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A Cementitious Compound with Composition 3CaO·Al₂O₃·CaCO₃·11H₂O

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Abstract

The tetracalcium dialuminium hydroxide carbonate pentahydrate Ca₄Al₂(OH)₁₂CO₃·5H₂O is a layered compound constituted by positively charged [Ca₄Al₂(OH)₁₂]²⁺ main layers and negatively charged [CO₃·5H₂O]²⁻ interlayers. The Al³⁺ and Ca²⁺ ions are six- and sevenfold coordinated by O atoms, respectively. A water molecule occupies the seventh coordination site of

each of three Ca²⁺ ions among the four contained in the main layer. Thus, among the five water molecules contained in the interlayer, two of them can be considered as only slightly bonded. One O atom of the carbonate group occupies the seventh coordination site of the remaining Ca²⁺ ion. Moreover, every O atom of the carbonate groups contributes to the formation of relatively strong hydrogen bonds with water molecules, providing cohesion of the interlayer. The planar CO₃²⁻ groups are tilted by 21.8 (9)° from the planes formed by the layers.

Comment

The compound 3CaO·Al₂O₃·CaCO₃·11H₂O and several of the many related basic salts called AFm phases are important because they are formed on hydration of cements. They form positively charged brucite-like [Ca₂(Al,Fe)(OH)₆]⁺ layers and negatively charged [X_z·nH₂O]⁻ interlayers to attain electroneutrality, where X is a monovalent anion (OH⁻, Cl⁻, NO₃⁻, AlO₂⁻) with z = 1, or a bivalent anion (CO₃²⁻, SO₄²⁻) with z = ½, and where n can vary depending on the humidity and on the nature of the inserted anions. To date, structures based on single-crystal data have been determined for the monosulfate 3CaO·Al₂O₃·CaSO₄·12H₂O (Allmann, 1977) and the chloride 3CaO·Al₂O₃·CaCl₂·11H₂O (Tersis *et al.*, 1987) only. A structural model for the carbonate equivalent has been proposed but not refined (Ahmed & Taylor, 1967). In fact, many uncertainties persist concerning the symmetry and the composition, such as the number of water molecules, of the carbonate compound. Triclinic lattice parameters based on single-crystal measurements have been published by Fischer & Kuzel (1982).

The title compound crystallizes in the non-centrosymmetric space group P1. It contains 27 crystallographic

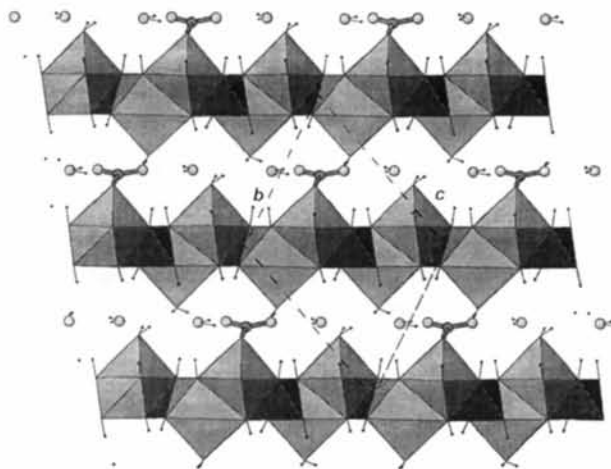


Fig. 1. Projection of the layer structure of 3CaO·Al₂O₃·CaCO₃·11H₂O along [100].

non-H atomic sites. There is one formula unit ($3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaCO}_3\cdot 11\text{H}_2\text{O}$) per unit cell. All the occupation factors are equal to unity; thus, the structure is perfectly ordered.

A general view of the structure projected along the [100] direction is shown in Fig. 1. It can be described by the stacking sequence of planes $[\text{Ca}_4\text{Al}_2(\text{OH})_{12}]^{2+} - 2\text{H}_2\text{O} - [\text{CO}_3\cdot 3\text{H}_2\text{O}]^{2-}$, etc., parallel to (011). Two adjacent $[\text{Ca}_4\text{Al}_2(\text{OH})_{12}]^{2+}$ main layers are separated by a distance of 7.55 Å. This distance is 8.93 and 7.87 Å in the corresponding sulfate and chloride compounds, respectively. The water molecules and the carbonate group in the interlayer of composition $[\text{CO}_3\cdot 5\text{H}_2\text{O}]^{2-}$ connect the main layers. The planar CO_3^{2-} groups are tilted by $21.8(3)^\circ$ from the (011) planes, *i.e.* from the main layers. This result is not compatible with a model proposed by Ahmed & Taylor (1967), in which carbonate groups were supposedly parallel to the layers and not connected directly to them.

The O-atom environments of the cations Ca^{2+} and Al^{3+} are represented in Fig. 2. The coordination numbers are six and seven for the Al^{3+} and Ca^{2+} cations,

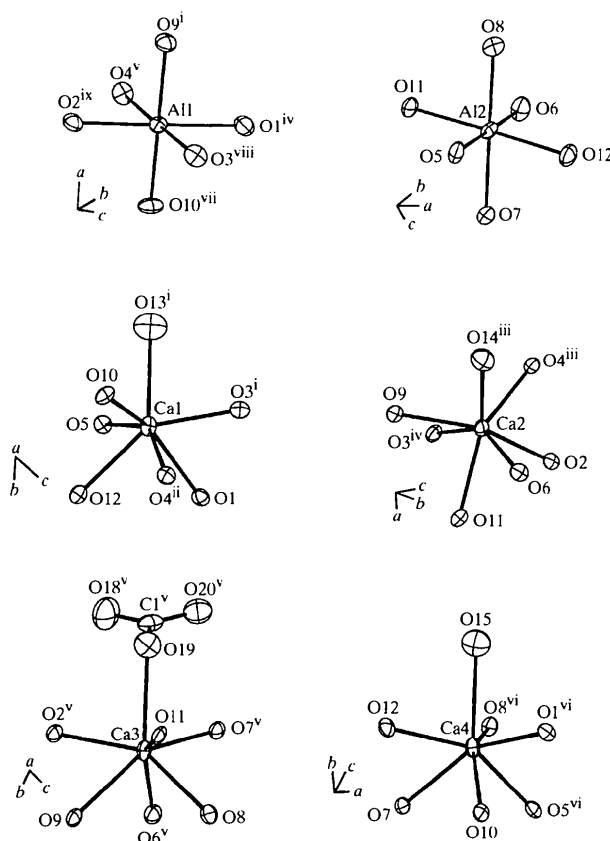


Fig. 2. O-atom environments of the Ca^{2+} and Al^{3+} cations within the main layers $[\text{Ca}_4\text{Al}_2(\text{OH})_{12}\cdot 3\text{H}_2\text{O}]^{2+}$. Displacement ellipsoids are drawn at the 70% probability level (ORTEPII; Johnson, 1976). Symmetry codes as in Table 1.

respectively. The seventh coordination site of each of Ca1, Ca2 and Ca4 is occupied by a water molecule ($\text{H}_2\text{O}13$, $\text{H}_2\text{O}14$ and $\text{H}_2\text{O}15$, respectively), and that of Ca3 is occupied by O19 of the carbonate group. Each Ca^{2+} cation is shifted out of the centre of its octahedron formed by hydroxy groups and thus approaches an H_2O molecule or a carbonate group from the interlayer. These shifts have values of -0.56 , 0.61 , -0.52 and 0.58 Å for Ca1, Ca2, Ca3 and Ca4, respectively. A shift of 0.57 Å was found in the monosulfate parent compound [the sign indicates a shift up or down from the (011) layer plane].

The hydrogen-bond network formed in the interlayer is represented in Fig. 3 and the corresponding distances are reported in Table 2. Water molecules $\text{H}_2\text{O}14$ – $\text{H}_2\text{O}17$ and the carbonate group in the interlayer form a group of six hydrogen bonds shorter than 1.90 Å. The $\text{H}_2\text{O}16$ and $\text{H}_2\text{O}14$ molecules link two adjacent carbonate groups belonging to the same interlayer. The lengths of the hydrogen bonds $\text{H}16\text{B}\cdots\text{O}19$ and $\text{H}16\text{A}\cdots\text{O}18$ connecting $\text{H}_2\text{O}16$ with adjacent carbonate groups are 1.75 (3) and 1.79 (3) Å, respectively. In the same manner, the lengths of hydrogen bonds $\text{H}14\text{A}\cdots\text{O}19$ and $\text{H}14\text{B}\cdots\text{O}20$ connecting $\text{H}_2\text{O}14$ with two adjacent carbonate groups are 1.86 (3) and 1.74 (4) Å, respectively. Thus, $\text{H}_2\text{O}14$ and $\text{H}_2\text{O}16$ can be considered as bidentate in the hydrogen-bond network. The two remaining hydrogen bonds, $\text{H}15\text{B}\cdots\text{O}18$ [1.71 (2) Å] and $\text{H}17\text{B}\cdots\text{O}14$ [1.85 (3) Å], occur between $\text{H}_2\text{O}15$ and a carbonate group, and between two water molecules, $\text{H}_2\text{O}17$ and $\text{H}_2\text{O}14$. Thus, each O atom (O18, O19 and O20) of the carbonate group contributes to the hydrogen-bond network with $\text{H}_2\text{O}14$ – $\text{H}_2\text{O}16$, bringing about cohesion of the interlayer part of the structure. $\text{H}_2\text{O}17$ is connected to $\text{H}_2\text{O}14$ only. Thus, the two water molecules $\text{H}_2\text{O}16$ and $\text{H}_2\text{O}17$ which are not con-

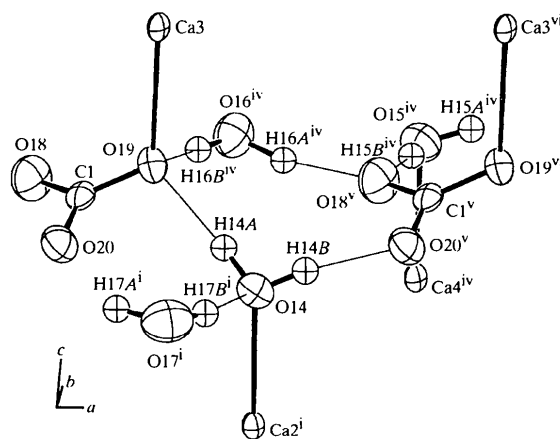


Fig. 3. View of the $[\text{CO}_3\cdot 5\text{H}_2\text{O}]^{2-}$ interlayers showing the network formed by hydrogen bonds (marked by thin lines) and the connection between two consecutive main layers. Displacement ellipsoids are drawn at the 70% probability level (ORTEPII; Johnson, 1976) and H-atom ellipsoids have been reduced for clarity. Symmetry codes as in Table 1.

nected to Ca²⁺ cations do not play the same role. H₂O17 should be the first water molecule to be removed when the compound is heated gradually. The connection between two adjacent [Ca₄Al₂(OH)₁₂]²⁺ main layers via the -2H₂O-[CO₃·3H₂O]²⁻ interlayer is also seen clearly in the drawing. The carbonate groups link the upper part of the main layer to the interlayer through Ca3—O19 bonds, and water molecules H₂O14—H₂O15 link the lower side of the main layer to the interlayer through Ca2—O14 and Ca4—O15 bonds.

Experimental

The single crystal of the title compound was prepared by hydrothermal synthesis. The starting powders Ca(OH)₂, Al(OH)₃ and CaCO₃ in a 3.5:2:0.5 ratio were mixed with water (ratio solid:water 0.5) and loaded into a silver capsule (length 100 mm, diameter 5 mm, thickness 0.1 mm) sealed under normal atmosphere. The experiment was performed over a period of one month at 393 K at 2 Kbar (1 mbar = 100 Pa).

Crystal data

Ca₄Al₂(OH)₁₂CO₃·5H₂O

M_r = 568.47

Triclinic

*P*1

a = 5.7747 (14) Å

b = 8.4689 (11) Å

c = 9.923 (3) Å

α = 64.77 (2)°

β = 82.75 (2)°

γ = 81.43 (2)°

V = 433.0 (2) Å³

Z = 1

D_x = 2.180 Mg m⁻³

D_m not measured

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 25 reflections

θ = 7.0–15.0°

μ = 1.453 mm⁻¹

T = 293 (2) K

Plate

0.360 × 0.225 × 0.040 mm

Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer

ω/2θ scans

Absorption correction:

ψ scan fitted by spherical harmonic functions (SORTAV; Blessing, 1995)

T_{min} = 0.57, *T_{max}* = 0.94

3271 measured reflections

2490 independent reflections

2218 reflections with

I > 2σ(*I*)

R_{int} = 0.026

θ_{max} = 29.9°

h = -7 → 8

k = -10 → 11

l = 0 → 13

3 standard reflections

frequency: 180 min

intensity decay: 3.8%

Refinement

Refinement on *F*²

R [*F*² > 2σ(*F*²)] = 0.027

wR (*F*²) = 0.083

S = 1.062

2414 reflections

310 parameters

H atoms: see below

w = 1/[σ²(*F_o*²) + (0.0478*P*)² + 0.0122*P*]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} = 0.037

Δρ_{max} = 0.546 e Å⁻³

Δρ_{min} = -0.675 e Å⁻³

Extinction correction: none

Scattering factors from

International Tables for Crystallography (Vol. C)

Absolute structure: Flack

(1983)

Flack parameter = 0.08 (3)

Table 1. Selected geometric parameters (Å, °)

Ca1—O10	2.350 (3)	Ca4—O1 ^{vi}	2.354 (3)
Ca1—O5	2.351 (3)	Ca4—O12	2.358 (3)
Ca1—O3 ⁱ	2.359 (3)	Ca4—O7	2.389 (2)
Ca1—O4 ⁱⁱⁱ	2.445 (3)	Ca4—O10	2.449 (3)
Ca1—O1	2.455 (2)	Ca4—O5 ^{vii}	2.464 (2)
Ca1—O12	2.457 (2)	Ca4—O15	2.553 (3)
Ca1—O13 ⁱ	2.546 (3)	Al1—O10 ^{viii}	1.897 (3)
Ca2—O9	2.349 (3)	Al1—O3 ^{viii}	1.901 (3)
Ca2—O4 ⁱⁱⁱ	2.360 (2)	Al1—O4 ⁱ	1.907 (3)
Ca2—O6	2.366 (3)	Al1—O2 ^{ix}	1.916 (3)
Ca2—O3 ^{iv}	2.447 (3)	Al1—O9 ⁱ	1.918 (3)
Ca2—O11	2.457 (2)	Al1—O1 ^{ix}	1.923 (3)
Ca2—O2	2.472 (2)	Al2—O8	1.898 (3)
Ca2—O14 ⁱⁱⁱ	2.518 (3)	Al2—O7	1.899 (3)
Ca3—O2 ^v	2.346 (3)	Al2—O11	1.909 (3)
Ca3—O11	2.355 (3)	Al2—O12	1.917 (3)
Ca3—O7 ^v	2.365 (2)	Al2—O6	1.918 (3)
Ca3—O9	2.446 (2)	Al2—O5	1.925 (3)
Ca3—O8	2.447 (3)	O18—C1	1.283 (3)
Ca3—O6 ^v	2.508 (3)	O19—C1 ⁱ	1.299 (4)
Ca3—O19	2.515 (3)	O20—C1	1.284 (3)
Ca4—O8 ^{vi}	2.348 (2)		
H13A—O13—H13B	98 (2)	O18—C1—O19 ⁱⁱ	120.2 (2)
O18—C1—O20	120.2 (2)	O20—C1—O19 ⁱⁱ	119.6 (3)

Symmetry codes: (i) *x*, *y* - 1, *z*; (ii) *x*, *y*, 1 + *z*; (iii) *x*, 1 + *y*, *z*; (iv) *x*, *y*, *z* - 1; (v) *x* - 1, *y*, *z*; (vi) 1 + *x*, *y*, *z*; (vii) *x* - 1, *y*, *z* - 1; (viii) *x*, *y* - 1, *z* - 1; (ix) *x* - 1, *y* - 1, *z*.

Table 2. Hydrogen-bonding geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O17 ⁱ —H17B ⁱ ...O14	0.92 (3)	1.85 (3)	2.746 (4)	163 (3)
O15 ^{ix} —H15B ^{ix} ...O18	0.92 (2)	1.71 (2)	2.631 (4)	171 (3)
O16 ^{ix} —H16A ^{ix} ...O18	0.97 (3)	1.79 (3)	2.750 (4)	165 (5)
O16 ^{ix} —H16B ^{ix} ...O19	0.95 (3)	1.75 (3)	2.681 (4)	165 (4)
O14—H14A...O19	0.92 (3)	1.86 (3)	2.774 (4)	173 (3)
O14—H14B...O20	0.90 (4)	1.74 (4)	2.626 (4)	171 (4)

Symmetry codes: (i) *x*, *y* - 1, *z*; (iv) *x*, *y*, *z* - 1.

An attempt to refine the structure in the centrosymmetric space group *P* $\bar{1}$ was not conclusive and led to an *R* value of 0.10. The centrosymmetric space group *P*1 allows the ordering of one carbonate group and five water molecules in the unit cell. H atoms were located from difference Fourier maps and refined with fixed individual isotropic displacement parameters [*U*_{iso} = 1.20*U*_{eq}(O)], using a riding model with geometric constraints O—H 0.95 Å and H—O—H 104° for water molecules.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *DREAR* (Blessing, 1987). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*b*). Molecular graphics: *ATOMS* (Dowty, 1995) and *ORTEPII* (Johnson, 1976).

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V₂MnTeO₇

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Abstract

The title compound, divanadium manganese tellurite, V₂MnTeO₇, was obtained by hydrothermal methods. The structure of this compound is made up of slabs, running parallel to the *xy* plane, that contain TeO₃₊₁ units and MnO₆ octahedra, along with distorted VO₅ square pyramids and VO₆ octahedra. Examination of the metal environments and bond-valence-sum calculations show that this compound is an Mn^{II}/V^{IV}/Te^{IV} compound.

Comment

Recently, we have become interested in tellurium(IV) oxides due to their complex structures, as well as their potential as glass-forming materials (Stanworth, 1952). In our studies, we have explored the chemistry of first row transition metal tellurites, including the M₂Te₃O₈ series (Feger *et al.*, 1998), the mineral rodalquilarite, H₃Fe₂(TeO₃)₄Cl (Dusausoy & Protas, 1969; Feger & Kolis, 1998c), and two chloride compounds, Ba₂Cu₄Te₄O₁₁Cl₄ and BaCu₂Te₂O₆Cl₂ (Feger & Kolis, 1998b). With these results, and with the discovery of Na₃Mn₄Te₂O₁₂ (Feger & Kolis, 1998a), a Te^{VI} compound, we have decided to explore the chemistry of manganese tellurites further. We have previously isolated the known mineral spiroffite, Mn₂Te₃O₈, and recently we have attempted to add other unique building

blocks, such as vanadates, to influence the structure. This has led to the synthesis and characterization of the new compound, V₂MnTeO₇, the first transition metal vanadate–tellurite.

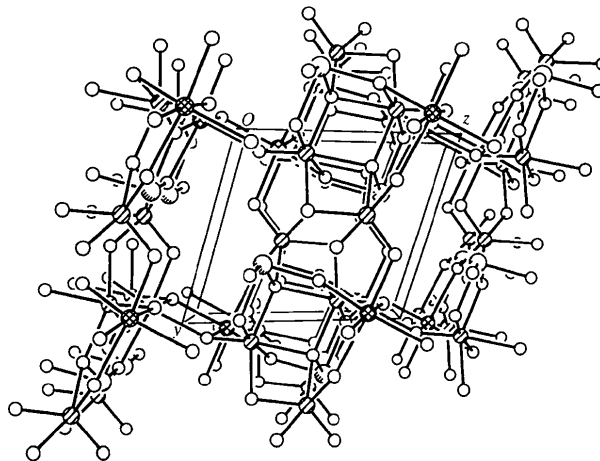


Fig. 1. Unit-cell view of V₂MnTeO₇ shown down the *x* axis. The striped spheres are V atoms, the cross-hatched spheres are Mn, the large shaded spheres are Te atoms, and the small open spheres are O atoms.

The structure of V₂MnTeO₇ is best viewed in terms of slabs running parallel to the *xy* plane (Fig. 1). These slabs are interconnected through Mn–O interactions, and can be further broken down into metal layers. Each slab consists of two of these layers containing the metal atoms, connected through O atoms. The metal coordination environments (Fig. 2) are typical, with the Mn atom in an octahedral environment, and the two V atoms in distorted octahedral and distorted square-pyramidal geometries. These V environments are both highly similar to those in the VTeO₄ phases, with the distorted octahedron of V1 nearly identical to

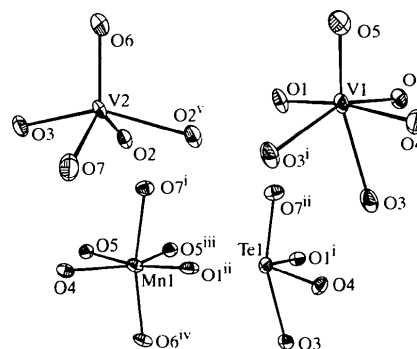


Fig. 2. Displacement ellipsoid plots of the four crystallographically distinct metal environments in V₂MnTeO₇, shown at the 70% probability level. Symmetry codes are as in Table 1.