SUPPLEMENTARY MATERIAL

Density functional theory study of the crystal structure and infrared spectrum of a synthetized ettringite mineral

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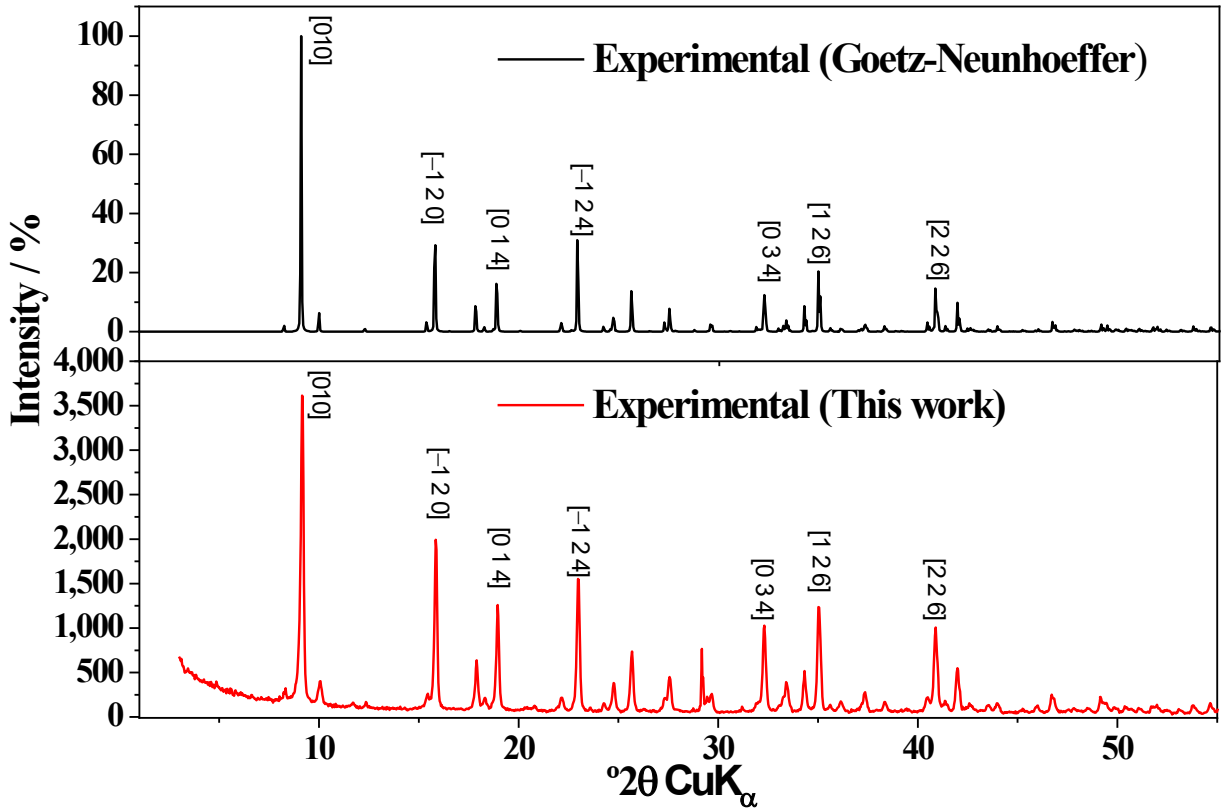


Figure. S1. X-ray diffraction patterns of ettringite: (a) Derived from the experimental crystal structure from Goetz-Neunhoeffer and Neubauer [59] obtained from a synthetized sample; (b) This work (synthetized sample).

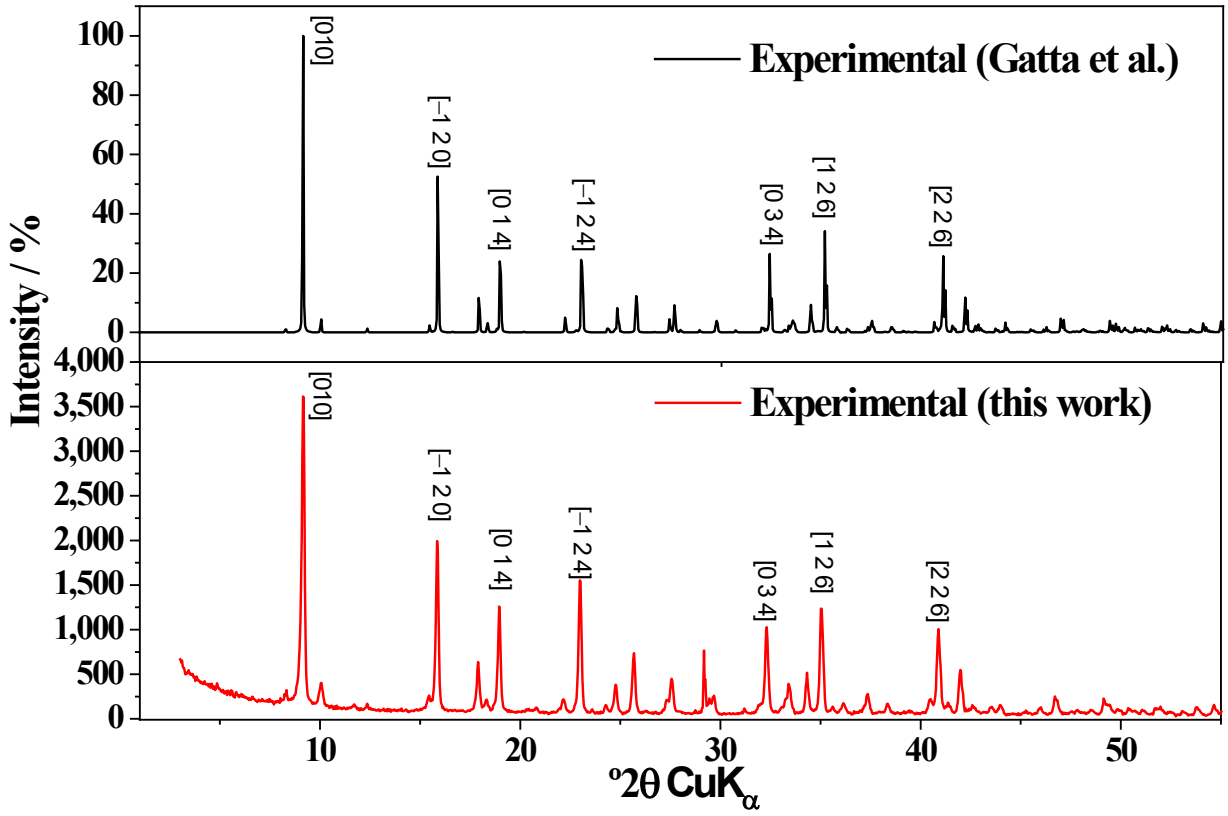


Figure S2. X-ray diffraction patterns of ettringite: (a) Derived from the experimental crystal structure from Gatta et al. [60] obtained from a natural sample; (b) This work (synthetized sample).

Table S1. Experimental vibrational frequencies and assignments obtained in this work and in that from Scholtzová et al. [76], referred in the table to as SKKT. The vibrational frequencies reported by Frost et al. [100] are also given.

Band Name	Vibrational frequency (cm^{-1})			Assignment	
	This work	SKKT [76]	Frost et al. [100]	This work	SKKT
a	3637	3637	3626	ν_{OH}	ν_{OH}
c	3426	3482	3398	ν_{OH}	ν_{OH}
g	2117	-	-	$\delta(AlOH)$	-
h	1683	1667	1676	$\delta(H_2O)$	$\delta(H_2O)$
i	1635	1633	1636	$\delta(H_2O)$	$\delta(H_2O)$
j	1473	1410	1403	$\delta(H_2O)$	-
k	1114	1113	1109	$\nu(AlO_6) + \delta(SO_4) + T(H_2O)$	$\nu^{as}(SO_4^{2-})$
l	1011	-	1078, 1053	$\nu(SO_4^{2-})$	-
m	988	989	986, 941	$\nu(SO_4^{2-})$	$\nu^{s}(SO_4^{2-})$
n	873	885	877, 851	$l(H_2O)$	$\delta(Al-OH)$
l	854	839	-	$l(H_2O)$	$\delta(Al-OH)$
o	667	-	-	$l(H_2O)$	
p	615	616	-	$\tau(H_2O)$	$\delta(Al-OH)$
q	542	542	-	$\omega(H_2O)$	$\nu(S-O)$
r	418	418	-	$\omega(H_2O)$	$\delta(Al-OH)$

THERMOGRAVIMETRIC ANALYSIS

Chemical composition cannot be obtained for ettringite because the H_2O content is variable [57]. The ideal structural formula of ettringite is $3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}32\ H_2O$ contains 45.93 wt.% H_2O. Ettringite is thermally stable merely up to ~110-120°C and its dehydration occurs during the final stage of its decomposition. There is a general agreement that a large water loss occurred at ~110-120°C, followed by amorphization of the sample after the loss of 20 units of water with the dehydration completed by 175°C. This led to the loss of its crystallization water and an amorphous state (monosulfate) appearing [106,109, 110]. In the course of thermal decomposition of deuterated ettringite, the molecular and hydroxyl water are removed simultaneously, throughout the whole temperature range [58].

The main dehydration process of ettringite is a multistep process (Figure S.3 and Figure S.4). The dehydration of ettringite could be separated for several stages, including 25-230 ºC, 230-350 °C, 350-835 °C and 825–1000 °C. The majority number of water molecules escape in a single step up to 230ºC, the remaining water molecules being liberated at higher temperatures. The total mass loss observed in the TG-DSC curves of the synthetized ettringite is 43.638 wt.%, indicating a total of 30.4 molecules of water, i.e., $3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}30.04\ H_2O$ (MW= 1192.42 g/mol). There are two well-defined DTG-DSC peaks at 146 and 267 °C (Figure S3. and Figure S.4), although the DSC curve suggests a first dehydration process until 70 °C. The sharp peak at 146 ºC corresponds to a net loss in weight of 34.17 wt.% (22.6 H_2O molecules, exothermic peak of 1551.62 J/g), and the second one at 267 ºC correspond to a weight loss of 6.34 wt.% (4.2 H_2O molecules, exothermic peak of 24.27 J/g). Thus, up to 400ºC, the number of water molecules removed is 26.8. After the second stage, both the TG and DTG curves show a progressive weight loss (3.1 wt.%) until the end of the experiment (1000 °C). A third peak is observed at 717 ºC corresponding to a net loss in weight of 1.195 wt.%. Between 400 and 825 ºC the mass loss is 2.74 wt.%. A final mass loss of 0.282 wt.% is observed at 899.63ºC corresponding to an endothermic peak.

In the TG-DSC curves (Figure S.3 and Figure S.4), the large mass loss between 50 ˚C and 230 ˚C is attributed to the decomposition of ettringite to a new solid phase, a partially dehydrated ettringite, called metaettringite, AFM-nH ($3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}nH_2O$, $n \neq 0$), which contains various water molecules numbers, n, ranging between 8 and 13 [109,110], and to basanite [$CaSO_4{\cdot}0.5H_2O$]. Further dehydration of basanite appears at 230 °C °C and complete dehydration of AFm-nH at 725 °C, respectively. At 900 °C ettringite is fully decomposed. The overall expected mass loss, assuming pure ettringite and conversion to 3 mole of calcium sulfate, 3 mole of calcium oxide, and 1 mole of aluminum oxide is 43.638%, which matches with the bound water content of ettringite. According to Table S.2, the number of water molecules of the synthezed ettringite is 30.4, the number of zeolitic water molecules being of 0.4 H_2O.

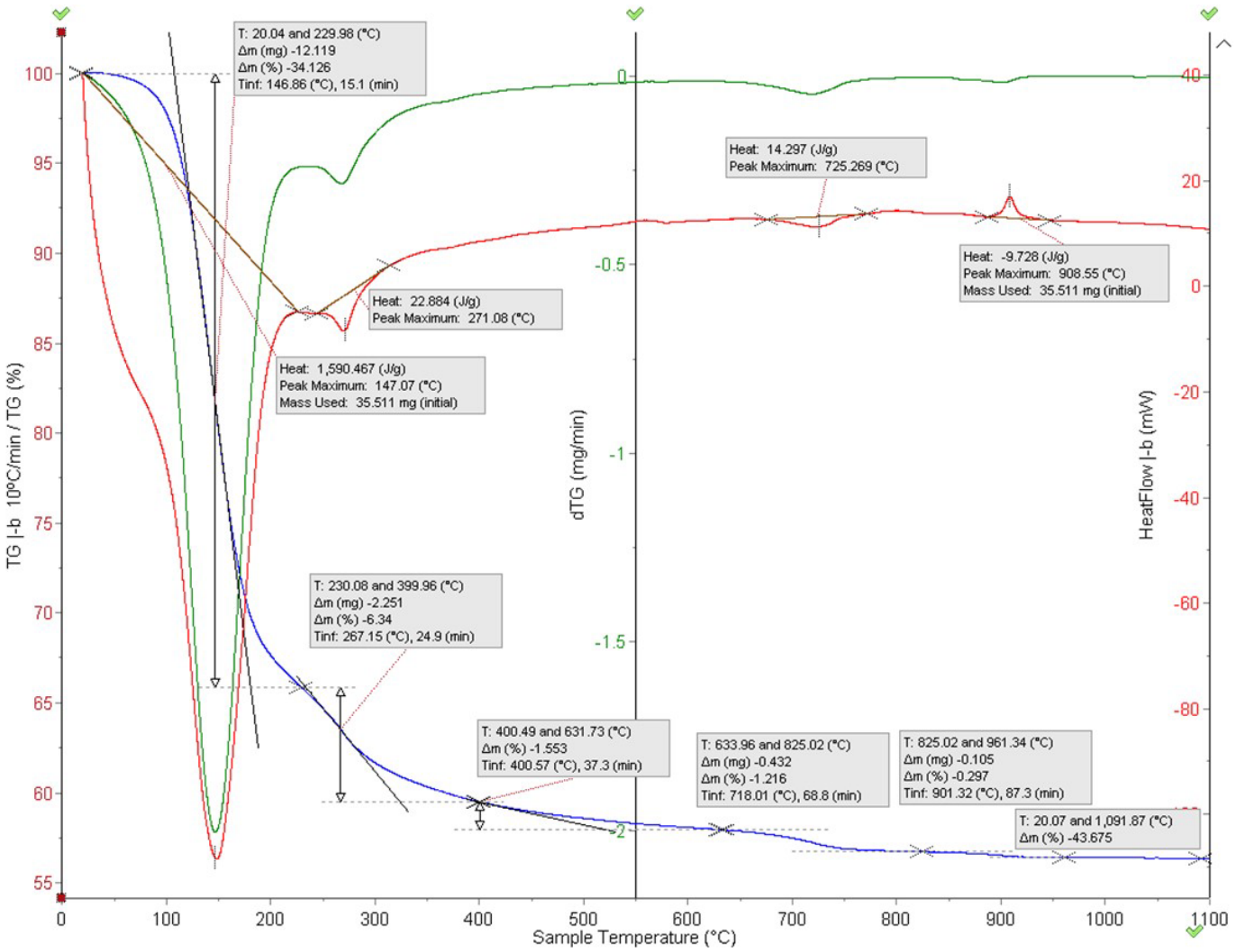


Figure S3. TG-DSC curves of the synthetized ettringite mineral (mass used = 35.511 mg).

Table S2. Dehydration process of synthetized ettringite based on TG-DSC analyses.

Theoretical: $3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}32\ H_2O$ [57, 106, 108]						
Total mass loss: 45.93%	32 H_2O → (n=26)	30 H_2O → (n=24)	18 H_2O → (n=12)	12 H_2O → (n=6)	6 H_2O → (n=0)	0 H_2O
Number of water removed		2	12	6	6	6
Location		intercolumn channel	12 H_2O Apices A	6 H_2O Apices B	6 H_2O Apices B	6 H_2O Al and Ca polyhedra
This work: $3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}30.4\ H_2O$						
Dehydration process	30.4 H_2O → (n=24.4)	30 H_2O → (n=24.0)	18.02 H_2O → (n=12.02)	11.98 H_2O → (n=5.98)	6.04 H_2O → (n=0.0)	0 H_2O
Mass loss	20-1100ºC: 43.638%		20-225ºC: 34.171%	225-400 ºC: 6.338%	400-630 ºC: 1.546%	630-1100°C: 1.195 + 0.282%

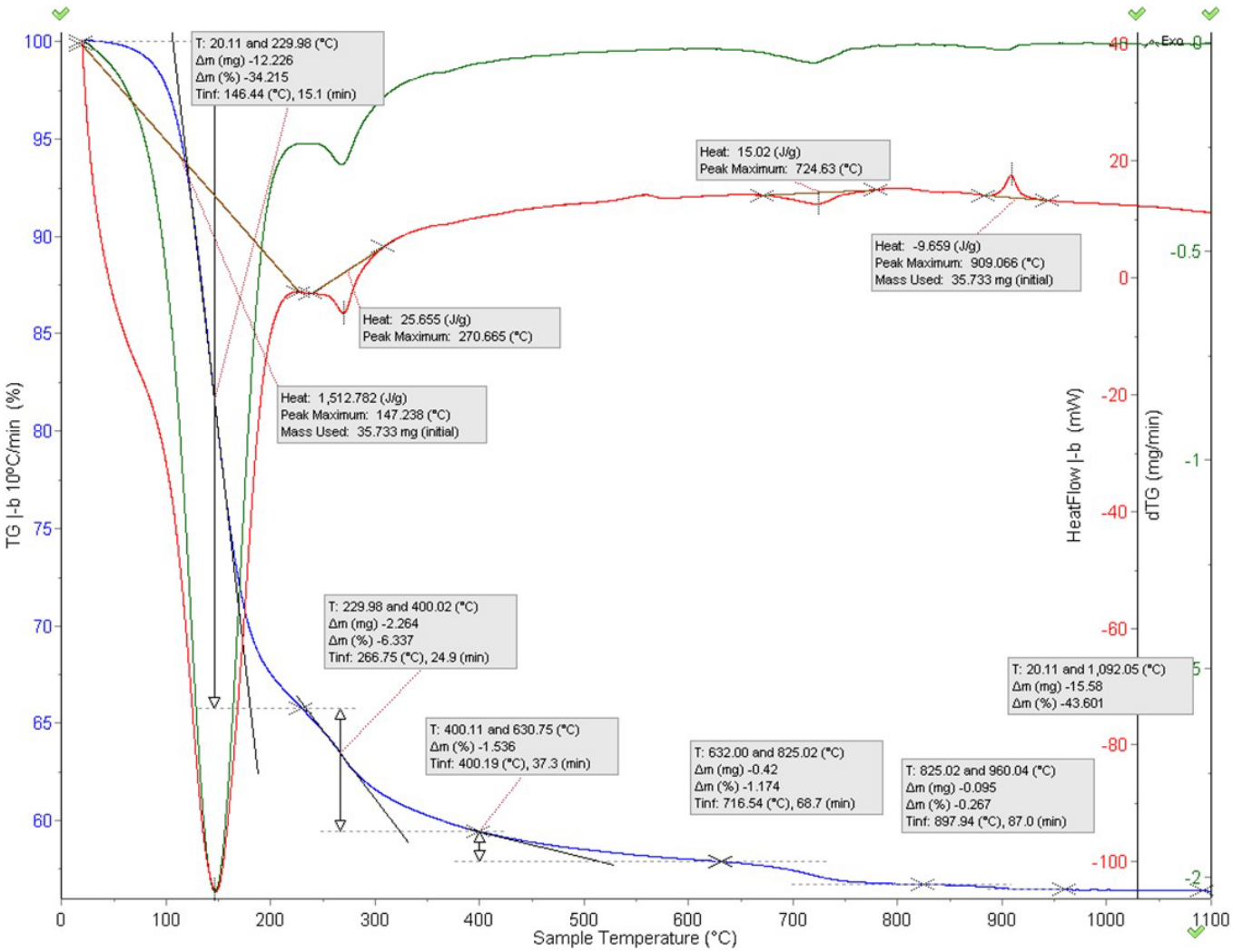


Figure S4. TG-DSC curves of the synthetized ettringite mineral (duplicate, mass used = 35.733 mg).

REFERENCES

See main text.