

ture enabling more such connections to be made at the expense of regularity of atomic arrangement.

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## The Unit Cell of Orthorhombic Pentacalcium Trialuminate, $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$

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The orthorhombic form of  $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$  has been found to belong to space group  $C222_1-D_2^2$ , 4 formula units per unit cell of  $a = 10.975$ ,  $b = 11.250$ ,  $c = 10.284$  Å (probable error  $\pm 0.005$  Å). Single crystals were investigated with copper radiation. Density  $3.03\text{--}3.06$  g.cm.<sup>-3</sup>. Optical constants: colourless, non-pleochroic, biaxial negative  $2V = 88.5 \pm 0.8^\circ$ ,  $\alpha = 1.680 \pm 0.001$ ,  $\beta = 1.682 \pm 0.001$ ,  $\gamma = 1.685 \pm 0.001$ ,  $\gamma - \alpha = 0.005$ . Acute bisectrix ( $X$ ) perpendicular to cleavage face (001), obtuse bisectrix ( $Z$ ) parallel to crystallographic  $a$  axis.

The similarity of the X-ray powder pattern to that of gehlenite,  $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ , is pointed out.

### Introduction

Over forty years ago, Shepherd, Rankin & Wright (1909) reported a stable and an unstable form of  $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$  with distinct optical characteristics. The structure of the stable form has been determined by Büssem & Eitel (1936) by single-crystal methods; the unit cell is cubic,  $a = 11.95$  Å. The measured density of  $2.69$  g.cm.<sup>-3</sup> did not agree with that calculated on the basis of a composition of  $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$  and to bring the calculated density in line with the measured, the formula  $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$  was suggested. It was then necessary to assume that two excess oxygens out of a total of 66 must be statistically distributed over the unit cell.

Lagerquist, Wallmark & Westgren (1937) subsequently suggested a slightly different alternative structure, with vacancies in aluminium locations. Their formula,  $9\text{CaO} \cdot 5\text{Al}_2\text{O}_3$ , as with  $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ , does not allow an integral number of molecules to fit into the measured unit cell.

Dyckerhoff (1924) investigated laboratory melts and thought that the unstable form of  $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$  might be found in high-alumina cement. This was further

investigated by Sundius (1939), who found in certain high-alumina cements a needle- or lath-shaped pleochroic mineral which had optical properties similar to unstable  $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ , as described by Shepherd *et al.* (1909); (Rankin & Wright (1915*a, b*) give more details). Henceforth in the literature this pleochroic cement mineral has been referred to as 'unstable  $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ ', although Sundius himself had observed that there is an appreciable amount of  $\text{SiO}_2$  and  $\text{Fe}_2\text{O}_3$  present.

Parker (1954), as a result of phase equilibrium studies in the system  $\text{CaO}-\text{Al}_2\text{O}_3-\text{MgO}-\text{SiO}_2$ , has demonstrated that the blue pleochroic mineral found in high-alumina cements is not unstable  $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$  but a quaternary compound with a probable formula  $6\text{CaO} \cdot 4\text{Al}_2\text{O}_3 \cdot (\text{Mg, Fe})\text{O} \cdot \text{SiO}_2$ . Recently single crystals of an orthorhombic form of  $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$  were prepared by Welch using the high-temperature microscope device (Welch, 1954).

There is obviously a very great possibility of confusion because the name 'unstable  $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ ' has been applied to different phases. Moreover, the orthorhombic  $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ , although closely resembling Rankin & Wright's unstable compound, may prove

in fact to be a stable phase in the binary system. It is proposed therefore to refer to the substance under discussion as 'orthorhombic  $5\text{CaO}\cdot 3\text{Al}_2\text{O}_3$ ', although a slight range of composition is not excluded.

### Preparation of samples

The crystals were grown (Welch, private communication, to be published) in the high-temperature microscope device from melts of  $\text{CaO}$  and  $\text{Al}_2\text{O}_3$  in molar ratios ranging from 12:7 to 5:3. Either cubic  $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$  or orthorhombic  $5\text{CaO}\cdot 3\text{Al}_2\text{O}_3$  crystals, with small or very small amounts of glass or crystalline impurity, could be obtained from these melts, depending on the heat treatment. For instance, from a melt with  $\text{CaO}:\text{Al}_2\text{O}_3$  ratio slightly less than 12:7 orthorhombic crystals with least residue were obtained when the preparation was completely melted at  $1600^\circ\text{C}$ ., then cooled rapidly to  $1070^\circ\text{C}$ . and held for 2–3 sec. when nucleation took place. The temperature was raised to  $1360^\circ\text{C}$ . until only one crystal remained, the melt then being slowly cooled to  $1300^\circ\text{C}$ .

### Optical constants

The optical description (by H. G. Midgley) of the single crystal is as follows: colourless, non-pleochroic, biaxial negative,  $2V = 88.5 \pm 0.8^\circ$ ,  $\alpha = 1.680 \pm 0.001$ ,  $\beta = 1.682 \pm 0.001$ ,  $\gamma = 1.685 \pm 0.001$ ,  $\gamma - \alpha = 0.005$  (for sodium light). Acute bisectrix ( $X$ ) perpendicular to the cleavage face (001) and the obtuse bisectrix ( $Z$ ) parallel to the crystallographic  $a$  axis.

### X-ray analysis

The beads obtained from the high-temperature microscope cleave fairly readily into thin flakes parallel to (001), but breaking up or cutting into smaller fragments causes distortions. Specimens crushed in a mortar give powder patterns with high-order Debye lines broadened or missing. Data of the powder pattern are available from the Building Research Station.

Laue, oscillation and Weissenberg photographs show that  $5\text{CaO}\cdot 3\text{Al}_2\text{O}_3$  is orthorhombic, space group  $C222_1-D_2^5$ , with four formula units in the unit cell of

$$a = 10.975, \quad b = 11.250, \quad c = 10.284 \text{ \AA}.$$

The error is probably under  $\pm 0.005 \text{ \AA}$ , as estimated from measurement of several specimens.  $\text{Cu } K\alpha$  radiation was used, wavelength  $1.54178 \text{ \AA}$ . Reflexions  $hkl$  were present only if  $h+k$  was even, and reflexions  $00l$  only if  $l$  was even.

Density was measured on two single-crystal flakes by flotation in a mixture of methylene iodide and bromoform, and on two polycrystalline lumps, of 0.7 and 1.8 g. weight respectively, by weighing in kerosene. The flotation method gave 3.011 and 3.031

$\text{g.cm.}^{-3}$  and the two lumps gave 3.068 and 3.064  $\text{g.cm.}^{-3}$  respectively. The first flake was contaminated by a very small amount of cubic  $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ , which is considerably lighter (specific gravity 2.70). The second flake from a different stock, too, may have appeared lighter because of some remnant glass (specific gravity about 2.87). The polycrystalline 'lump' specimens contained a very little tricalcium aluminate, density about  $3.03 \text{ g.cm.}^{-3}$ .

The number of formula units in the unit cell of  $1270 \text{ \AA}^3$  are 3.95 or 3.99 for measured densities of 3.03 and  $3.06 \text{ g.cm.}^{-3}$  respectively, assuming the  $5\text{CaO}\cdot 3\text{Al}_2\text{O}_3$  formula (formula weight =  $586.2$  atomic weight units). This is sufficiently close to the integral number 4. The  $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$  formula on the other hand, does not fit at all satisfactorily and gives 1.7 molecules instead of 2.

It will be noted that crystal-density considerations compelled Büsser & Eitel to suggest  $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$  as the formula for the compound named by Rankin as 'stable  $5\text{CaO}\cdot 3\text{Al}_2\text{O}_3$ ', whereas in the case of the orthorhombic mineral the original formula gives a better fit.

The dimensions of the unit cell seem unaffected by the composition of the stock melt from which the crystal was grown. However, the polycrystalline lump specimen which was weighed to  $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$  composition but was annealed in an atmosphere of dry nitrogen showed an increase of about  $0.02 \text{ \AA}$  or 0.2% in its axial lengths ( $10.997$ ,  $11.277$  and  $10.302 \text{ \AA}$  for  $a$ ,  $b$  and  $c$  respectively) as measured on a powder photograph.

### Structural comparisons

It is not possible at present to undertake a complete structure determination but some comparisons can be drawn:

1. The X-ray powder patterns of cubic  $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$  and orthorhombic  $5\text{CaO}\cdot 3\text{Al}_2\text{O}_3$  compounds show no resemblance, although the cube edge of the one ( $11.95 \text{ \AA}$ ) is quite close to the orthorhombic axes ( $10.975$ ,  $11.250$ ,  $10.284 \text{ \AA}$ ) of the other compound of only slightly different composition. Large changes in specific gravity and unit-cell contents would discourage any attempts to view the orthorhombic structure as derived from the cubic structure by simple deformation.

2. The X-ray powder pattern of orthorhombic  $5\text{CaO}\cdot 3\text{Al}_2\text{O}_3$  bears some resemblance to the pleochroic mineral of high-alumina cement, but it is undoubtedly a completely different compound. Parker (1954) has shown that  $\text{SiO}_2$  and  $\text{FeO}$  or  $\text{MgO}$  are essential constituents of the latter and K. A. Gross (private communication; also Lea, 1956) has determined its orthorhombic unit cell as  $27.7 \times 10.85 \times 5.14 \text{ \AA}$ . Both patterns are similar to gehlenite,  $2\text{CaO}\cdot \text{Al}_2\text{O}_3\cdot \text{SiO}_2$  which is tetragonal (Raaz, 1930)  $a = b = 7.69$ ,  $c = 5.10 \text{ \AA}$ . Now the Weissenberg photograph of the

*ab* plane of the orthorhombic pentacalcium trialuminate has two conspicuous rows of spots, approximately at  $45^\circ$  to the orthorhombic *a* and *b* axis chosen above. On this basis it could be indexed as monoclinic with  $a'=b'=7.87 \text{ \AA}$ ,  $c=10.28 \text{ \AA}$ ,  $\gamma=91.5^\circ$ , space group  $P2_1$  or  $P2_1/m$ . This unit cell is readily comparable with that of gehlenite. In the composition it would imply the replacement of all the silicon in gehlenite by aluminium, and the introduction of two more calcium ions for every 28 oxygens. From space-filling considerations this seems feasible, but the introduction of  $\text{Al}_2\text{O}_7$  groups as in gehlenite might lower the orthorhombic symmetry proposed for orthorhombic  $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ .

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## Anwendung eines Elektronenfilters auf das Elektronenbeugungsdiagramm des Glimmers und des Anthrazen: Kikuchi-Linien und diffuse Flecken

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A description is given of the use of an electron filter in electron diffraction. It is applied to the analysis of the energy loss of the electrons which contribute to the Kikuchi lines in the diagrams of mica and to the areas of diffuse blackening in the diagrams of anthracene.

### Einführung

Die Zerstreung der unelastischen Elektronen bei ihrem Durchgang durch die Materie hat ein besonderes Interesse in den Elektronenbeugungsdiagramm und beim Anwenden des Filters, welches sich auf die Gegenfeld-Methode gründet. Wir haben dieses Filter bei den Elektronenbeugungsdiagrammen des Glimmers und des Anthrazen angewandt, um im ersten Fall den Energieverlust der Elektronen zu analysieren, welche die Kikuchi-Linien bilden und im zweiten Fall die diffusen Flecken, die sich symmetrisch verteilen und von Charlesby & Wilman entdeckt worden sind.

### Elektronenfilter

Wir benutzen ein Elektronenfilter mit einem Silbernetz, das die Zentral-Elektrode darstellt, gemäss dem

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von Boersch (1949, 1953) konstruierten, an dem wir aber einige Neuerungen angebracht haben, und unter Anwendung eines parallelen Elektronenbündels.

In dem Filter benutzen wir ein neues Silbernetz mit einer Gitterkonstanten von  $30\mu$  und 70% Durchlässigkeit, was uns erlaubt, Photographien herzustellen, ohne dass das Schattenbild des Netzes den Bildern überlagert ist.

### Anwendungen

(a) *Anwendung des Filters auf die Elektronenbeugungsdiagramme des Goldes*

Wendet man das Filter bei einem Elektronenbeugungsdiagramm des Goldes an, so beobachtet man einen grossen Unterschied zwischen den Aufnahmen mit und ohne Filter (Fig. 1).

Wendet man das Filter bis zu einem Wert von 3 e.V. an (Fig. 1(b)), verschwindet der Hintergrund