31·2, 31·3	+19, +17, +10 .

Conversely, if the unit-cell dimensions are calculated from reflections of different zones somewhat different values are obtained. Similar or more marked differences have been obtained with other hexagonal calcium aluminate hydrates. This effect is usually marginal, but it may prove significant. It is known that some imperfections of the structure, such as 'stacking faults', can cause displacements of some diffraction lines; whether such displacements can also be of a size to cause the errors met with in the indexing of other hydrates of this series cannot be said at the moment.

Secondly, there are sometimes, from one specimen to another, notable changes in relative intensities of certain lines, after allowing for any possible overlap from other known phases. For instance comparing the intensities of films No. 6104L and 5390L one finds that on 6104L there are:

00·l reflections much weaker,
11·0 much weakened relative to 11·2, other 11·l's seem unaltered,
20·0 much weakened relative to 20·1, other 20·l's seem unaltered,
21·0 somewhat weakened relative to 21·1, other 21·l's seem unaltered,
30·0 perhaps weakened,
22·0 the same,
31·0 perhaps stronger relative to 31·2.

Preferred orientation is known to affect intensities and the reduction of 00·l intensities is understandable, but it is difficult to see the cause for intensity changes of some of the other reflections.

α_1-4 CaO . Al_2O_3 . 19 H_2O

The phase of tetra-calcium aluminate hydrate which is first precipitated in contact with mother-liquor, designated as α_1-4 CaO . Al_2O_3 . 19 H_2O by Jones & Roberts, has a strong resemblance to the α_2-19 H_2O-hydrate just described. In fact, both have the same basal spacings, and the 11·l, 30·l, and 22·l reflections coincide (although relative intensities may differ). There are, however, several lines of strong or medium intensity which are not accounted for by the unit cell chosen for the α_2 phase. These lines can be indexed in terms of another hexagonal unit cell with the same a axis, but with $c''=32{\cdot}04$ Å. The two c axes are in a simple ratio 21·36:32·04 = 2:3. The set of reflections which coincide with some of those in the α_2-phase have indices with $-h+k=3n$ only, for even orders of index l (in terms of $c'=21{\cdot}36$ Å cell). The remainder have indices with $-h+k \neq 3n$ (except 00·l reflections which of course overlap) for all orders of l except $l=3n$ (in terms of the $c''=32{\cdot}04$ Å cell). The agreement between the calculated and observed 4 $\sin^2\theta$ values is very good. Of the 55 reflections observed only nine weak or broad reflections have a difference greater than 0·0010.

For a uniform description of all the observed reflections a cell with $c=32{\cdot}04$ Å would suffice, but for some observations made on the single crystal photographs of α-4 CaO . Al_2O_3 . 13 H_2O and by a certain analogy to di-calcium aluminate hydrates (to be published) it seems preferable at this stage to adopt a larger unit cell, $c=3c'=2c''=64{\cdot}08$ Å, which would also accommodate an integral number ($Z=3$) of molecular units.

Single crystal oscillation photographs of α-4 CaO . Al_2O_3 . 13 H_2O show spots and streaks placed in rows parallel to the c axis. Because of the streaky nature of most of the reflections, and the long c spacing, accurate orientation of the specimen is difficult. The layer lines remain somewhat indistinct, and it would be unwise to infer from this a 50 Å indentity period. But on measuring the indentity period of stronger spots along individual row lines it was found to be 16·5 Å in some rows (the first basal reflection of a powder photograph of this hydrate is at $d=8{\cdot}3$ Å) and 24·9 Å in some other rows. These two indentity periods are also in the ratio of 2 to 3. In view of the ready change from the 19 H_2O-hydrate into the 13 H_2O-hydrate, it is reasonable to assume that they follow an analogous structural packing scheme, which accounts for this very interesting systematic absence of certain reflections.

In conclusion, the following unit cell is proposed for the α_1-4 CaO . Al_2O_3 . 19 H_2O: (F.W. 668·6). Hexagonal (possibly rhombohedral)

$$a=5{\cdot}77\pm0{\cdot}01,\quad c=64{\cdot}08\pm0{\cdot}1\ \text{Å}\ (=3\times21{\cdot}36)\,.$$

Volume of unit cell, $U=1846$ Å^3, measured density $D_m=1{\cdot}79$ g.cm.$^{-3}$ (by weighing in kerosene). The calculated density, for three 'molecules' per unit cell ($Z=3$) is $D_x=1{\cdot}804$ g.cm.$^{-3}$ and is in fairly good agreement with the measured density. After making a choice of indices between a few overlapping reflections it appears that only even orders of the index l are observed. But the c axis cannot be halved without also halving the molecular unit. Reflections with $-h+k=3n$ ($n=0, 1, 2$ etc.) occur only with $l=6n$. Reflections with $-h+k \neq 3n$ occur in all even orders of l except $l=6n$. The first group of reflections clearly satisfied the condition of hexagonal indexing of a rhombohedral lattice, $-h+k+l=3n$. But, as on a powder photograph it is impossible to distinguish between the $+l$ and $-l$ and between the l rows for which h^2+k^2+hk is the same, it cannot be said with certainty that the rhombohedral conditions would be satisfied in the second group. However, the absence of reflections with $l=6n$ in the second group makes it possible. If that is so, the space group of α_1-phase would probably be $R3c$–C^6_{3v} or $R\bar{3}c$–D^6_{3d}. If the rhombohedral conditions are not satisfied, then the choice is between six hexagonal space groups.

Mixtures of α_1- *and* α_2-4 CaO . Al_2O_3 . 19 H_2O

It seems that preparations can be made in which α_1 and α_2 phases in any ratio can coexist, for a limited period at least. On the whole, the X-ray picture is of a simple physical mixture, with one possible exception. Films, where the α_1 phase still dominates, but where there is already a considerable amount of α_2 phase, show appreciably broader basal reflections compared with other films. The 20·2 line of the α_1 phase, and possibly a few others, also seems to be broader. It is possible that this broadening of lines is due to effective reduction of coherently scattering particle size in the c direction during the rearrangement of atomic positions in the $\alpha_1 \rightarrow \alpha_2$ transformation. These line broadenings do not suggest that there is any difference in the size of unit cells of the two polytypes other than the 1:3 ratio of the *c* axes. A difference of say 0·1% should have been observable.

Solid solution of $4CaO.Al_2O_3.19H_2O$ in $2CaO.Al_2O_3.8H_2O$

Jones & Roberts concluded that a solid solution between α_1- (or α_2-) $4CaO.Al_2O_3.19H_2O$ and α_1-$2CaO.Al_2O_3.8H_2O$ exists in the aqueous system with a limiting composition corresponding to $2{\cdot}4CaO.Al_2O_3.10{\cdot}2H_2O$. They were, however, unable to differentiate between pure α_1-$2CaO.Al_2O_3.8H_2O$ and the solid-solution phase by optical or X-ray examination. Although the X-ray patterns of the two pure compounds are quite distinctive, the unit cell sizes are very similar (the di-calcium aluminate hydrate is larger by 0·45% in the *a* direction, and 0·91% in the *c* direction). By comparing the mixtures of the suspected solid solution and the pure components, good agreement was obtained between calculated and estimated values for the *a* and *c* axes. However, detailed analysis of the results from different zones of reflections suggested that the expected differences were of the same order as certain systematic deviations mentioned above in describing the α_2-phase, and it must be concluded that the X-ray data does not provide adequate proof of the existence of a solid solution series.

I should like to thank my colleague Dr M. H. Roberts for allowing me to use the X-ray films he took for his work on the system of CaO–Al_2O_3–H_2O. The work described is part of the research programme of the Building Research Board of the Department of Scientific and Industrial Research, and this paper is published by permission of the Director of Building Research. Crown Copyright is reserved.

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The Crystal Structure of Disordered Trimethylamine Triborane

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The crystal structure of the disordered high temperature (transition temperature −64 °C.) modification of trimethylamine triborane, $B_3H_7N(CH_3)_3$, has been determined by single-crystal X-ray diffraction techniques. It has been possible to roughly determine the molecular configuration, and to estimate bond parameters. The nature of the disorder also is indicated.

1. Introduction

Coordination compounds containing the triborane group, B_2H_7, were first prepared by Edwards, Hough & Ford (1957) in these laboratories. The preparation of trimethylamine triborane, the most stable and most easily purified of the compounds prepared, is typical of the reactions used:

$$B_4H_{10}+2\ (CH_3)_3N \rightarrow (CH_3)_3NB_3H_7+(CH_3)_3BH_3\ .$$

This reaction was postulated to proceed by a 'symmetrical' cleavage of the hydrogen bridge bonds in tetraborane by analogy with the reactions of Lewis bases with diborane (Edwards, Hough & Ford, 1957). Shortly following this work, the compound ammonia triborane, $NH_3B_3H_7$, was prepared in the laboratory of R. W. Parry at the University of Michigan (Kodama, Parry & Carter, 1959).

Thermodynamic studies have shown that trimethylamine triborane and ammonia triborane both undergo low temperature phase transitions of a similar type (Westrum & Levitin, 1959; Levitin & Westrum, 1959). Crystal structure analyses have been reported recently for both the disordered high temperature, and ordered low temperature phases of ammonia triborane (Nordman & Reimann, 1959). The B_3H_7 group was found to have a structure close to the one expected for the 'symmetrical' cleavage fragment of tetraborane. The work reported herein establishes a similar structure for the B_3H_7 radical in trimethylamine triborane and affords further corroboration for the symmetrical cleavage reaction mechanism.

2. Experimental

Several specimens of crude reaction product were supplied by Messrs. W. V. Hough and M. D. Ford of these laboratories. The crude material was purified by

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