Crystallographic analysis of akermanite, gehlenite and akermanite-gehlenite solid solutions that may appear in low carbon cements/binders

(*akermanite was already studied as a "bone substitute bioceramic"*)

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What is melilite?

Melilite group

$Ca_2M(XSiO_7)$

having a tetragonal crystallographic unit cell

M= Mg, Al, rarely Fe, B. Zn, Si, Be, *etc.*
X=Si, Al, rarely B or Be

a group of tetragonal (*i.e.*, tetragonal crystal lattice) sorosilicates with disilicate (*a.k.a.*, pyrosilicate or diorthosilicate) anions $(Si_2O_7)^{6-}$.

M in the general formula given above denotes a small- to medium-sized divalent or trivalent cations (mostly Mg and Al). In petrology, **melilite usually refers to minerals in the akermanite-gehlenite series, by far the most abundant members of the group**.

Melilite

originally described in 1796 based on natural samples of Capo di Bove (*an archaeological site*), Alban Hills, Rome province, Lazio, Italy

$Ca_2(Al,Mg,Fe)((Al,Si,B)SiO_7)$

having a tetragonal crystallographic unit cell

What are akermanite and gehlenite?

Akermanite

$Ca_2Mg(Si_2O_7)$ → a ceramic scientist writes akermanite as $2CaO{\cdot}MgO{\cdot}SiO_2$
having a tetragonal crystallographic unit cell

first described (in 1884) from samples of slags from furnace iron production found at three furnace localities: Hofors, Löfsjöen and Mölnbo, Sweden; named in honor of Anders Richard **Åkerman**, Swedish metallurgist. Akermanite (and gehlenite) has a Mohs hardness of 5 to 6. (To compare, Mohs hardness of gypsum, calcite, sapphire (or corundum) and diamond are 2, 3, 9 and 10, respectively.)

Gehlenite

$Ca_2Al(AlSiO_7)$ → a ceramic scientist writes gehlenite as $2CaO{\cdot}Al_2O_3{\cdot}SiO_2$
having a tetragonal crystallographic unit cell

named in 1815 in honor of Adolf Ferdinand **Gehlen;**
natural gehlenite crystals were found in
Trentino-South Tyrol, Italy

Akermanite as a “bone substitute” bioceramic
(to be discussed only in the next page)

Akermanite was shown, as early as 2006, to be a suitable material for use in **bone substitute** applications.

1.) C. Wu, J. Chang, W. Zhai, S. Ni, and J. Wang, "Porous akermanite scaffolds for bone tissue engineering: preparation, characterization, and *in vitro* studies," *J. Biomed. Mater. Res. Part B: Appl. Biomater.*, 78B, 47-55 (2006)

This article proved that when akermanite was immersed in an SBF (synthetic/simulated body fluid) at 37°C, it was "not inert" and the surfaces of akermanite particles were covered with carbonated, non-stoichiometric, apatitic calcium phosphate mimicking the composition and chemistry of the newly formed bone. SBF solutions contain HCO_3^- (*aq*) ranging from 4.2 to 27 mM.

27 mM is the HCO_3^- concentration of human blood plasma. Under the light of the first article above, it **will not be surprising to find that pure akermanite would rapidly carbonate when it is stirred in water with intentional CO2 bubbling through that water body at high CO2 injection rates, when pure gehlenite would not.** Our crystallographic analyses to be presented in the following pages of this note will shed light on that difference between akermanite and gehlenite.

2.) L. Xia *et al.*, *Scientific Reports (Nature)*, 6, Article number: 22005 (2016)

3.) J. M. G. Ventura, D. U. Tulyaganov, S. Agathopoulos, and J. M. F. Ferreira, "Sintering and crystallization of akermanite-based glass–ceramics," *Mater. Lett.*, 60, 1488-1491 (2006)

4.) A. Dasan, A. Talimian, J. Kraxner, D. Galusek, H. Elsayed, and E. Bernardo, "Akermanite glass microspheres: Preparation and perspectives on sinter-crystallization," *Int. J. Appl. Glass Sci.*, 12, 551-561 (2021)

If the composition of a low carbon cement/binder would fall into the CaO-SiO_2-Al_2O_3-MgO quaternary system, then one will find the phase stability regions of akermanite and gehlenite in that system.

Note: While **ternary** phase diagrams map three components (*e.g.*, CaO, SiO_2 and Al_2O_3), **quaternary** phase diagrams map four components (*e.g.*, CaO, SiO_2, Al_2O_3 and MgO).

BFS = blast furnace slag

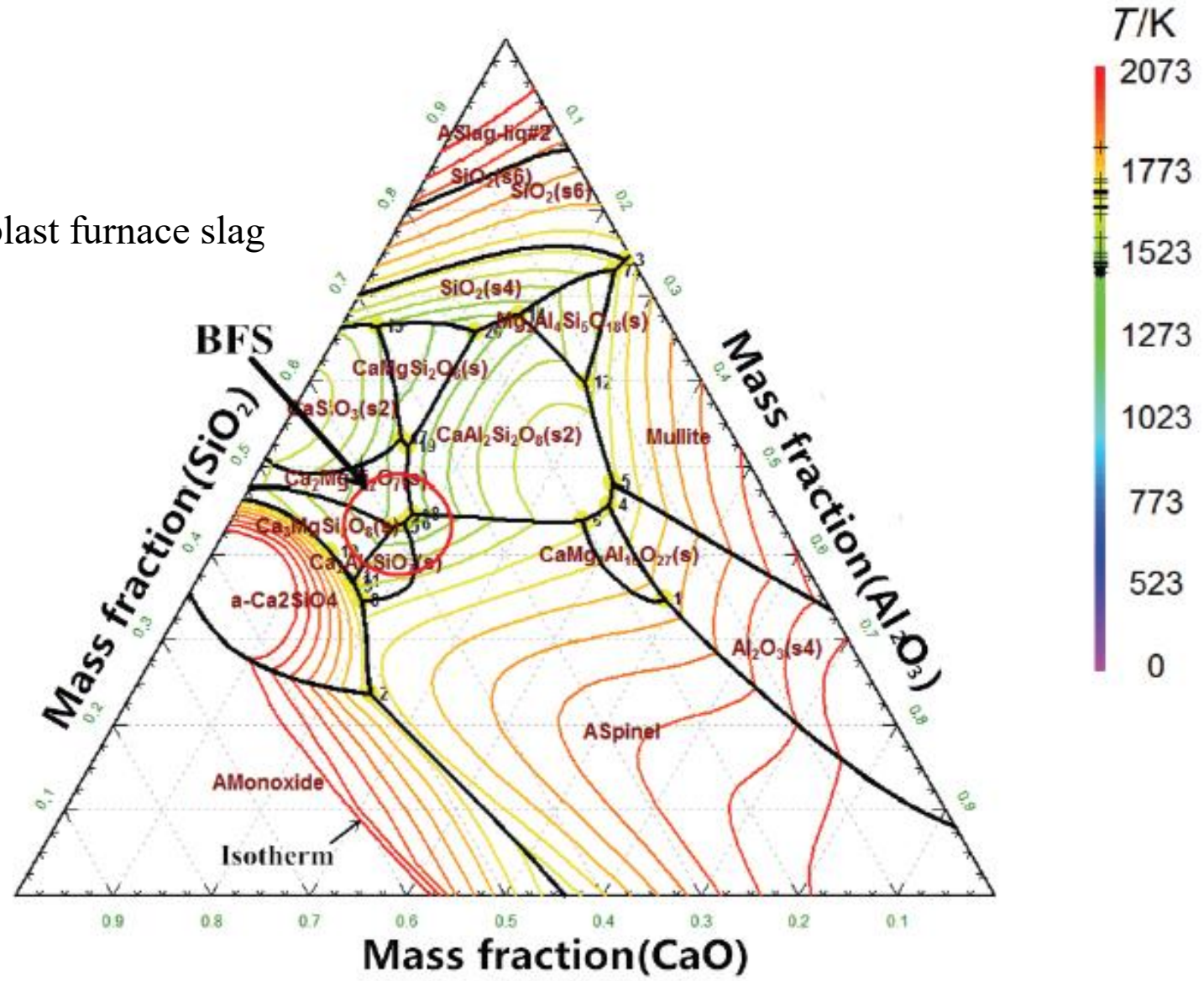

Fig. 1. Phase diagram of SiO_2–Al_2O_3–CaO–MgO (ω_{MgO} = 8.64 mass %) obtained using FactSage 7.1.

This (quaternary) diagram explains how one can form akermanite ($Ca_2MgSi_2O_7$) and/or gehlenite ($Ca_2Al_2SiO_7$) when the composition of the feedstock of a cement kiln (to undergo heating at around 1250°C) is close to the phase stability region of wollastonite ($CaSiO_3$).

Source: K. Yue, L. Chao, Z. Yuzhu, X. Hongwei, L. Yue, and J. Maofa, "Study on mineralogical crystallization of granulation of gas quenching blast furnace slag," *J. Serbian Chem. Soc.*, 83, 1031-1045 (2018).

The world's very first "low carbon binder" (non-hydraulic) clinker was produced numerous times (at the "thousands of tons" scales in a single cement production campaign), starting back in 2014, by Lafarge and then Lafarge-Holcim, based on the idea of Solidia Technologies in an ordinary cement kiln, while running it at a much lower temperature (than that practiced in the ordinary Portland cement production campaigns).

The clinker of the Solidia binder was designed to have a "low Ca/Si molar ratio" (simply achieved by reducing the mass of the limestone used but still using the same constituents taken from the cement kiln's quarry) in the feedstock entering the cement kiln, therefore, had lower CO2 emissions (from the kiln) in comparison to the production of ordinary Portland cement and the large volumes of concrete made by using the Solidia binder was cured in specially-designed CO2 chambers (CO2 being absorbed by the green concrete to *in situ* form $CaCO_3$) in as short as 6 h (U.S. Patent Application No. 2020/0062660 A1). The simultaneous lowering of the Ca/Si ratio of the feedstock and the lowering of the kiln's max temperature (*i.e.*, carbonaceous fuel consumption decrease) resulted in reduced CO2 emissions from the cement kiln.

One distinguishing feature of the Solidia cement/binder (U.S. Patent No. 11,718,566 B2) was that it did not contain any trace of the phases of alite (C_3S), tricalcium aluminate (C_3A) and tetracalcium aluminoferrite (C_4AF) of the ordinary Portland cement. Its belite (C_2S) content came out to be negligible. It was essentially composed of wollastonite (CS, $CaSiO_3$), akermanite-gehlenite solid solution, rankinite (C_3S_2, $3CaO{\cdot}2SiO_2$) together with an amorphous content. The reason for having an akermanite-gehlenite solid solution phase in the clinker of that low C cement/binder should be obvious from the FactSage-calculated quaternary phase diagram reproduced in the previous page.

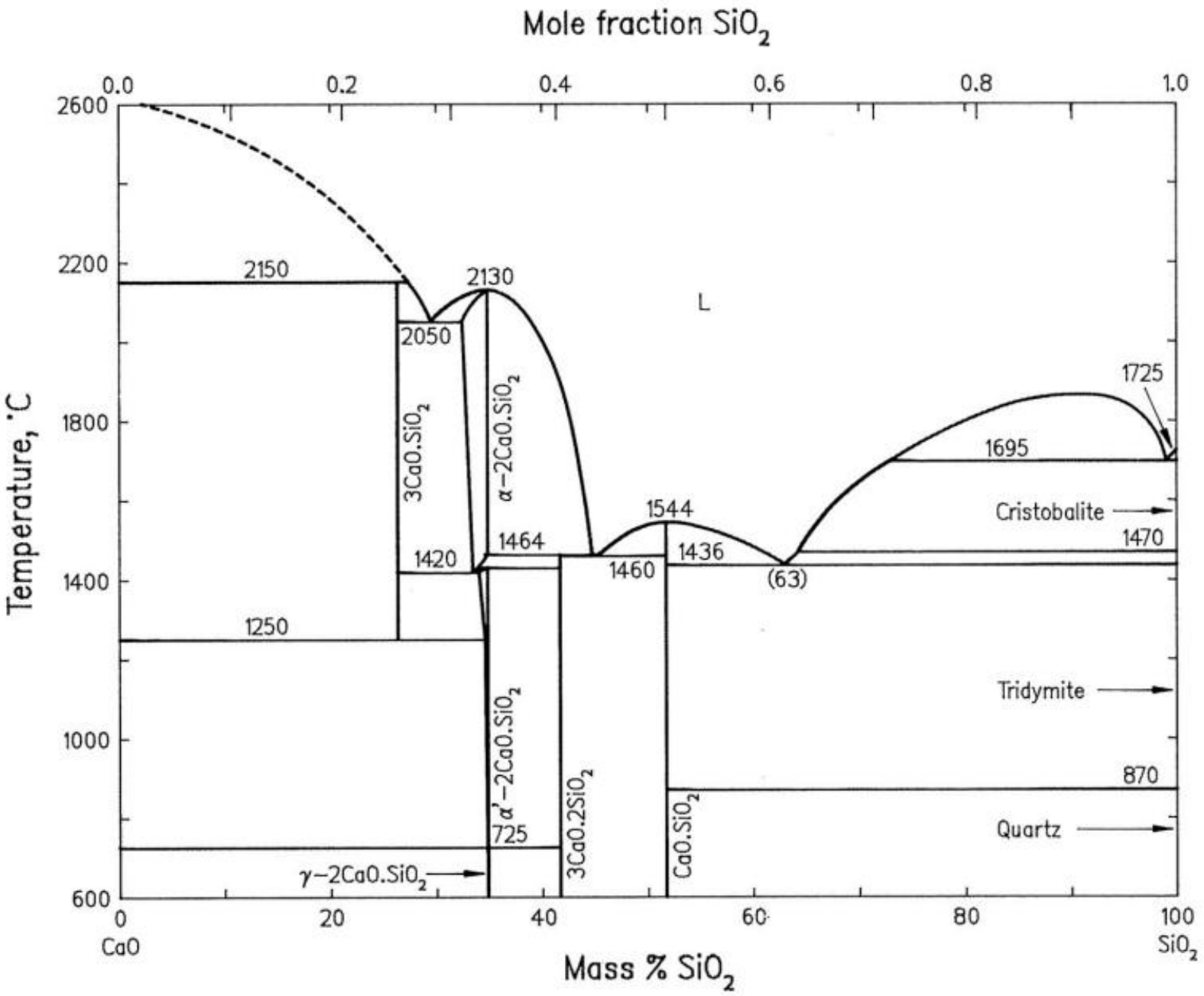

Fig. from: J. F. White *et al.*, *Metall. Mater. Trans. B*, 48, 506-515 (2017)

According to this CaO-SiO_2 binary phase diagram, if one wants to produce a Ca-silicate using the raw meal/feedstock of a cement kiln, but by only reducing the limestone content in it, then there is not a calcium silicate phase with a calcium content lower than that of wollastonite ($CaSiO_3$). Under these conditions, the targeted product phase will be $CaSiO_3$.

Complete carbonation (exothermic; -87 kJ/mol) 1 mole of $CaSiO_3$ will generate 1 mole of $CaCO_3$ and 1 mole of amorphous silica, the latter of which will be mostly covered with $CaCO_3$ crystals, when carbonation is done by using moist CO2(g).

If the CaO formed in the cement kiln (by the calcination of limestone) will not completely react with all SiO_2, then the chances of C_3S_2 (=rankinite, which is a fast carbonating material) formation together with $CaSiO_3$ will be high.

Crystallography (*via* X-ray or neutron diffraction) is the only analytical tool to ascertain the amount of gehlenite (or akermanite) present in an "akermanite-gehlenite solid solution."

Ternary or quaternary phase diagram determinations are based on tedious and consecutive X-ray diffraction work supplemented by electron microscopy and EPMA / EDXS analyses.

Notes:
(1) While X-ray diffraction (XRD) is based on the interaction of the incident X-rays with the electron clouds, neutrons in neutron diffraction interact with the atomic nuclei and magnetic moments.
(2) In X-ray diffraction, the scattering intensities decrease with an increase in the 2θ angle (consult Bragg's Law). This is not the case for neutron diffraction.
(3) While neutrons in neutron diffraction come from a nuclear reactor or spallation neutron sources (getting a time of analysis from a nuclear reactor is not that easy and inexpensive), the X-rays in X-ray diffraction are readily obtained from lab-scale diffractometers which are not that expensive ($75K (bench-top diffractometers) to $180K-$500K for full size).

The crystallography of akermanite-gehlenite solid solutions as well as phase-pure akermanite and phase-pure gehlenite was first studied (by using neutron diffraction) by **Swainson *et al.* in 1992**.

This was a well-designed, meticulously performed and written article which should be studied/cited by every new researcher coming into this specific field focusing on the melilitic phases/materials.

I. P. Swainson, M. T. Dove, W. W. Schmahl, and A. Putuis, "Neutron powder diffraction study of the akermanite-gehlenite solid solution series," *Phys. Chem. Minerals*, 19, 185-195 (1992).

The above authors prepared synthetic samples of **0** (=gehlenite), **25, 50, 75** and **100% akermanite** prior to their neutron diffraction study. This article resulted in the generation of five (each corresponding to the above-listed phase percentages) CIF files (*i.e.*, Crystallographic Information File) which can be reached at AMCSD (American Mineralogist Crystal Structure Database) by using https://www.rruff.net/ or at COD (Crystallography Open Database) The readers (inexperienced with CIF files) having any difficulty in accessing those *open-to-public* CIF files may contact me *via* LinkedIn.

••• The crystallographic analysis I will provide in the rest of this note **will use those CIF files**. *(I also experimentally determined, using XRD, the akermanite and gehlenite contents of the akermanite-gehlenite solid solutions present in the Solidia cement when I was working for Solidia Technologies from July 2015 to December 2022.)*

The next page gives, as an example, the CIF file of 50% akermanite-50% gehlenite solid solution, which was generated from the 1992 study of Swainson *et al*.

The CIF files, *when they are available at https://www.rruff.net/amcsd/ or at COD for a given material/phase/compound*, will let anyone to study and analyze the crystallographic info without a need for having an access to subscription-based databases such as MDI-JADE or ICSD.

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AlT2 0.03923 0.03923 -0.00514 -0.00274 -0.00237 -0.00237
SiT2 0.03923 0.03923 -0.00514 -0.00274 -0.00237 -0.00237
O1 0.07906 0.07906 -0.00334 -0.04470 0.00000 0.00000
O2 0.08818 0.00000 -0.00373 0.00000 0.01364 0.01364
O3 0.11251 0.06903 0.00206 -0.01551 -0.00731 -0.00474
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AlT1 0.00000 0.00000 0.00000 0.54000
AlT2 0.14190 0.35810 0.94270 0.22500
SiT2 0.14190 0.35810 0.94270 0.76000
O1 0.50000 0.00000 0.17820 1.00000
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```

A CIF file starts by giving full credit to those who performed the experimental work, then provides the formula of the compound, space group, lattice parameters, and the density of the compound.

A CIF file also list symmetry operators, anisotropic U-tensor values, atomic coordinates (as x, y, z fractions in a unit cell) and site occupancies for the atoms/ions present in the studied compound.

In order to use such CIF files (available at Crystallography Open Database or AMCSD), one may use three shareware (yet highly competent) softwares listed below.

VESTA: https://jp-minerals.org/vesta/en/download.html

MERCURY: https://www.ccdc.cam.ac.uk/solutions/software/free-mercury/

AVOGADRO: https://avogadro.cc/

• VESTA and MERCURY can calculate the powder X-ray diffraction pattern (as a text file that can then be opened with Excel, Origin, *etc*.) only by using the CIF file.

• MERCURY and AVOGADRO can calculate the bond lengths (in Å) in a structure by using a given CIF file.

• VESTA, MERCURY and AVOGADRO can generate the rotatable crystal structures for visualization purposes by using the CIF files.

• H-M space group notation explained: http://img.chem.ucl.ac.uk/sgp/misc/notation.htm

Summary of the lattice parameters of the five CIF files

100% akermanite	75% akermanite + 25% gehlenite	50% akermanite + 50% gehlenite	25% akermanite + 75% gehlenite	100% gehlenite
a = b = 7.8288 Å	a = b = 7.7853 Å	a = b = 7.7475 Å	a = b = 7.7115 Å	a = b = 7.6850 Å
c = 5.0052 Å	c = 5.0211 Å	c = 5.0359 Å	c = 5.0498 Å	c = 5.0636 Å
V = 306.769 Å^3	V = 304.333 Å^3	V = 302.274 Å^3	V = 300.298 Å^3	V = 299.100 Å^3
ρ = 2.941 g/cm^3	ρ = 2.969 g/cm^3	ρ = 2.997 g/cm^3	ρ = 3.026 g/cm^3	ρ = 3.047 g/cm^3
$\alpha = \beta = \gamma = 90°$	$\alpha = \beta = \gamma = 90°$	$\alpha = \beta = \gamma = 90°$	$\alpha = \beta = \gamma = 90°$	$\alpha = \beta = \gamma = 90°$
$Ca_2Mg_{0.96}Si_2O_7$	$Ca_2Mg_{0.71}Al_{0.51}Si_{1.74}O_7$	$Ca_2Mg_{0.46}Al_{0.99}Si_{1.52}O_7$	$Ca_2Mg_{0.21}Al_{1.54}Si_{1.24}O_7$	$Ca_2Al_{2.06}Si_{0.95}O_7$
COD: 9006116	COD: 9006115	COD: 9006114	COD: 9006113	AMCSD: 0007694
H-M: P -4 21 *m*	H-M: P -4 21 *m*	H-M: P -4 21 *m*	H-M: P -4 21 *m*	H-M: P -4 21 *m*
SG: 113	SG: 113	SG: 113	SG: 113	SG: 113

COD: Crystallography Open Database, AMCSD: American Mineralogist Crystal Structure Database
H-M: Hermann-Mauguin symmetry symbol, SG: space group number

Source of table's data: I. P. Swainson, M. T. Dove, W. W. Schmahl, and A. Putnis, "Neutron diffraction study of the akermanite-gehlenite solid solution series," *Physics and Chemistry of Minerals (Germany)*, 19, 185-195 (1992).

The above table showed

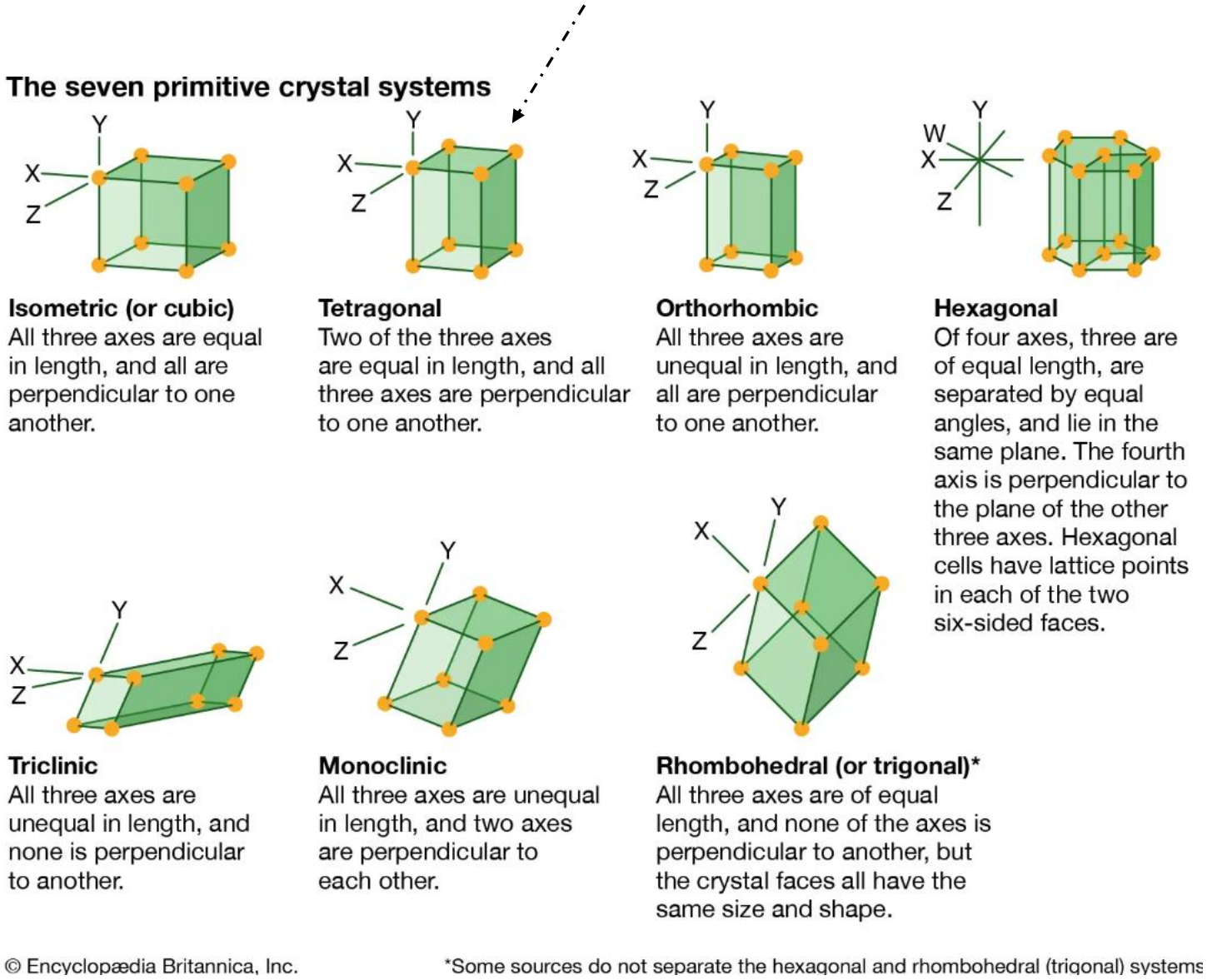
(a) pure akermanite, pure gehlenite and their 25, 50, and 75% solid solutions all had a **tetragonal** structure,

(b) pure akermanite, pure gehlenite and their solid solutions all had the same space group of **P -4 21 *m*** (number **113**).

A tetragonal structure (*i.e.*, crystal lattice) is identified by having:

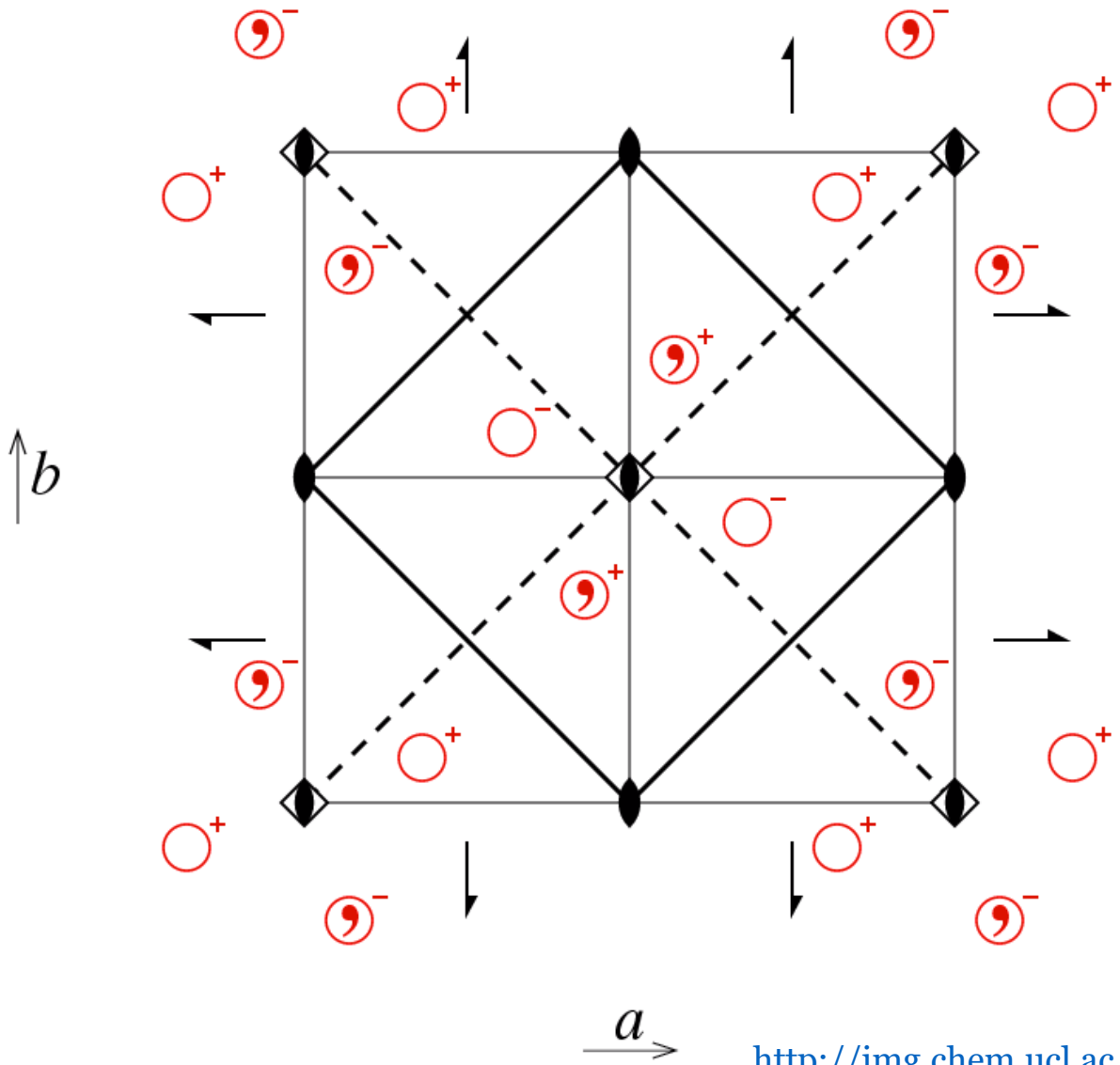
$a = b \neq c$

$\alpha = \beta = \gamma = 90°$



This is what a crystallographer enjoys by looking at the space group No. 113.

$P\bar{4}2_1m$ $P\,\bar{4}\,2_1\,m$ $\bar{4}2m$ No. 113



1 x, y, z

2 $\bar{x}, \bar{y}, z$

3 $y, \bar{x}, \bar{z}$

4 $\bar{y}, x, \bar{z}$

5 $\frac{1}{2} + x, \frac{1}{2} - y, \bar{z}$

6 $\frac{1}{2} - x, \frac{1}{2} + y, \bar{z}$

7 $\frac{1}{2} + y, \frac{1}{2} + x, z$

8 $\frac{1}{2} - y, \frac{1}{2} - x, z$

http://img.chem.ucl.ac.uk/sgp/large/115az1.htm

Akermanite, gehlenite, melilite, hardystonite, umangite, ferroakermanite, bennesherite and gugiaite all have the same space group and all have a tetragonal structure.

Summary of the atomic coordinates (directly taken from the five CIF files)

	100% Aker	75% Ak + 25% Gh	50% Ak + 50% Gh	25% Ak + 75% Gh	100% Gehl
	x *y* *z* *Occup*	*x* *y* *z* *Occup*	*x* *y* *z* *Occup*	*x* *y* *z* *Occup*	*x* *y* *z* *Occup*
Ca	0.332, 0.168, 0.505, 1.000	0.3345, 0.1655, 0.5083, 1.000	0.3369, 0.1631, 0.5093, 1.000	0.3377, 0.1623, 0.5100, 1.000	0.3389, 0.1611, 0.5104, 1.000
Mg (*T*)	0.000, 0.000, 0.000, 0.960	0.000, 0.000, 0.000, 0.710	0.000, 0.000, 0.000, 0.460	0.000, 0.000, 0.000, 0.210	--
Al (*T1*)	--	0.000, 0.000, 0.000, 0.290	0.000, 0.000, 0.000, 0.540	0.000, 0.000, 0.000, 0.790	0.000, 0.000, 0.000, 1.000
Al (*T2*)	--	0.1407, 0.3593, 0.9370, 0.110	0.1419, 0.3581, 0.9427, 0.225	0.1421, 0.3579, 0.9503, 0.375	0.1434, 0.3566, 0.9540, 0.500
Si (*T*)	0.1395, 0.3605, 0.9334, 1.000	0.1407, 0.3593, 0.9370, 0.870	0.1419, 0.3581, 0.9427, 0.760	0.1421, 0.3579, 0.9503, 0.620	0.1434, 0.3566, 0.9540, 0.500
O1	0.500, 0.000, 0.1775, 1.000	0.500, 0.000, 0.1788, 1.000	0.500, 0.000, 0.1782, 1.000	0.500, 0.000, 0.1793, 1.000	0.500, 0.000, 0.1765, 1.000
O2	0.1409, 0.3591, 0.2547, 1.000	0.1417, 0.3583, 0.2621, 1.000	0.1423, 0.3577, 0.2676, 1.000	0.1430, 0.3570, 0.2756, 1.000	0.1427, 0.3573, 0.2835, 1.000
O3	0.0816, 0.1870, 0.7879, 1.000	0.0833, 0.1816, 0.7931, 1.000	0.0850, 0.1778, 0.7980, 1.000	0.0861, 0.1717, 0.8030, 1.000	0.0876, 0.1678, 0.8078, 1.000

What does this table tell?

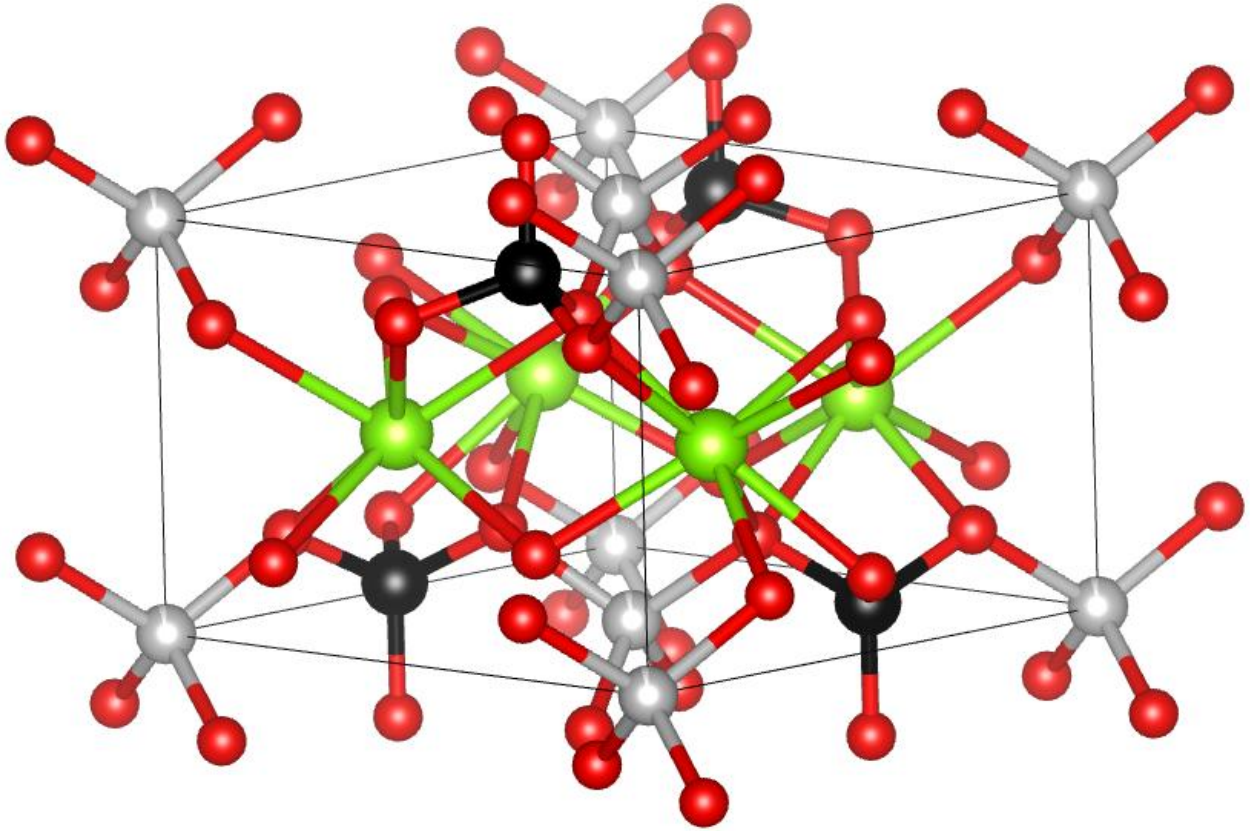
1.) An atom/ion with the x, y, z coordinates of 0.0, 0.0, and 0.00 means that it is occupying the 8 corners of the tetragonal unit cell. All other shown in the above table occupy positions within the unit cell but not at the corners.

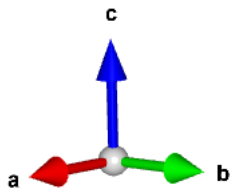
2.) Occupancy factors were determined by chemical analysis which also helps to assign a formula to the compound/material under investigation. It is a requirement that the CIF files must have an experimentally determined formula. 1.00 as the occupancy factor means that that position is fully occupied by that atom/ion, where values smaller than 1.00 indicate either there are some vacancies at those atomic sites or the same site is shared by two different atoms/ions. The site sharing by Mg (*T*), which means Mg is sitting at the center of a tetrahedron, and Al (*T1*) means that in going from 75% akermanite to 25% akermanite, magnesiums are substituted by aluminums in the same tetrahedra. Similarly, in going from 75% akermanite to 100% gehlenite, the silicons, *i.e.*, Si (*T*), in the SiO_4 tetrahedra are progressively substituted by aluminums (*i.e.*, by Al (*T2*)).

3.) At this point, it will be good to remember the formula of pure akermanite and pure gehlenite.

Pure akermanite: $Ca_2Mg(Si_2O_7)$ Pure gehlenite: $Ca_2Al(AlSiO_7)$ The way the formula of gehlenite was written here is the correct one, which tells that aluminums occupy two different sites in samples of 25% gehlenite, 50% gehlenite, 75% gehlenite and 100% gehlenite. Writing the gehlenite formula as "$Ca_2Al_2SiO_7$" does not point to this.

VESTA-generated structure drawings



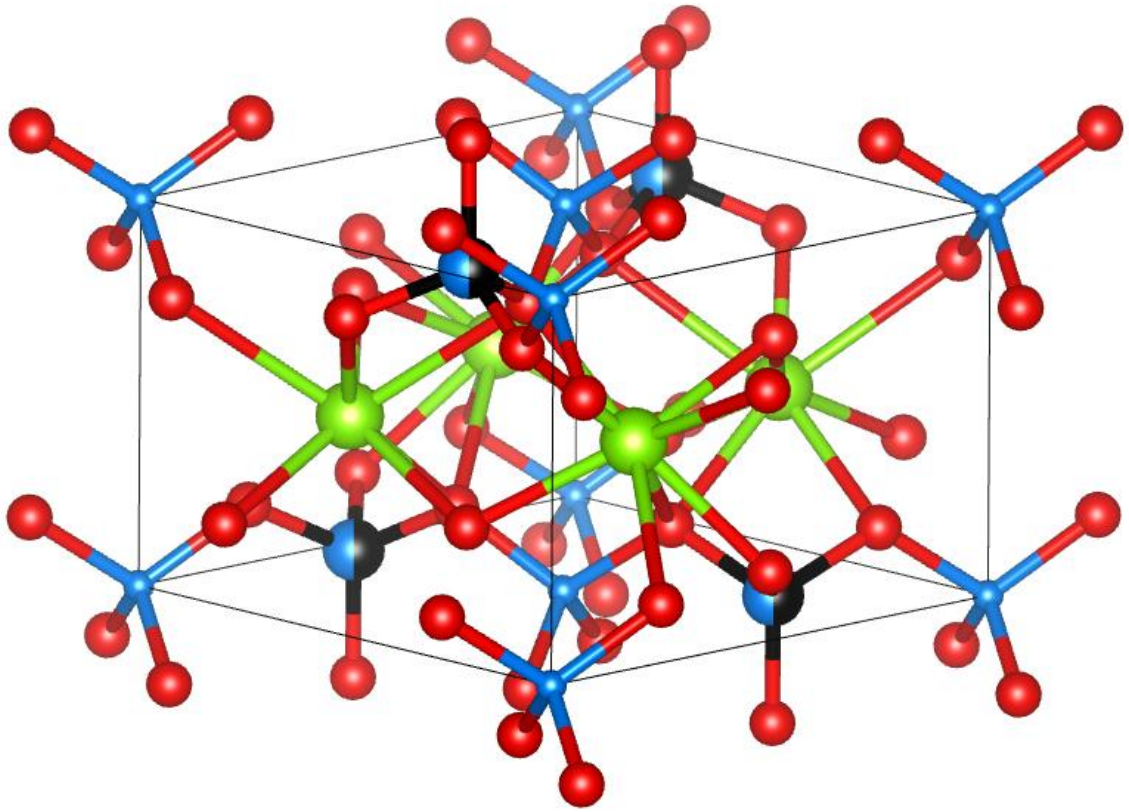


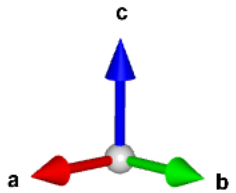
pure akermanite

$Ca_2Mg(Si_2O_7)$

Mg: silver
Si: black
Ca: green
O: red

Mg^{2+} ions occupy the unit cell corners while located at the centers of MgO_4 tetrahedra.





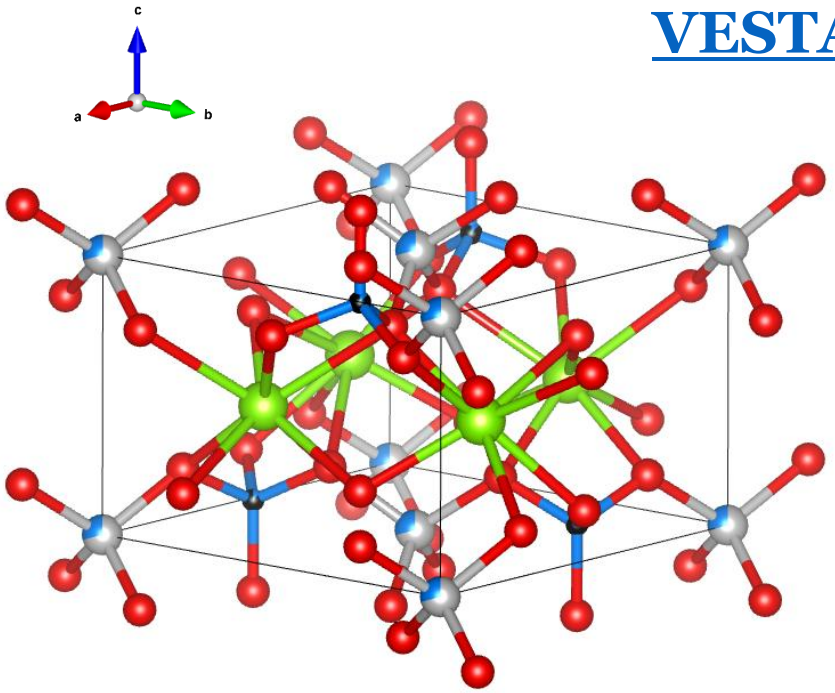
Pure gehlenite

$Ca_2Al(AlSiO_7)$

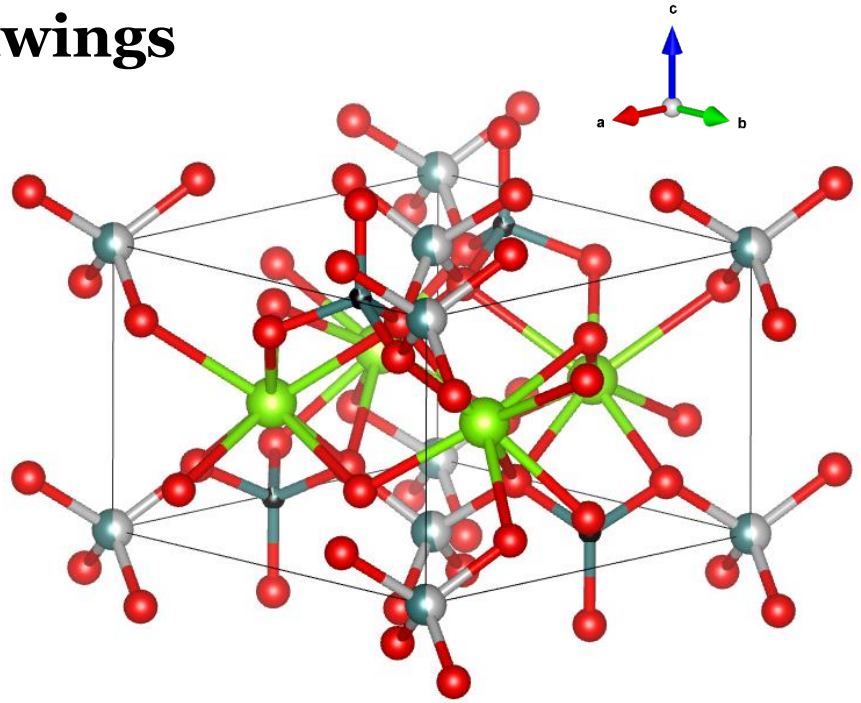
Al: blue
Si: black
Ca: green
O: red

Al^{3+} ions sit at the unit cell corners and substitute for silicon of the SiO_4 tetrahedra. (Half blue, half black spheres denote that substitution.)

VESTA-generated structure drawings



Mg: silver
Si: black
Al: blue
Ca: green
O: red

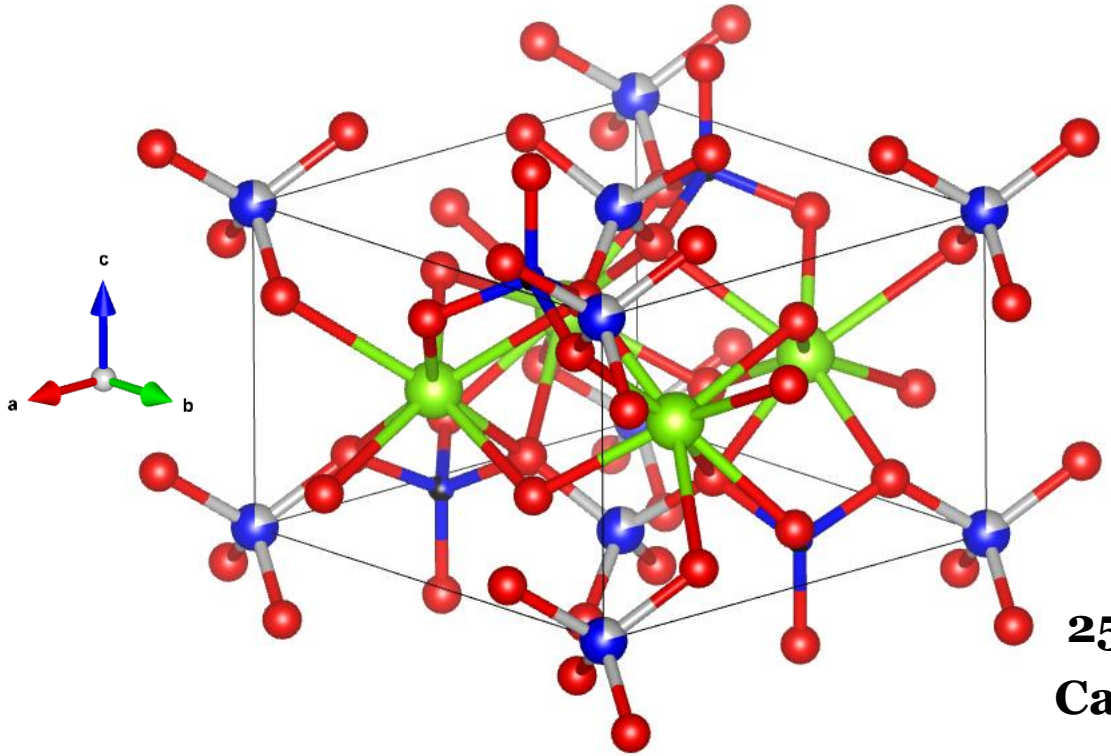


75% Aker + 25% Gehl

$Ca_2Mg_{0.71}Al_{0.51}(Si_{1.74}O_7)$

50% Aker + 50% Gehl

$Ca_2Mg_{0.46}Al_{0.99}(Si_{1.52}O_7)$



25% Aker + 75% Gehl

$Ca_2Mg_{0.21}Al_{1.54}(Si_{1.24}O_7)$

A. C. Tas

Why does akermanite react with a carbonate ion-containing solution while gehlenite would not?

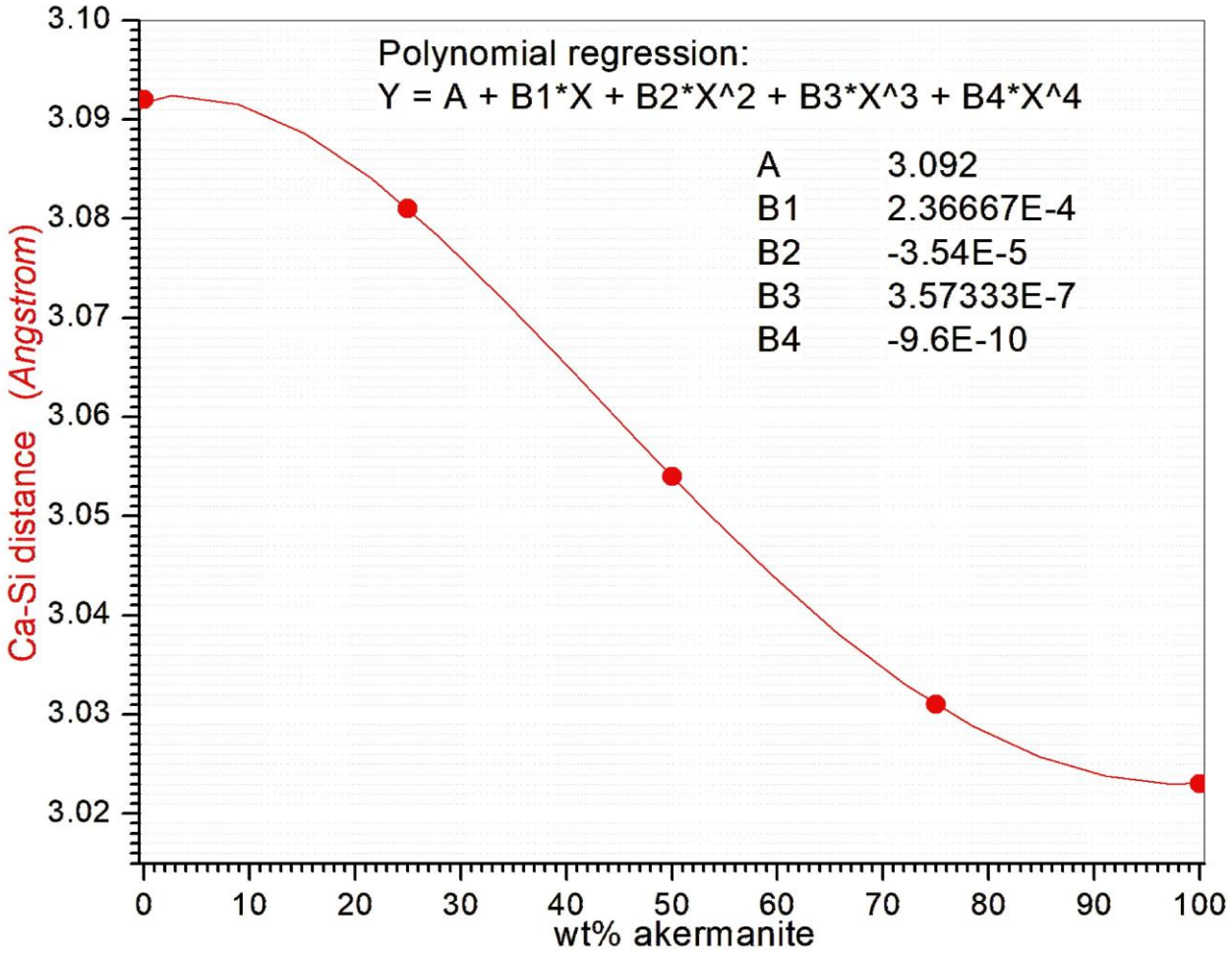
three links for supporting evidence: (1), (2), (3)

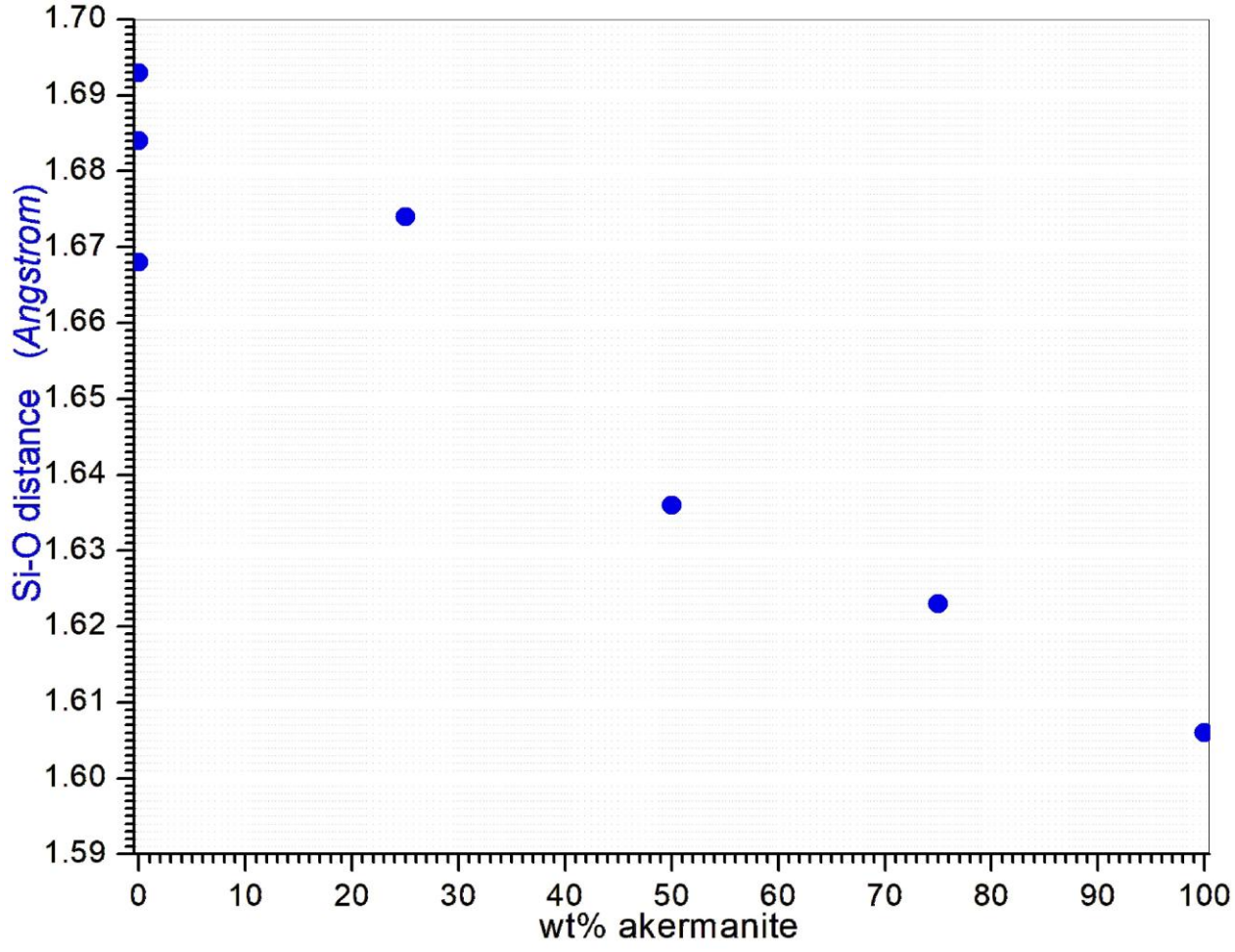
One strong reason for that is the location of Mg^{2+} ions in akermanite: at the 8 corners of the tetragonal unit cell, and they are not located inside the unit cell. The crystal lattice is pinned by its 8 corners. Typically, if one wants to see a crystal structure to completely collapse and transform into something else, then the corner atoms/ions should be able to readily interact with their surroundings (water, carbonated water, weak organic acids, *etc.*).

Mg^{2+} ions (aqueous of course) do have a high affinity for water and they typically form an octahedra with 6 molecules of water as shown here. When the Mg^{2+} ions of akermanite starts forming such octahedra with, water, then the crystal structure of akermanite becomes unstable, it starts to collapse and as a result of this, the surrounding water film (*i.e.*, the water film surrounding the akermanite powder particles) becomes increasingly richer in silicic acid and Ca^{2+} concentrations. The released Ca^{2+} ions (those originally residing inside the lattice in a polyhedral configuration as shown in the previous pages) will then be free to react with the carbonate ions of the water. Therefore, when a low C cement/binder composition has pure akermanite as a primary, secondary or tertiary phase, then this component of the cement/binder will be "carbonatable." On the other hand, the unit cell corners of gehlenite are occupied by Al^{3+} ions.

Based on our past experience, gehlenite is more than difficult to carbonate; and this was also confirmed by this recent study.

Bond distances/lengths calculated by MERCURY (using the five CIF files)

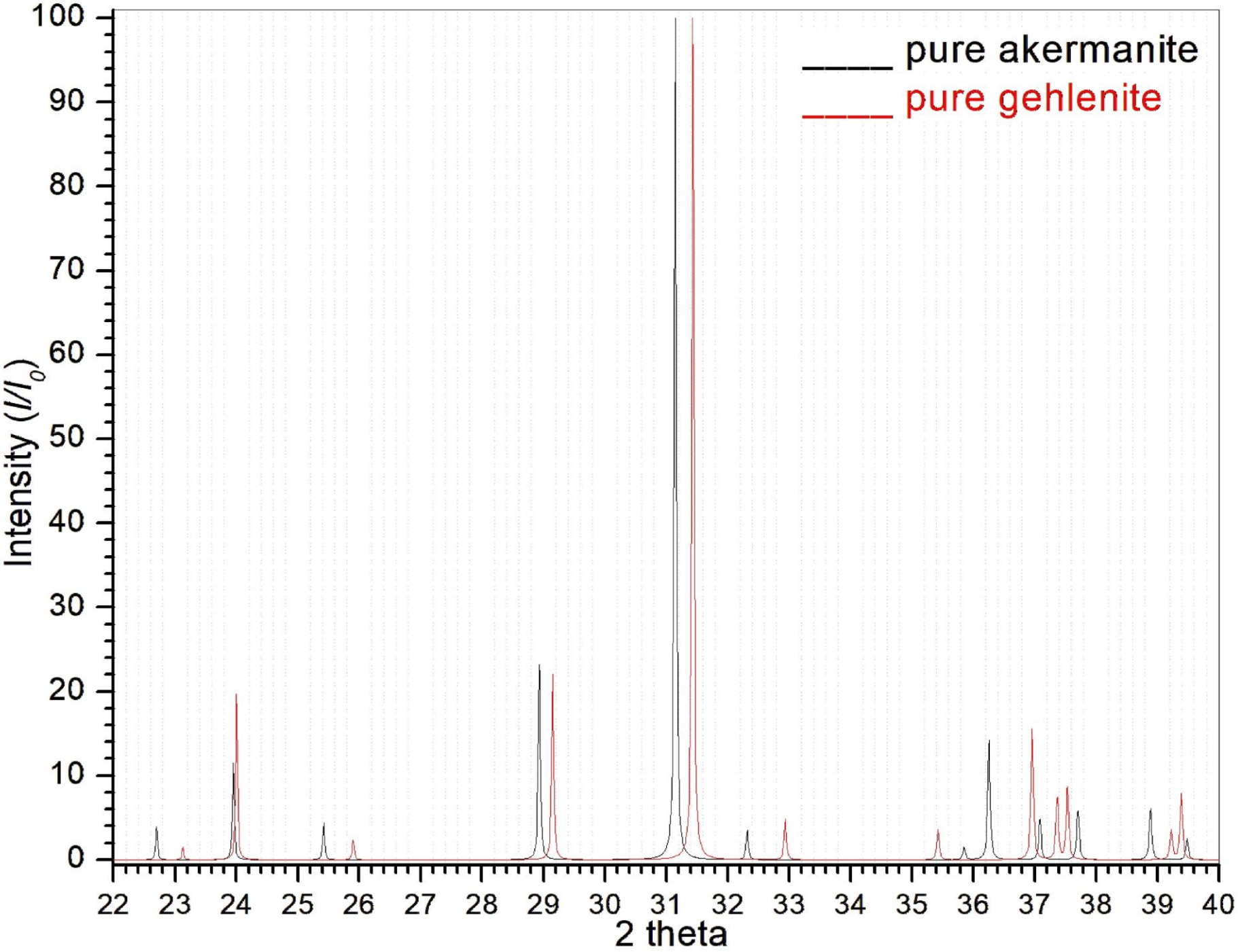




The Si-O bond distance in silicic acid (*i.e.*, $Si(OH)_4$) is known to be 1.62 Å. As seen from the above plot, the Si-O bond distance/length of akermanite is much closer to 1.62 Å than those of gehlenite. This similarity becomes important when one talks about the release of silicic acid from an akermanite particle in carbonated water having both carbonic acid and carbonate ions over the reaction time.

The data of this Table was generated by VESTA for Cu $K_{\alpha 1}$ radiation, we tabulated here only the 21 peaks of significantly high intensities (of the calculated full XRD patterns).

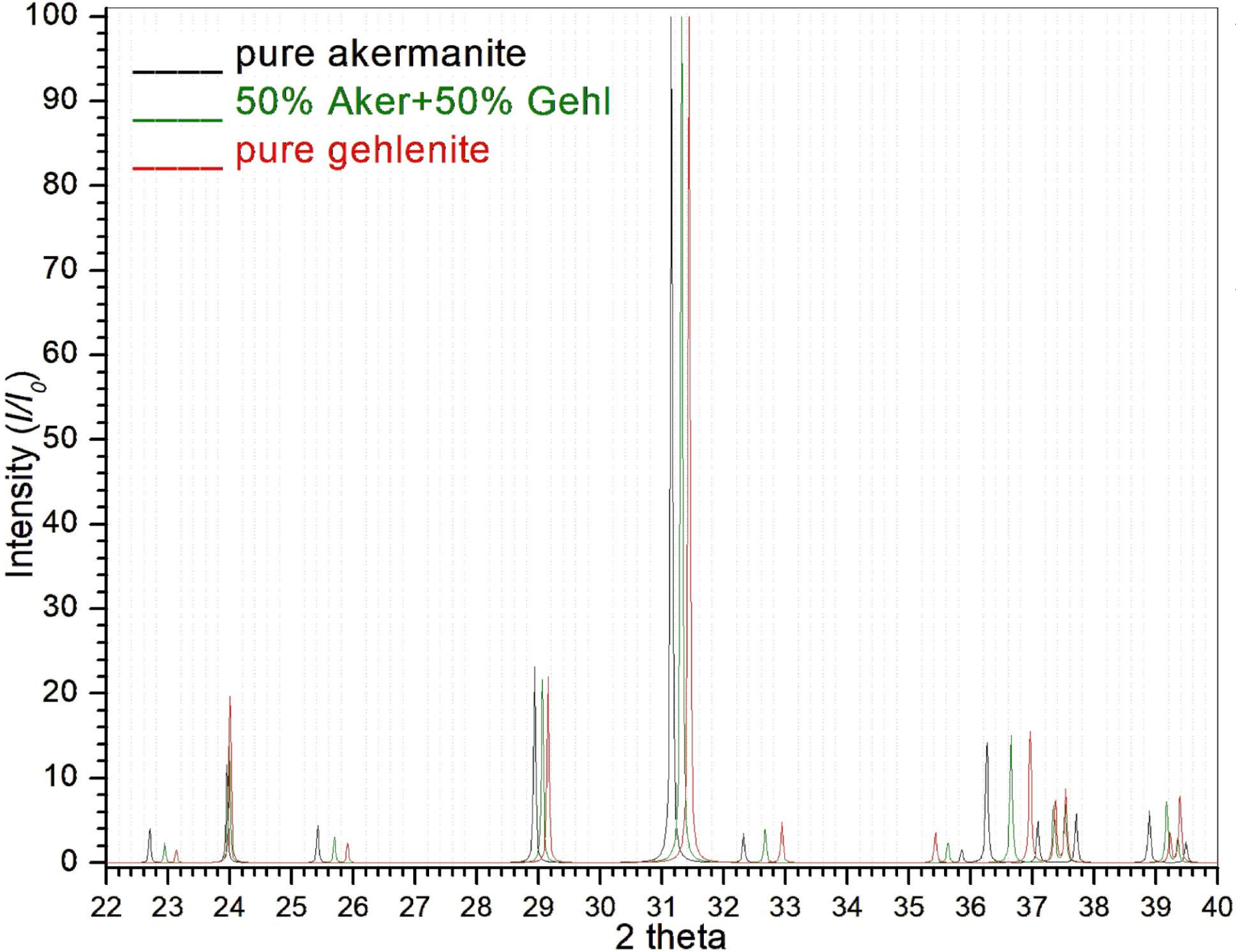
	100% Ak	75%Ak+25%Gh	50%Ak+50%Gh	25%Ak+75%Gh	100% Gh
h k l	**2θ / I/I_o**	**2θ / I/I_o**	**2θ / I/I_o**	**2θ / I/I_o**	**2θ / I/I_o**
1 1 0	15.9971 / 19.7	16.0871 / 15.4	16.1661 / 13.9	16.2421 / 11.5	16.2985 / 10.0
1 0 1	21.0499 / 14.3	21.0367 / 11.0	21.0232 / 8.4	21.0117 / 6.1	20.9932 / 4.9
2 0 0	22.6981 / 6.8	22.8266 / 4.9	22.9395 / 3.9	23.0480 / 3.0	23.1286 / 2.5
1 1 1	23.9492 / 10.4	23.9682 / 13.1	23.9832 / 14.4	23.9991 / 15.4	24.0023 / 17.4
2 1 0	25.4196 / 7.7	25.5640 / 6.1	25.6908 / 5.4	25.8128 / 4.6	25.9034 / 4.8
2 0 1	28.9336 / 45.1	29.0008 / 44.6	29.0587 / 41.2	29.1156 / 41.8	29.1506 / 40.1
2 1 1	31.1497 / 100	31.2366 / 100	31.3118 / 100	31.3853 / 100	31.4332 / 100
2 2 0	32.3171 / 7.2	32.5027 / 8.0	32.6657 / 8.2	32.8225 / 9.1	32.9389 / 9.0
0 0 2	35.8532 / 3.3	35.7358 / 4.0	35.6273 / 5.0	35.5260 / 6.4	35.4259 / 8.2
3 1 0	36.2565 / 31.6	36.4662 / 32.7	36.6504 / 32.9	36.8276 / 33.1	36.9592 / 32.2
2 2 1	37.0859 / 5.2	37.2222 / 6.3	37.3410 / 7.2	37.4563 / 8.5	37.5363 / 9.4
1 0 2	37.7061 / 13.3	37.6141 / 14.8	37.5283 / 15.1	37.4488 / 15.2	37.3663 / 16.4
3 0 1	38.8884 / 14.1	39.0391 / 16.0	39.1705 / 16.6	39.2981 / 18.0	39.3873 / 17.0
2 1 2	44.4625 / 14.9	44.4532 / 14.6	44.4412 / 13.4	44.4327 / 11.8	44.4061 / 9.7
4 0 0	46.3537 / 12.5	46.6280 / 14.3	46.8690 / 16.1	47.1010 / 18.0	47.2733 / 17.2
4 1 0	47.8679 / 15.4	48.1523 / 13.6	48.4022 / 11.5	48.6427 / 10.5	48.8214 / 6.9
3 3 0	49.3467 / 22.8	49.6410 / 22.1	49.8998 / 21.4	50.1488 / 21.1	50.3337 / 17.7
4 1 1	51.4299 / 11.1	51.6778 / 10.2	51.8951 / 9.3	52.1051 / 8.8	52.2567 / 7.2
3 1 2	51.9100 / 21.2	51.9807 / 23.4	52.0396 / 24.6	52.0993 / 26.4	52.1258 / 25.6
4 2 0	52.2110 / 13.3	52.5250 / 13.9	52.8010 / 14.0	53.0667 / 13.5	53.2641 / 12.6
3 3 1	52.8352 / 3.6	53.0940 / 3.9	53.3209 / 3.7	53.5401 / 3.8	53.6987 / 2.8



VESTA-calculated full XRD patterns of akermanite and gehlenite overlayed (*shown here only the 22 to 40° 2θ region*)

It is, therefore, quite easy to distinguish between akermanite and gehlenite by using X-ray diffraction.

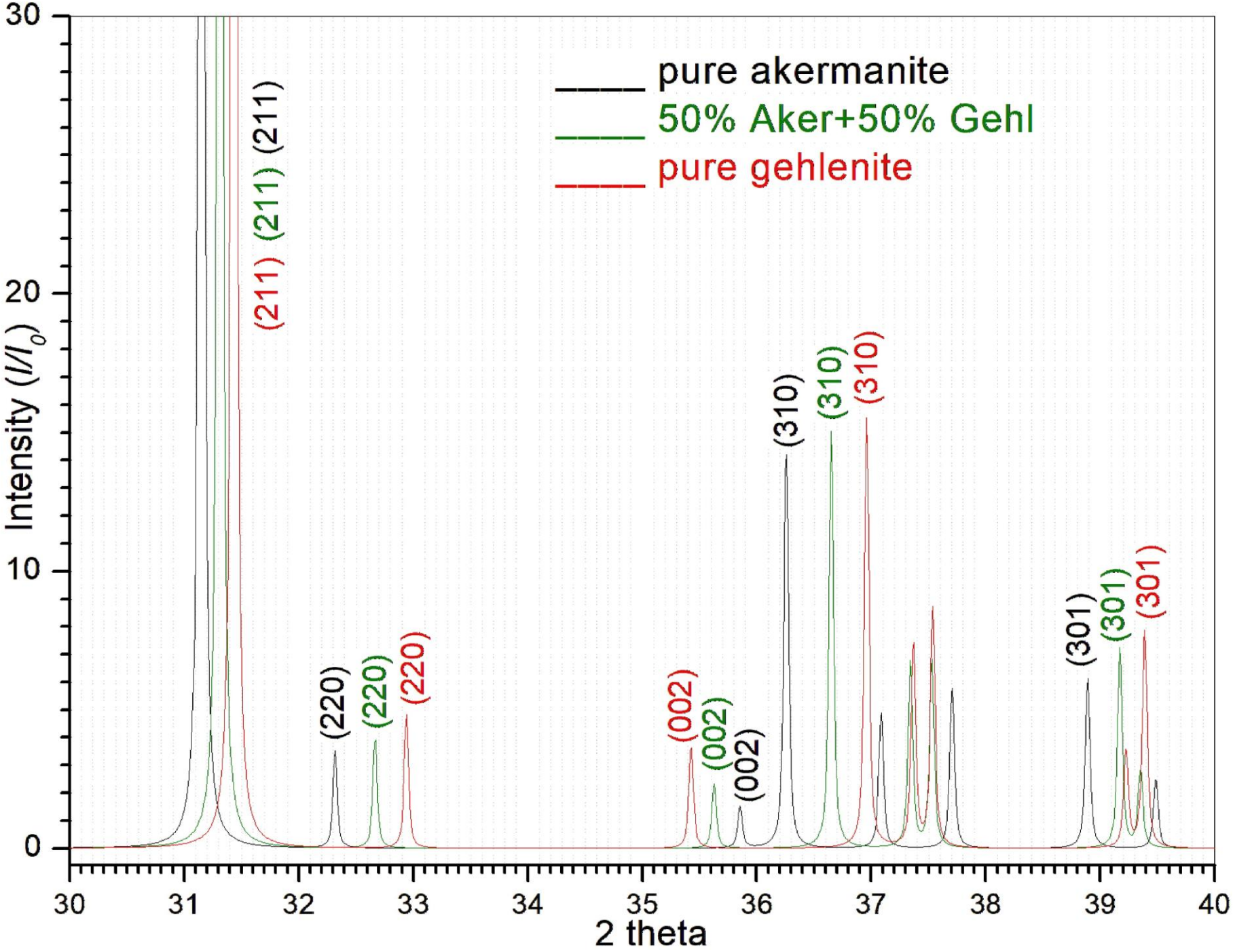
If one's initial composition does not have enough free magnesium oxide to react with CaO and SiO2 at high temperatures indicated by the quaternary phase diagram given before, then one would mostly produce gehlenite.



VESTA-calculated full XRD patterns of akermanite, gehlenite and 50% akermanite+50% gehlenite overlayed (*shown here only the 22 to 40° 2θ region*)

It hereby becomes evident that one can confidently assess the presence or absence of a "50%-50% solid solution of akermanite and gehlenite" in a sample as long as one knows the peak positions of pure akermanite and pure gehlenite.

The data plot of the next page will further explain that.

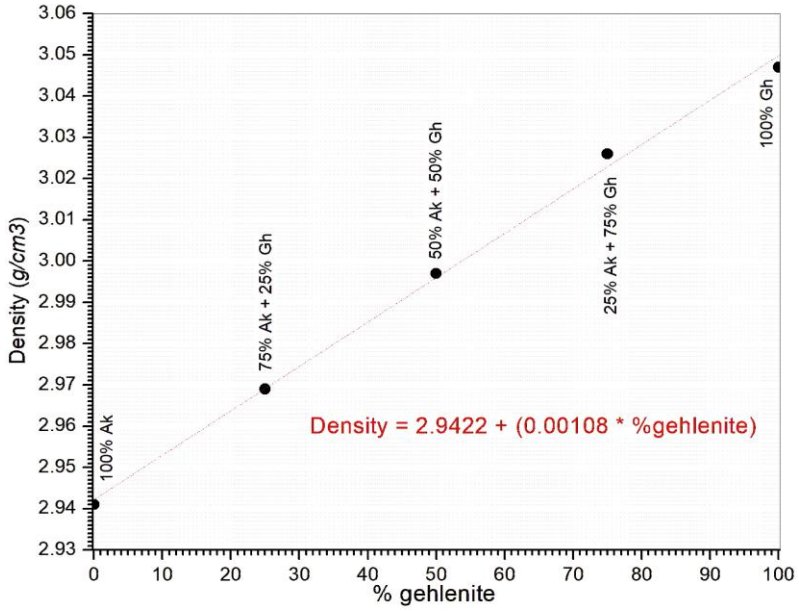


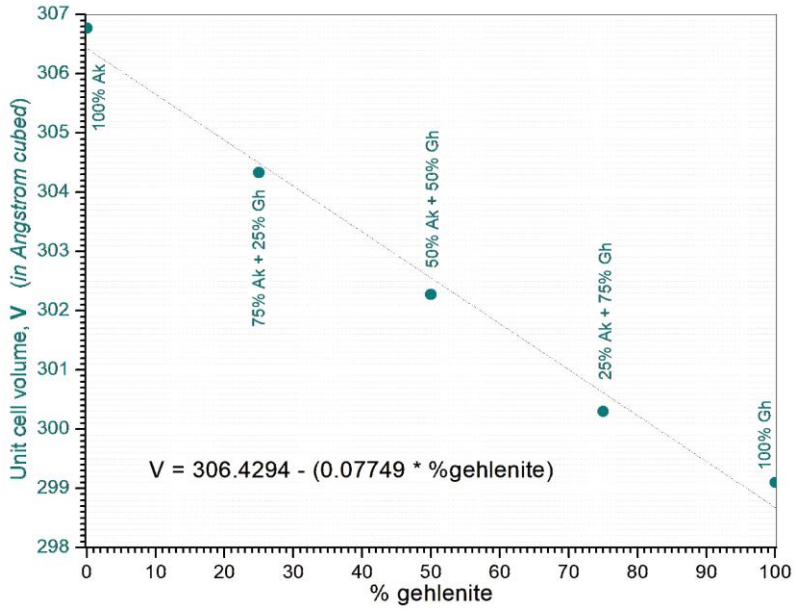
VESTA-calculated full XRD patterns of akermanite, gehlenite and 50% akermanite+50% gehlenite overlayed (*shown here only the 30 to 40° 2θ region*)

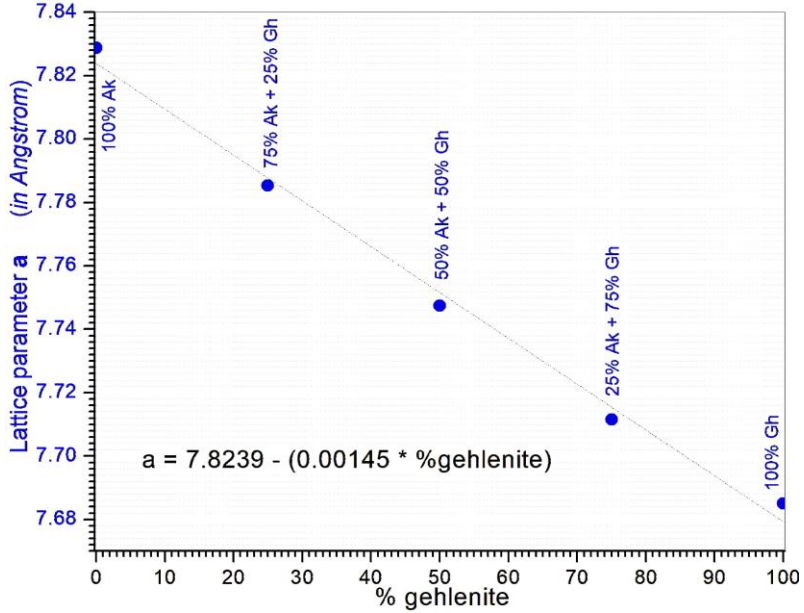
Most of the peaks are well-separated from one another.

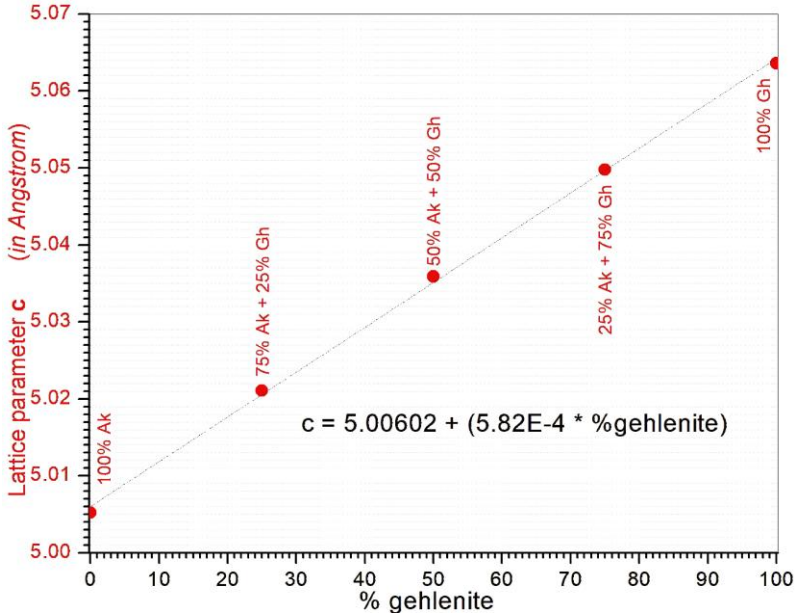
I suggest, for a sample that is suspected of containing a solid solution of akermanite and gehlenite, first collecting a high resolution XRD data by using 45 kV-40 mA, 30 to 40° scan, 2 h scan with a step size of 0.02° parameter settings.

The below plots are generated by using the data of table of p. 17. The akermanite-gehlenite solid solutions can be visualized by such plots.









Real solid solutions typically display such linear relationships for density, unit cell volume, lattice parameter a and lattice parameter c with varying composition (*x-axis* in all plots).

If and when the goal was to synthesize the powders of pure akermanite, pure gehlenite and a number of solid solutions between the two, then the linear regression equation inscribed in the top left plot can be used in follow-up quite simple and robust "pycnometric (either by using Gay-Lussac bottles or He-pycnometry) powder density" measurements. XRD analyses may then follow.

Experimental Details

Samples

Synthetic samples of nominal composition 0, 25, 50, 75 and 100% åkermanite content were produced by annealing glasses of appropriate composition (prepared by the National Physical Laboratory, England) at 1250° C for 2 days. The compositions of the glasses were checked by energy-dispersive electron microprobe; the results are given in Table 1. Pure åkermanite crystals proved to be particularly difficult to grow, and X-ray powder diffraction patterns always showed small contamination of other phases, including wollastonite. No other compositions showed signs of impurity phases. The presence of impurity phases in the nominally pure åkermanite did not cause appreciable problems in the analysis of the neutron powder diffraction data (see below) because the Bragg peaks of the impurity phases were much weaker than those of åkermanite (of less than 1% of the intensities of typical åkermanite reflections), and the high resolution of the neutron powder diffractometer enabled us to separate the åkermanite Bragg peaks from those of the impurity phases. The annealed samples were ground to fine powders of typical volume 5 cm^3 for the neutron powder diffraction experiments.

Before finishing this document, it it might be useful to reproduce the sample preparation procedure developed and practiced by Swainson *et al.* (1992).

Their selection of 1250°C as the temperature to anneal glasses (*i.e.*, glasses when prepared carefully at higher temperatures would have uniform compositions) corroborates both the cement kiln operation temperature of Solidia Technologies to produce its low C cement/binder and the quaternary phase diagram given in p. 9.