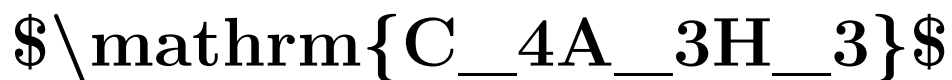


# CRYSTAL STRUCTURE OF TETRACALCIUM TRIHYDROTRIALUMI- NATE



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## Abstract

## Full Text

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# CRYSTAL STRUCTURE OF TETRACALCIUM TRIHYDROTRIALUMINATE $C_4A_3H_3$

Tetracalcium trihydrotrialuminate

$C_4A_3H_3 = 4CaO \cdot 3Al_2O_3 \cdot 3H_2O$ , formed as a result of hydrothermal synthesis in the system  $CaO-Al_2O_3-H_2O$ , and also during the hardening of alumina cements at elevated temperatures, is regarded as the most high-temperature-stable calcium hydroaluminate. Since its discovery in 1943 <sup>(1)</sup>, it has been studied by various authors, chiefly on powders, since obtaining sufficiently large and perfect single crystals is a difficult task.

Our objects were transparent single crystals of "rhomboid" form, the result of hydrothermal synthesis at  $450^\circ$  and  $P = 1000-1500$  atm <sup>(2)</sup>. The preliminary stage of the X-ray structural analysis of faceted crystals was carried out on a DRON-1 diffractometer in accordance with the method <sup>(3)</sup>. In rhombic crystals of  $4CaO \cdot 3Al_2O_3 \cdot 3H_2O$  the cell is body-centered,  $a = 12.426 \pm 0.002$  Å,  $b = 12.809 \pm 0.002$  Å,  $c = 8.864 \pm 0.0001$  Å. The systematic extinctions correspond to two Fedorov groups:  $C_{2v}^{17} = Ab2a$ ,  $D_{2h}^{18} = Abma$ ,  $Z = 4$ . These data agree with those reported earlier <sup>(4)</sup>.

**Table 1**

$Ca_2(AlO_2)_3(OH) \cdot H_2O$ . Coordinates of the basis atoms and parameters of isotropic thermal vibrations

Atoms	$x/a$	$y/b$	$z/c$	$B$ (Å <sup>2</sup> )
Ca <sub>1</sub>	0	0.1422	0	0.18
Ca <sub>2</sub>	0.3492	0	0.2107	0.12
Al <sub>1</sub>	0.1296	0.1229	0.3630	0.12
Al <sub>2</sub>	0.250	0.250	0.1106	0.14
O <sub>1</sub>	0.3663	0.2186	0.0026	0.54
O <sub>2</sub>	0.2222	0.1393	0.2195	0.64
O <sub>3</sub> (OH)	-0.0025	0.1310	0.2769	0.85
O <sub>4</sub>	0.1467	0	0.4463	0.66
O <sub>5</sub> (H <sub>2</sub> O)	0.3913	0	0.4640	0.80

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

Accuracy of atom localization:

Ca  $-0.002 \text{ \AA}$ , Al  $-0.003 \text{ \AA}$ , O  $-0.004 \text{ \AA}$ .

Accuracy in the parameters of isotropic thermal vibrations:

Ca and Al  $-0.07 \text{ \AA}^2$ , O  $-0.12-0.17 \text{ \AA}^2$ .

A three-dimensional set of structural-amplitude moduli was obtained on an equi-inclination automatic diffractometer controlled by a computer <sup>(5)</sup>. Experimental conditions: spherical specimen  $d = 0.302 \pm 0.005 \text{ mm}$ , nonsphericity 3.2%, mosaicity 0.4°,  $\text{CuK}_\alpha$  radiation with a  $\beta$ -filter (Ni), BSV-11 tube, voltage 34 kV, current 15 mA. The spectral interval  $\Delta\lambda/\lambda = 0.0078$  was used, the counter was scintillation-type, intensities were corrected in the diffractometer for the  $LP$  factors and for absorption for  $\mu R = 2.64$ . Reflections were measured only in a single passage of the crystal through the calculated interval  $\Delta\omega$  at a rate of  $6^\circ/\text{min}$ ; the combined  $\omega-\omega/2\omega$  method was used <sup>(6)</sup>. The average data-collection rate under these conditions was 54 reflections per hour. After averaging equivalent reflections, we

had 598  $|F| \neq 0$  on 10 layers ( $hk0-hk9$ ). The mean error for equivalent reflections was 2.3%, and the error in the measured  $|F|$  was 1.1%.

The data of the goniometric study of the crystals, the absence of a piezoelectric effect, and the statistical test for an inversion center made the holohedral symmetry group more probable.

In solving the structure of  $\text{C}_4\text{A}_3\text{H}_3$ , substantial assistance, along with analysis of the Patterson function, was provided by ideas about the topotactic mechanism of the transformation of rhombic  $4\text{CaO} \cdot 3\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$  into cubic  $4\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ , the structure of which had been solved earlier <sup>(7)</sup>. The assumption that the structures of  $\text{C}_4\text{A}_3\text{H}_3$  and  $\text{C}_4\text{A}_3$  are close was made in <sup>(8)</sup> on the basis of an analysis of powder patterns obtained at different degrees of dehydration of  $\text{C}_4\text{A}_3\text{H}_3$ . The coordinates of the basic atoms (Table 1) were found from two-dimensional and three-dimensional syntheses of the electron density. The discrepancy factor reached in the course of least-squares refinement was 0.084.

**Fig. 1.**  $\text{C}_4\text{A}_3\text{H}_3$ . Projection of the structure along  $[010]$ . Al tetrahedra along  $a$  are joined into discrete packets three tetrahedra thick. Black circles are Ca atoms, large spheres are  $\text{H}_2\text{O}$  particles.

In the crystal structure of  $\text{C}_4\text{A}_3\text{H}_3$  the principle of the arrangement of atoms according to the laws of closest packing is clearly realized; O atoms together

Fig. 3

Figure 3: Fig. 3

**Fig. 2**

**Fig. 3**

**Fig. 2.**  $C_4A_3H_3$ . Projection of the structure along  $[001]$ . Sodalite motif of the structure. The two halves of the sodalite cage are connected by a horizontal second-order axis along  $b$ . A cut through the vertices of tetrahedra shows the points of linkage with tetrahedra located above and below; a broken cut denotes the absence of a connection between tetrahedra.

**Fig. 3.**  $C_4A_3H_3$ . Connecting detail of adjacent packets of aluminosilicate tetrahedra. The acute vertices of an isolated rhombus of Ca octahedra are located in different packets, the obtuse ones—between packets.

form a cubic closest packing (layer index in the rhombic cell  $(20\bar{1})$ ) with Al atoms in  $3/16$  of the tetrahedral voids and Ca atoms in  $1/4$  of the octahedral ones ( $A_2B_3X_8$ ). Large Ca cations and strong hydrogen bonds somewhat distort the ideal packing.

Another guiding principle may be considered to be the tendency, characteristic of aluminosilicates and most pronounced in calcium aluminates, of Al atoms to form frameworks of alumino-oxygen tetrahedra.

Strong hydrogen bonds prevent complete—throughout—polymerization of the tetrahedra, and the structure consists of block-packets: within the repeat period  $a$  there are 2 blocks, each 3 tetrahedra thick along the  $a$  axis and infinite in the other two directions (Fig. 1). Each of the two packets

**Table 2**

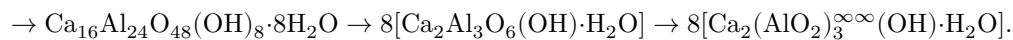
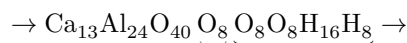
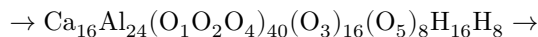
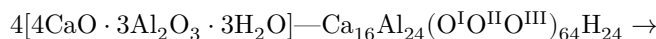
$Ca_2(AlO_2)_3(OH)H_2O$ . Interatomic distances (in angstroms)

Al tetrahedra		Ca octahedra	
<b>Al<sub>1</sub>-tetrahedron</b>		<b>Ca<sub>1</sub>-octahedron</b>	
Al <sub>1</sub> —O <sub>1</sub>	1.743	Ca <sub>1</sub> —O <sub>1</sub>	2.440 (2)
Al <sub>1</sub> —O <sub>2</sub>	1.725	Ca <sub>1</sub> —O <sub>3</sub>	2.459 (2)
Al <sub>1</sub> —O <sub>3</sub>	1.812	Ca <sub>1</sub> —O <sub>5</sub>	2.292 (2)
Al <sub>1</sub> —O <sub>4</sub>	1.752	(Ca <sub>1</sub> —O) <sub>avg</sub>	2.394
(Al <sub>1</sub> —O) <sub>avg</sub>	1.758	O <sub>1</sub> —O <sub>1</sub>	2.993
O <sub>1</sub> —O <sub>2</sub>	2.919	O <sub>1</sub> —O <sub>3</sub>	2.793 (2)
O <sub>1</sub> —O <sub>3</sub>	2.793	O <sub>1</sub> —O <sub>5</sub>	2.852 (2)
O <sub>1</sub> —O <sub>4</sub>	2.848	O <sub>1</sub> —O <sub>5</sub>	3.634 (2)
O <sub>2</sub> —O <sub>3</sub>	2.835	O <sub>3</sub> —O <sub>5</sub>	3.021 (2)
O <sub>2</sub> —O <sub>4</sub>	2.845	O <sub>3</sub> —O <sub>5</sub>	3.526 (2)

Al tetrahedra		Ca octahedra	
O <sub>3</sub> –O <sub>4</sub>	2.916	O <sub>5</sub> –O <sub>5</sub>	2.783
(O–O) <sub>avg</sub>	1.858	(O–O) <sub>avg</sub>	3.117
<b>Al<sub>2</sub>-tetrahedron</b>		<b>Ca<sub>2</sub>-octahedron</b>	
Al <sub>2</sub> –O <sub>1</sub>	1.776 (2)	Ca <sub>2</sub> –O <sub>2</sub>	2.384 (2)
Al <sub>2</sub> –O <sub>2</sub>	1.751 (2)	Ca <sub>2</sub> –O <sub>3</sub>	2.497 (2)
(Al <sub>2</sub> –O) <sub>avg</sub>	1.763	Ca <sub>2</sub> –O <sub>4</sub>	2.344
O <sub>1</sub> –O <sub>1</sub>	2.993	Ca <sub>2</sub> –O <sub>5</sub>	2.305
O <sub>1</sub> –O <sub>2</sub>	2.817 (2)	(Ca–O) <sub>avg</sub>	2.402
O <sub>1</sub> –O <sub>2</sub>	2.864 (2)	O <sub>2</sub> –O <sub>2</sub>	2.922
O <sub>2</sub> –O <sub>2</sub>	2.817	O <sub>2</sub> –O <sub>3</sub>	3.428 (2)
(O–O) <sub>avg</sub>	2.862	O <sub>2</sub> –O <sub>4</sub>	3.423 (2)
		O <sub>2</sub> –O <sub>5</sub>	3.206 (2)
		O <sub>3</sub> –O <sub>3</sub>	3.086
		O <sub>3</sub> –O <sub>4</sub>	3.471 (2)
		O <sub>3</sub> –O <sub>5</sub>	3.024 (2)
		(O–O) <sub>avg</sub>	3.250

consists of halves of a sodalite “lantern”; in alternating packets these halves are displaced relative to one another along (100) by 2.5 Å and are mutually linked by a twofold axis lying in (100) (Figs. 1, 2). In the packets both six-membered and four-membered windows of Al tetrahedra are preserved (Fig. 2).

In the structure, the O atoms occupy 5 nonequivalent positions and, according to their role in the alumino-oxygen framework, are divided into three groups: O<sup>I</sup> –these are O<sub>1</sub>, O<sub>2</sub>, O<sub>4</sub>, common to two tetrahedra and therefore fully included in the framework; O<sup>II</sup>–O<sub>3</sub>, belonging to one tetrahedron, enters the framework only “by half”; O<sup>III</sup>–O<sub>5</sub>, does not participate in the formation of the framework. The distinction between the O atoms of the three groups determines the character and position of the water. In accordance with the established structure, the multiplicity of the positions, and the known chemical formula, the crystal-chemical formula of the compound is represented as follows:



The Ca atoms are located at the large six-membered windows ( $\text{Ca}_2$ ) and in the gaps between packets of aluminum tetrahedra ( $\text{Ca}_1$ ). Four Ca-octahedra, joined by two  $\text{O}_5$  atoms into isolated rhombi parallel to only one of the four series of planes of cubic closest packing ( $20\bar{1}$ ), serve as a linkage (Fig. 3).

The interatomic distances and the parameters of anisotropic thermal vibrations in the structure (Table 2) obey crystal-chemical principles: shortened distances between O atoms that are connected by a strong hydrogen bond, 2.783 Å ( $\text{O}_5\text{—O}_5$ ); elongated Al— $\text{O}_3$  distances (1.812 Å) in the tetrahedron with the OH group; the largest thermal vibrations at  $\text{O}_3$  and  $\text{O}_5$ . The short Ca bonds with free  $\text{H}_2\text{O}$ —2.292 and 2.305 Å—are apparently responsible for the fairly high strength and thermal stability of  $\text{Ca}_2(\text{AlO}_2)_3(\text{OH}) \cdot \text{H}_2\text{O}$  (endothermic effect at 540°). The cleavage plane (100), as usual in lamellar structures, passes between two packets of Al tetrahedra that are connected by hydrogen bonds and paired calcium octahedra ( $\text{Ca}_1$ ).

The structural features of  $\text{Ca}_2(\text{AlO}_2)_3(\text{OH}) \cdot \text{H}_2\text{O}$  explain the mechanism of dehydration of this compound, which will be presented by the authors in a separate communication.

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named after M. V. Lomonosov

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*Note: Figure translations are in progress. See original paper for figures.*

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