On the heat of formation of ye'elimite $\text{Ca}_4\text{Al}_6\text{O}_{12}\cdot\text{SO}_4$ using density functional theory

Alexander Pisch, Alain Pasturel

► To cite this version:

Alexander Pisch, Alain Pasturel. On the heat of formation of ye'elimite $\text{Ca}_4\text{Al}_6\text{O}_{12}\cdot\text{SO}_4$ using density functional theory. *Advances in Cement Research*, 2018, 31 (3), pp.1 - 7. 10.1680/jadcr.18.00128 . hal-01931195

HAL Id: hal-01931195

<https://hal.science/hal-01931195>

Submitted on 28 Nov 2019

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

On the heat of formation of ye'elimite $\text{Ca}_4\text{Al}_6\text{O}_{12}\cdot\text{SO}_4$ using density functional theory

Author 1

- Alexander PISCH, CNRS research fellow
- Univ. Grenoble Alpes, CNRS, Grenoble INP, SIMaP, F-38000 Grenoble, France
- ORCID number: 0000-0003-3451-5224

Author 2

- Alain PASTUREL, CNRS senior researcher
- Univ. Grenoble Alpes, CNRS, Grenoble INP, SIMaP, F-38000 Grenoble, France
- ORCID number: 0000-0001-6334-9005

Full contact details of corresponding author.

Dr. Alexander Pisch

Laboratoire SIMaP

UGA/CNRS/Grenoble INP

1130 Rue de la Piscine – BP75

F-38402 St Martin d'Hères Cedex

France

Phone : +33 476826510

Mail : alexander.pisch@simap.grenoble-inp.fr

Abstract (150 words)

The heat of formation of ye'elimite $\text{Ca}_4\text{Al}_6\text{O}_{12}\cdot\text{SO}_4$ was calculated using density functional theory (DFT). The crystallographic ground state of ye'elimite is the orthorhombic Pcc2 modification in agreement with experimental information. Three different many-body interaction functionals were used for DFT calculations: the generalised gradient approximation (GGA), the Armiento/Mattsson 2005 functional (AM05) and the strongly constrained and appropriately normed function (SCAN). The best results were obtained with the Scan functional and a heat of formation at 298K of -35.5 kJ/mol referred to pure CaO, Al_2O_3 and CaSO_4 was found. All other reported modifications of ye'elimite (cubic, tetragonal, monoclinic) are unstable with endothermic heat of transformations ranging from +18 to +78 kJ/mol.

Keywords chosen from ICE Publishing list

Modelling; Crystallography/crystal structure; Thermodynamics; Sulfate-based cements;

List of notation

a,b,c	lattice parameter
C_P	heat capacity at constant pressure
C_V	heat capacity at constant volume
F	Helmholtz free energy
H	enthalpy
$\hbar$	Planck constant
k_B	Boltzmann constant
q	phonon frequency
S	entropy
s	phonon band
T	temperature
V_0	volume at 0K
β	lattice angle
ω	frequency

1. Introduction

The mineral ye'elimite $\text{Ca}_4\text{Al}_6\text{O}_{12}\cdot\text{SO}_4$ has its name from its natural occurrence in the Hatrurim basin, west of the Dead Sea near Har Ye'elim and Nahal Ye'elim (Israel). The artificial version of this compound is used in calcium-sulfo-aluminate (CSA) cements due to its high reactivity with water. Key characteristics of CSA binders are rapid setting, high early strength and low shrinkage (Mehta & Monteiro, 2006). CSA clinkers and cements were developed by Alexander Klein at UC Berkley in the 1960's which explains the second name of ye'elimite – Klein's compound (Klein, 1963). Ye'elimite gained growing interest in recent times due to its use in a novel class of low CO_2 binders called BYF (belite-ye'elimite-ferrite) cements. Overall emissions of CO_2 are reduced by 20 to 30% in these binders due to a reduced level of limestone in the clinker, a lower burning temperature (typically not exceeding 1573K) and a lower grinding energy (Gartner, 2004).

The crystal structure of ye'elimite belongs to the sodalite family with a generic formula $\text{M}_4(\text{T}_6\text{O}_{12})\text{X}$. The sodalite mineral, $\text{Na}_8[\text{Al}_6\text{Si}_6\text{O}_{24}]\text{Cl}_2$ is the prototype of a series with related structures. The symmetry relations within the sodalite family was reviewed by Fischer and Baur (Fischer and Baur, 2009). Ye'elimite exists in two distinct crystal structures with an allotropic phase transition at 737K (Depmeier, 1988) or 711K (Kurokawa *et al*, 2014). The stable modification at low temperature is orthorhombic of the Pcc2 space group type (Calos *et al*, 1995; Cuesta *et al*, 2013). Additional crystal structures are reported in the literature. (Peixing *et al*, 1992) proposed a tetragonal cell of the P-4c2 space group type. (Cuesta *et al*, 2013) in their theoretical study using DFT calculations reported that this is not a stable modification of ye'elimite. In fact, it transforms into the stable Pcc2 modification during the relaxation step in the calculation. The high temperature modification is of the I-43m space group type (Cuesta *et al*, 2014; Kurokawa *et al*, 2014) with some statistically disordered SO_4 groups. Both authors claim, that in fact the I-43m modification is only a sub-cell of the $\text{I}4_132$ space group of the full system. However, due to the large number of atoms in the potential unit cell, the experimental data do not allow to fit the observed reflections to this space group and to derive corresponding atomic positions. (Cuesta *et al*, 2013) in their theoretical study proposed therefore two alternative approximations of the high temperature modification: a tetragonal I-4 cell and a monoclinic Cm cell. Both of them are less stable than the stable orthorhombic Pcc2 cell but present interesting

approximations for a deeper understanding of the high temperature disordered cubic modification reported at a later stage.

Thermodynamic data for the heat of formation of ye'elimite are rare and scarce. The knowledge of the Gibbs energy, the enthalpy and the entropy as a function of temperature is important to calculate optimum chemical and mineralogical compositions in industrial clinkers. In addition, high quality thermodynamic data is mandatory to be able to perform high quality heat and mass balance simulations of the clinker production process (Meyer *et al*, 2016) and for modeling the hydration behaviour (Martin *et al*, 2015). (Costa *et al*, 1972) determined the heat of reaction for $3 \text{ CaO} + 3 \text{ Al}_2\text{O}_3 + \text{CaSO}_4 = \text{Ca}_4\text{Al}_6\text{O}_{12}.\text{SO}_4$ using acid solution calorimetry. Pure calcium oxide (CaO), calcium sulfate (CaSO₄) and ye'elimite (Ca₄Al₆O₁₂.SO₄) were dissolved in a 4N hydrochloric acid (HCl) aqueous solution at 25°C and the observed heat of dissolution was recorded in an adapted calorimetric set-up. Pure Al₂O₃ could not be dissolved for kinetic reasons and its heat of dissolution was estimated. The heat of reaction of ye'elimite from calcium carbonate (CaCO₃), aluminium oxide (Al₂O₃) and calcium sulfate dehydrate (CaSO₄.2H₂O) was measured at 1623K by (Ayed *et al*, 1992) using drop calorimetry. Unfortunately, the authors did not perform a drop of the final product to determine the heat content from room temperature to 1623K. Therefore, the heat of formation at room temperature can only be approximated using tabulated or estimated heat capacity data for all compounds participating in the reaction. (Hanein *et al*, 2015) derived the heat of formation of ye'elimite from sulphur dioxide SO₂(g) vapour pressure measurements in the 1290K-1675K temperature range (Choi & Glasser, 1988). The most recent experimental determination of the heat of formation of ye'elimite uses hydrations experiments (Skalamprinos *et al*, 2018). They derived their value from measurements of the heat of hydration with pure ye'elimite and ye'elimite + anhydrite mixtures. In addition to the experimental values, different estimations exist in the literature. (Sharp *et al*, 1999) published a value without any further explanation on how it was obtained. (Wang *et al*, 2011) used two different empirical methods based on relative contribution of ions and functional groups to derive the heat and entropy of formation as well as the heat capacity at constant pressure.

A modern way to determine the standard heats of formation of crystalline solids are DFT calculations. Examples for the validity of this approach in the field of oxides are publications

from Wattez et al (Wattez *et al*, 2011) for the heat of formation of C_2S , C_3S and C_4AF using the GGA functional and more recently from Kitchaev et al (Kitchaev *et al*, 2017) for the enthalpy difference in MnO_2 polymorphs using the SCAN functional. The potential of DFT calculations for crystal structure determinations was shown by (Cuesta *et al*, 2013) in their theoretical study of the different modifications of ye'elimite using the CASTEP code and the General Gradient Approximation (GGA) functional. They confirmed the ground state orthorhombic structure and reported relative energies for the different modifications. Unfortunately, the authors of the study did not calculate the energies of formation with respect to pure CaO , Al_2O_3 and $CaSO_4$. The purpose of this contribution is to determine the heat of formation of ye'elimite with respect to CaO , Al_2O_3 and $CaSO_4$ using DFT and three different functionals.

2. Theory

The ground state properties of all reported modifications of ye'elimite were determined using DFT (Hohenberg & Kohn, 1964, Kohn and Sham, 1965). The VASP software package (Kresse *et al*, 1996, 1999) in its most recent version (5.4.4) was used for the calculations. Three different many-body exchange correlation functionals were used for this study: the well-established General Gradient Approximation (GGA) (Perdew and Wang, 1992), the hybrid AM05 functional (Armiento and Mattsson, 2005, Mattson et al, 2008) and the recently developed Strongly Conditioned and Appropriately Normed (SCAN) semi-local density functional (Sun *et al*, 2015). For Ca, the 3s, 3p and 4s orbitals, for Al, the 3s and 3p orbitals, for S, the 3p and 3s orbitals and for O the 2s and 2p orbitals are considered as valence states in the calculations. The cut-off energy for the projector augmented plane-wave bases was set to 800 eV. The gamma centred grid of k-points in the irreducible part of the Brillouin zone was automatically generated following the Monkhorst-Pack scheme (Monkhorst and Pack, 1976). The lattice parameters as well as the internal atomic coordinates of all modifications of ye'elimite were fully relaxed. The linear tetrahedron method with Blöchl corrections (Blöchl et al 1994) was used to calculate the electronic density of states (DOS). The relaxations were performed with a convergence criterion of 10^{-6} eV/Å for the total energy. Finite temperature properties such as the Helmholtz free energy F and heat capacities at constant volume / pressure C_v / C_p can be approximated using lattice dynamics theory (Ziman,

2001). The phonon spectrum of the stable orthorhombic ye'elimite was determined using the frozen phonon (supercell) method. The vibrational modes were calculated using the phonopy code (Togo *et al*, 2015) coupled to VASP. The convergence criteria for the Hellman-Feynman forces was set to 10^{-5} eV/Å to avoid residual strain in the lattice. The total energy of formation at 0K in kJ/mol is obtained by subtracting the weighed sum of the simple constituents from the calculated ground state energy of the ternary compound:

$$\Delta H(\text{Ca}_4\text{Al}_6\text{SO}_{12}.\text{SO}_4) = E(\text{Ca}_4\text{Al}_6\text{SO}_{12}.\text{SO}_4) - (3 E(\text{CaO}) + 3 E(\text{Al}_2\text{O}_3) + E(\text{CaSO}_4))$$

The Helmholtz free energy F at constant volume can be calculated in the harmonic approximation (HA) using their phonon density of states as a function of frequency q of the bands:

$$F(V_0, T) = \frac{1}{2} \sum_{q,s} \hbar \omega(q, s) + k_B T \sum_{q,s} \ln \left[1 - \exp \left(\frac{-\hbar \omega(q,s)}{k_B T} \right) \right]$$

The vibrational entropy and the heat capacity at constant volume are then given by:

$$S = - \left(\frac{\partial F}{\partial T} \right)_V; C_V = -T \left(\frac{\partial^2 F}{\partial T^2} \right)_V$$

The standard heat of formation at 298K of $\text{Ca}_4\text{Al}_6\text{SO}_{12}.\text{SO}_4$ was calculated using the C_V data of ye'elimite and the tabulated heat content data for CaO, Al_2O_3 from Janaf (Chase, 1998) and for CaSO_4 from (Robie *et al*, 1989).

3. Results and Discussion

The calculated ground state properties of $\text{Ca}_4\text{Al}_6\text{SO}_{12}.\text{SO}_4$ in the Pcc2 space group are summed up in Table 1 (lattice parameters, cell volumes), Table 2 (atomic positions) and Table 3 (energies of formation). The calculated lattice parameters and cell volume with the GGA functional are close to results reported in the frame of the "materialsproject.org" consortium (Jain *et al*, 2013). The calculated values from (Cuesta *et al*, 2013) differ considerably despite the fact that the authors used also GGA for their calculations. A possible explanation may be

that the ground state was not reached in the total energy calculations or that the underlying atomic potentials for Ca, Al, O and S in CASTEP differ from those used in the VASP code. By comparing our calculated data with the experimental values, it is clear that the data calculated with GGA and AM05 are larger than the experimentally reported lattice parameters while the values calculated with SCAN gives more satisfactory results. The main difference to the experimental lattice parameters lies in the fact that the calculated parameters are more orthorhombic-type with an a to b difference of 0.0145 Å instead of 0.0009 nm / 0.00006 nm for the experimental values. As DFT values were calculated at 0K, the difference to the experimental values seems to indicate that the orthorhombic-type character becomes smaller with increasing temperature. This evolution makes sense because the structure tends to higher symmetry with increasing temperature and becomes cubic in the high temperature modification above 737K / 711K. The fully relaxed atomic positions as presented in Table 2 correspond to the calculations with SCAN. The agreement between the experimentally refined positions and the calculated ones is good. This is also the case if one compares mean bond energies between the experimental and calculated crystal structure for which differences lower than 2% are observed. It is important to mention, that such a comparison is biased by the fact, that the experimental data are obtained at room temperature and the calculated one at 0K. The calculated formation energies at 0 K with respect to CaO, Al₂O₃ and CaSO₄ (Table 3) depend also considerably on the used functional. The most negative value was observed with GGA. Our calculated GGA value is in agreement with data reported by (Jain et al, 2013) using the same dataset and software for the calculations. We find that AM05 and SCAN yield less negative values.

Table 1: Ground state properties at 0K– lattice parameters and cell volumes – of orthorhombic Ca₄Al₆SO₁₂.SO₄ (Pcc2). Comparison of experimental and calculated values.

	Experimental		Theoretical				
	(Calos et al , 1995)	(Cuesta et al, 2013)	GGA (Cuesta et al, 2013)	GGA (Jain et al, 2013)	GGA (This work)	AM05 (This work)	SCAN (This work)

a (nm)	1.3028	1.30356(7)	1.3397	1.3097	1.3102	1.3018	1.2975
b (nm)	1.3037	1.30350(7)	1.3445	1.3267	1.3264	1.3185	1.3120
c (nm)	9.161	9.1677(2)	9.398	9.255	9.264	9.208	9.157
V (nm ³)	1.55596	1.55779	1.69279	1.6081	1.6099	1.58048	1.55881

145

146

147 Table 2: Fully relaxed atomic positions of orthorhombic Ca₄Al₆SO₁₂.SO₄ (Pcc2) as compared to
148 experimental information from (Cuesta et al, 2013). Experimental data are printed in italics.

Atom	Wyckoff position	x	y	z
Ca1	4e	<i>0.0627(11)</i>	<i>0.2495(14)</i>	<i>0.1554(17)</i>
		0.0586	0.2502	0.1483
Ca2	4e	<i>0.2549(14)</i>	<i>0.9417(12)</i>	<i>0.2945(16)</i>
		0.2546	0.9354	0.2919
Ca3	4e	<i>0.2591(16)</i>	<i>0.5301(11)</i>	<i>0.2494(15)</i>
		0.2585	0.5238	0.2399
Ca4	4e	<i>0.4910(9)</i>	<i>0.2548(13)</i>	<i>0.2196(13)</i>
		0.4926	0.2546	0.2202
Al1	2d	<i>0.5</i>	<i>0.5</i>	<i>0.2242(15)</i>
		0.5	0.5	0.2287
Al2	2c	<i>0.5</i>	<i>0</i>	<i>0.2466(12)</i>
		0.5	0	0.2461
Al3	2a	<i>0</i>	<i>0</i>	<i>0.2292(15)</i>
		0	0	0.221
Al4	2b	<i>0</i>	<i>0.5</i>	<i>0.2011(11)</i>
		0	0.5	0.1961
Al5	4e	<i>0.6269(7)</i>	<i>0.1202(7)</i>	<i>0.9963(90)</i>
		0.6277	0.1216	0.9924
Al6	4e	<i>0.1238(6)</i>	<i>0.6282(7)</i>	<i>0.9519(8)</i>
		0.1197	0.6301	0.9493
Al7	4e	<i>0.3708(6)</i>	<i>0.6293(7)</i>	<i>0.9760(13)</i>
		0.3703	0.6311	0.9772
Al8	4e	<i>0.1233(7)</i>	<i>0.8793(7)</i>	<i>0.9787(13)</i>
		0.1215	0.8785	0.9694
S1	4e	<i>0.2691(7)</i>	<i>0.2693(7)</i>	<i>0.9654(10)</i>
		0.2774	0.266	0.9696
O1	4e	<i>0.6790(12)</i>	<i>0.2645(16)</i>	<i>0.6111(12)</i>
		0.6664	0.26722	0.6073
O2	4e	<i>0.8260(8)</i>	<i>0.2042(9)</i>	<i>0.4666(15)</i>

		0.8103	0.1929	0.4799
O3	4e	<i>0.7590(15)</i>	<i>0.3781(7)</i>	<i>0.4296(22)</i>
		0.7633	0.3684	0.4393
O4	4e	<i>0.6598(10)</i>	<i>0.2280(14)</i>	<i>0.3507(17)</i>
		0.6572	0.23	0.348
O5	4e	<i>0.3983(10)</i>	<i>0.2439(6)</i>	<i>0.4338(11)</i>
		0.4109	0.2451	0.4473
O6	4e	<i>0.5628(6)</i>	<i>0.4028(5)</i>	<i>0.1320(13)</i>
		0.5708	0.4071	0.1391
O7	4e	<i>0.5457(8)</i>	<i>0.1035(5)</i>	<i>0.1446(11)</i>
		0.553	0.0994	0.1471
O8	4e	<i>0.7546(5)</i>	<i>0.5910(9)</i>	<i>0.5102(9)</i>
		0.7573	0.6032	0.5128
O9	4e	<i>0.5957(5)</i>	<i>0.4375(6)</i>	<i>0.8201(13)</i>
		0.5955	0.4349	0.8213
O10	4e	<i>0.8984(5)</i>	<i>0.4459(7)</i>	<i>0.7976(8)</i>
		0.896	0.4457	0.7924
O11	4e	<i>0.7539(6)</i>	<i>0.9027(10)</i>	<i>0.5520(10)</i>
		0.7559	0.8958	0.5464
O12	4e	<i>0.8916(5)</i>	<i>0.0345(7)</i>	<i>0.8323(14)</i>
		0.8912	0.0344	0.825
O13	4e	<i>0.6069(5)</i>	<i>0.0378(8)</i>	<i>0.8490(11)</i>
		0.6071	0.0414	0.8453
O14	4e	<i>0.1050(11)</i>	<i>0.2433(6)</i>	<i>0.4026(11)</i>
		0.0965	0.2435	0.395
O15	4e	<i>0.9646(7)</i>	<i>0.1066(5)</i>	<i>0.1224(14)</i>
		0.9647	0.1071	0.1162
O16	4e	<i>0.9571(7)</i>	<i>0.3947(5)</i>	<i>0.0996(8)</i>
		0.9619	0.3933	0.0955

149

150

151 Table 3: Calculated energies of formation at 0K referred to CaO, Al₂O₃ and CaSO₄ using GGA,

152 AM05 and SCAN functionals.

Functional	Energy of formation at 0K referred to CaO, Al ₂ O ₃ and CaSO ₄ [kJ/mol]	Reference
GGA	-167.56	(Jain et al, 2013)
	-176.00	(This work)
AM05	-93.54	(This work)

SCAN	-42.70	(This work)
------	--------	-------------

In order to be able to compare the DFT calculated data with the experimental values, one must correct the value from 0K to 298K. To do this, the heat capacity at low temperature is used to calculate the heat content between these two temperatures. Unfortunately, there are no experimental data available in the literature for the heat capacity at constant pressure of orthorhombic ye'elimite at low temperature. However, the heat capacity at constant volume can be derived from phonon calculations in the harmonic approximation. The calculated phonon density of states of orthorhombic $\text{Ca}_4\text{Al}_6\text{SO}_{12}\cdot\text{SO}_4$ (Pcc2) is presented in Figure 1. It shows that there are more vibrational states at lower frequency (acoustical branch) which indicates that the transport properties are preferentially induced by collective displacements with same direction, amplitude and phase. It would be interesting to compare this theoretical results to experimental data using neutron diffraction. The derived Helmholtz free energy, entropy and heat capacity at constant volume in the harmonic approximation are plotted in Figure 2. The heat content between 298K and 0K is 75.7 kJ/mol. This value presents a lower boundary for the heat content due to the fact that it was calculated with heat capacity data at constant volume. The true value at constant pressure may therefore be slightly higher. Combined with the heat contents for CaO, Al_2O_3 from the JANAF thermodynamic data compilation (Chase, 1998) and CaSO_4 from (Robie *et al*, 1989) a correction of 8.1 kJ/mol is applied. The standard heat of formation of stable orthorhombic $\text{Ca}_4\text{Al}_6\text{SO}_{12}\cdot\text{SO}_4$ (Pcc2) at 298K becomes -35.5 kJ/moles. This calculated value is compared to the experimental data in Table 4. Our value agrees with the calorimetric one from (Costa *et al*, 1972) and the estimations from (Wang *et al*, 2011) and (Sharp *et al*, 1988). All other experimental values are considerably more negative. However, these values are either measured at high temperature and extrapolated to room temperature with estimated values for the heat capacity of $\text{Ca}_4\text{Al}_6\text{SO}_{12}\cdot\text{SO}_4$ (drop reaction, 2nd law analysis) or use secondary data for the reaction calculations (hydration).

Table 4: Calculated heats of formation at 298K for orthorhombic $\text{Ca}_4\text{Al}_6\text{O}_{12}\cdot\text{SO}_4$ (Pcc2) as compared to the available experimental information. The data are referred to CaO , Al_2O_3 and CaSO_4 (column 2) and Ca -fcc, Al -fcc, S -orthorhombic and $\frac{1}{2} \text{O}_2(\text{g})$ (column 3). All supplementary thermodynamic data for the calculation are taken from JANAF (Chase, 1998)

Technique	Heat of formation with respect to CaO , Al_2O_3 and CaSO_4 (298K) [kJ/mol]	Heat of formation with respect to Ca , Al , S and $\frac{1}{2} \text{O}_2(\text{g})$ (298K) [kJ/mol]	Reference
Acid solution calorimetry	-49.37	-8415.8	(Costa et al, 1972)
Drop reaction calorimetry (1623K)	-81.22	-8447.7	(Ayed et al, 1992)
Heat of hydration	-156.52	-8523.0	(Skalamprinos et al, 2018)
2 nd law analysis (1290- 1675K)	-174.52	-8541.0	(Hanein et al, 2015)
Estimation (Mostafa)	+66.08	-8300.4	(Wang et al, 2011)
Estimation (Wen)	-26.72	-8393.2	(Wang et al, 2011)
Estimation (Sharp)	-48.52	-8415.0	(Sharp et al, 1999)
DFT calculation corrected with heat content	-35.48	-8401.1	SCAN (This work)

The relative heats of transformation at 0 K of the other structural modifications of $\text{Ca}_4\text{Al}_6\text{SO}_{12}\cdot\text{SO}_4$ as compared to the stable orthorhombic modification are reproduced in Table 5. Cubic (I-43m), Tetragonal (P-4c2, I-4) and monoclinic (Cm) $\text{Ca}_4\text{Al}_6\text{SO}_{12}\cdot\text{SO}_4$ are less stable than orthorhombic (Pcc2) $\text{Ca}_4\text{Al}_6\text{SO}_{12}\cdot\text{SO}_4$. The calculated transformation energies are more endothermic than the observed value of 0.4 kJ/mol for the orthorhombic / cubic transition at 737K (Depmeier, 1988).

Table 5: Calculated structural modifications of $\text{Ca}_4\text{Al}_6\text{SO}_{12}\cdot\text{SO}_4$ using SCAN compared to the reported experimental data including the heat of transformation at 0K. The heats of transformation are given with respect to the stable Pcc2 modification.

Structure type	Lattice parameters	Cell volume	Heat of transformation at 0K vs. Pcc2 [kJ/mol]	Reference
I-43m	a = 0.920 nm	0.77869 nm ³		Experimental (Calos et al, 1995)
	a = 0.9385 nm	0.82661 nm ³		Calculated (Cuesta et al, 2013)
	a = 0.9076 nm	0.74762 nm ³	+75.5	Calculated (This work)
P-4c2	a = 1.3031 nm c = 0.9163 nm	1.55379 nm ³		Experimental (Peixing et al, 1992)
	a = 1.3108 nm c = 0.9217 nm	1.58366 nm ³	+28.9	Calculated (This work)
I-4	a = 0.9505 nm c = 0.9516 nm	0.85972 nm ³		Calculated (Cuertas et al, 2013)
	a = 0.9231 nm c = 0.9301 nm	0.79255 nm ³	+18.7	Calculated (This work)
Cm	a = 0.9455 nm b = 1.3333 nm c = 0.8246 nm $\beta = 54.5^\circ$	0.84560 nm ³		Calculated (Cuesta et al, 2013)
	a = 0.9179 nm b = 1.2937 nm c = 0.7950 nm $\beta = 55.22^\circ$	0.775.40 nm ³	+22.3	Calculated (This work)

4. Conclusions

The structural and thermodynamic properties of various structural modifications of $\text{Ca}_4\text{Al}_6\text{SO}_{12}\cdot\text{SO}_4$ were calculated using DFT. The stable modification at 0K and room temperature is the orthorhombic Pcc2 modification in agreement with experimental information. Three different functionals were used for the calculations: GGA, AM05 and SCAN. The latter one gives the closest agreement with the experimental data and was used to derive the heat of

formation, the entropy and the heat capacity at constant volume. A heat of formation of -35.5 kJ/mol at 298K (with respect to CaO, Al₂O₃ and CaSO₄) and -8401.1 kJ/mol (with respect to the stable elements) was found in agreement the calorimetric value from (Costa et al, 1972). The reported cubic, tetragonal and monoclinic modifications are all unstable with respect to orthorhombic Ca₄Al₆SO₁₂.SO₄. The calculated transformation energies are more positive than the measured value of 0.4 kJ/mol and therefore none of these structures corresponds to the high temperature modification in agreement with the most recent results from (Cuesta et al, 2013; Kurokawa et al, 2014).

Acknowledgements

The authors wish to thank the GDR CNRS n°3584 (TherMatHT) for fruitful discussions on this project.

References

- Armiento R., Mattsson AE (2005) *Functional designed to include surface effects in self-consistent density functional theory* Phys. Rev. B72, 085108
<https://doi.org/10.1103/PhysRevB.72.085108>
- Ayed F, LeHoux P, Sorrentino F (1992) *Calcium sulfoaluminate formation* Proceedings of the 14th international conference on cement microscopy, April 6-9, Costa Mesa, CA (USA), ed. International Cement Association, 325-332
- Blöchl PE, Jepsen O, Andersen OK (1994) *Improved tetrahedron method for Brillouin-zone integrations* Phys. Rev. B49(23) 16223.
- Calos NJ, Kennard CHL, Whittaker AK, Davis RL (1995) *Structure of Calcium Aluminate Sulfate Ca₄Al₆O₁₆S* Solid State Chem. 119(1), 1-7
- Chase, Jr MW (1998) *NIST-JANAF Thermochemical Tables*. 4th edition, Washington, DC : New York :American Chemical Society ; American Institute of Physics for the National Institute of Standards and Technology, 1998.
- Choi G-S, Glasser, FP (1988) *The sulphur cycle in cement kilns: vapour pressures and solid-phase stability of the sulphate phases* Cem. Conc. Res. 18(3), 367–374.
[https://doi.org/10.1016/0008-8846\(88\)90071-3](https://doi.org/10.1016/0008-8846(88)90071-3)

235 Costa U, Massazza F, Testolin M (1972) *Heats of formation of $4\text{CaO} \cdot 3\text{Al}_2\text{O}_3 \cdot \text{SO}_3$,*
 236 *$4\text{SrO} \cdot 3\text{Al}_2\text{O}_3 \cdot \text{SO}_3$ and their mixed crystals* II Cemento 69(2), 61–68.
 237 Cuesta A., De la Torre AG., Losilla ER., Peterson VK, Rejmak, P, Ayuela, A, Frontera C,
 238 Aranda MAG (2013) *Structure, Atomistic Simulations, and Phase Transition of Stoichiometric*
 239 *Yeelimite*. Chemistry of Materials 25(9), 1680–1687. <https://doi.org/10.1021/cm400129z>
 240 Cuesta A, De la Torre ÁG, Losilla ER, Santacruz I, Aranda MAG (2014) *Pseudocubic Crystal*
 241 *Structure and Phase Transition in Doped Ye'elimite* Crystal Growth & Design 14(10), 5158–
 242 5163. <https://doi.org/10.1021/cg501290q>
 243 Depmeier W (1988) *Aluminate Sodalites – A Family with Strained Structures and Ferroic Phase*
 244 *Transitions* Phys. Chem. Miner. 15(5), 419–426
 245 Fischer RX, Baur WH (2009) *Symmetry relationships of Sodalite (SOD) – type crystal structures*
 246 Z. Kristallogr. 224(4), 185–197 <https://doi.org/10.1524/zkri.2009.1147> Mehta PK, Monteiro
 247 PJM (2006) *Concrete Microstructure, Properties and Materials* 3rd edition, McGraw-Hill, New
 248 York, NY
 249 Gartner EMG (2004) *Industrially interesting approaches to “low-CO₂” cements* Cem. Conc. Res.
 250 34(9), 1489–1498 <https://doi.org/10.1016/j.cemconres.2004.01.021>
 251 Hanein T, Elhoweris A, Galan I, Glasser FP, Bannerman MC (2015). *Thermodynamic data of*
 252 *ye'elemite ($\text{C}_4\text{A}_3\text{S}$) for cement clinker equilibrium calculations*, in: Proceedings of the 35th
 253 Cement and Concrete Science Conference, Aberdeen, UK. Centre for Innovative Building
 254 Materials and Technologies, Aberdeen, UK.
 255 Hohenberg P, Kohn W (1964) *Inhomogeneous electron gas* Phys. Rev. 136 (3B) B864–B871.
 256 Kohn W, Sham L (1965) *Self-consistent equations including exchange and correlation effects*
 257 Phys. Rev. 140 (4A) A1133–1140.
 258 Jain A, Ong SP, Hautier G, Chen W, Richards WD, Dacek S, Cholia S, Gunter D, Skinner D,
 259 Ceder G, Persson KA (2013) *The Materials Project: A materials genome approach to*
 260 *accelerating materials innovation* APL Materials 1(1), 011002
 261 <https://doi.org/10.1063/1.4812323>
 262 Kitchaev DA, Peng H, Liu Y, Sun J, Perdew JP, Ceder G (2016) *Energetics of MnO_2*
 263 *polymorphs in density functional theory* Phys Rev. B93(4), 045132, 1–5
 264 <https://doi.org/10.1103/PhysRevB.93.045132>

265 Klein A (1963) *Calciumaluminosulfate and Expansive Cements Containing Same* US Patent N°
 266 3, 155, 526
 267 Kurokawa D, Takeda S, Colas M, Asaka, T, Thomas P, Fukuda K (2014) *Phase transformation*
 268 *of $\text{Ca}_4[\text{Al}_6\text{O}_{12}]\text{SO}_4$ and its disordered crystal structure at 1073K*. Journal of Solid State
 269 Chemistry 215, 265–270. <https://doi.org/10.1016/j.jssc.2014.03.040>
 270 Kresse G, Furthmüller J (1996) *Efficient iterative schemes for ab initio total-energy calculations*
 271 *using a plane-wave basis set* Phys. Rev. B 54 (16) 11169-11186.
 272 Kresse G, Joubert D (1999) *From ultrasoft pseudopotentials to the projector augmented-wave*
 273 *method* Phys. Rev. B 59 (3) 1758.
 274 Mattsson, AE, Armiento R, Paier J, Kresse G, Wills JM, Mattson TR (2008) *The AM05 density*
 275 *functional applied to solids* J. Chem. Phys. 128(8), 084714, 1-11
 276 <https://doi.org/10.1063/1.2835596>
 277 Martin LHJ, Winnefeld F, Müller CJ, Lothenbach B (2015) *Contribution of limestone to the*
 278 *hydration of calcium sulfoaluminate cement* Cem. Concr. Comp. 62, 204-211
 279 <https://doi.org/10.1016/j.cemconcomp.2015.07.005>
 280 Meyer V, Pisch A, Penttilä K, Koukkari P (2016) *Computation of steady state thermochemistry in*
 281 *rotary kilns: Application to the cement manufacturing process* Chem. Eng. Res. Design Part
 282 B, 115, 335-347 <https://doi.org/10.1016/j.cherd.2016.08.007>
 283 Monkhorst H, Pack J, (1976) *Special points for Brillouin-zone integrations*, Phys. Rev. B 13
 284 (1976) 5188-5192.
 285 Mehta PK, Monteiro PJM (2006) Concrete Microstructure, Properties, and Materials. 3rd edition;
 286 McGraw-Hill, New York, NY., 238-239
 287 Peixing Z, Yimin C, Piping S, Guanying Z, Wenmel H, Jiaguo W (1992) *The crystal structure of*
 288 *C4A3S* Proceedings of 9th Int. Congr. On the Chemistry of Cement, Vol.1, Tara Art Press:
 289 New Delhi, India, 201-208
 290 Perdew JP, Wang Y (1992) *Accurate and simple analytic representation of the electron-gas*
 291 *correlation energy* Phys. Rev. B45 (23) 13244-13249
 292 <https://doi.org/10.1103/PhysRevB.45.13244>

Robie RA, Russell-Robinson A, Hemingway BS (1989) *heat capacities and entropies from 8 to 1000K of Langbeinite ($K_2Mg_2(SO_4)_3$), anhydrite ($CaSO_4$) and of Gypsum ($CaSO_4 \cdot 2H_2O$) to 325K* Thermochimica Acta 139, 67-81

Sharp JH, Lawrence CD, Yang R (1999) *Calcium sulfoaluminate cements - low-energy cements, special cements or what?* Adv. Cem. Res. 11, 3–13.
<https://doi.org/10.1680/adcr.1999.11.1.3>

Skalamprinos S, Galan I, Hanein T, Glasser F (2018) *Enthalpy of formation of ye'elimite and ternesite* J. Therm. Anal. & Calorimetry 131(3), 2345–2359. <https://doi.org/10.1007/s10973-017-6751-0>

Sun J, Ruzsinszky A, Perdew JP (2015) *Strongly constrained and appropriately normed semilocal density functional*, Phys. Rev. Lett. 115(3) 036402.

Togo A, Tanaka I (2015) *First principles phonon calculations in materials science* Scr. Mater. 108, 1-5

Wang W, Chen X, Ying C, Dong Y, MA C (2011) *Calculation and verification for the thermodynamic data of $3CaO \cdot 3Al_2O_3 \cdot CaSO_4$* Chinese Journal of Chemical Engineering 19(3), 489–495. [https://doi.org/10.1016/S1004-9541\(11\)60011-6](https://doi.org/10.1016/S1004-9541(11)60011-6)

Wattez T, Pisch A, Pasturel A, (2011) *First principles calculations of anhydrous cement clinker phases*, Proceedings, International Conference on the Chemistry of Cement ICCC 14, Madrid (Spain) ed. A. Palomo, A. Zaragoza, J.C. Lopez-Agüi, Instituto de Ciencias de la Construcción "Eduardo Torroja", Madrid.

Ziman JM (2001) *Electron and Phonons* Oxford Classic Series, Oxford University Press, Oxford (UK)

322 **Figure captions (images as individual files separate to your MS Word text file).**

323

324 Figure 1. Calculated phonon DOS for orthorhombic $\text{Ca}_4\text{Al}_6\text{SO}_{12}\cdot\text{SO}_4$

325 Figure 2. Calculated heat capacity at constant volume and derived standard heat of formation
326 and standard entropy at 298K for orthorhombic $\text{Ca}_4\text{Al}_6\text{SO}_{12}\cdot\text{SO}_4$

327

328

329

330

Figure 1.

Figure 2.