Loughborough University

This item was submitted to Loughborough's Institutional Repository (https://dspace.lboro.ac.uk/) by the author and is made available under the following Creative Commons Licence conditions.

For the full text of this licence, please go to:
http://creativecommons.org/licenses/by-nc-nd/2.5/

1 **Synthesis and structural characterisation of new ettringite and thaumasite**

2 **type phases: $Ca_6[Ga(OH)_6.12H_2O]_2(SO_4)_3.2H_2O$ and**

3 **$Ca_6[M(OH)_6.12H_2O]_2(SO_4)_2(CO_3)_2$, M=Mn, Sn**

4 Rachel L. Norman,[a,b] Sandra E. Dann [a] , Simon C. Hogg [c] and Caroline A. Kirk[*a,b]

5 [a]Department of Chemistry, Loughborough University, Loughborough, LE11 3TU, U.K.

6 [b]Department of Mineralogy, The Natural History Museum, Cromwell Road, London,

7 SW7 5BD, U.K.

8 [c]Department of Materials, Loughborough University, Loughborough, LE11 3TU, U.K.

9 * corresponding author, C.A.Kirk@lboro.ac.uk

10

11

12 **Abstract**

13

14

15 Investigations into the formation of new ettringite-type phases with a range of

16 trivalent and tetravalent cations were carried out to further study the potential this

17 structure type has to incorporate cations covering a range of ionic radii (0.53-0.69 Å).

18 We report the synthesis and structural characterisation of a new ettringite-type phase,

19 $Ca_6[Ga(OH)_6.12H_2O]_2(SO_4)_3.2H_2O$, which was indexed in space group P31c with the

20 unit cell parameters a = 11.202(2) Å, c = 21.797(3) Å and two new thaumasite-type

21 phases $Ca_6[M(OH)_6.12H_2O]_2(SO_4)_2(CO_3)_2$, M = Mn, Sn which were indexed in space

1

22   group P6$_3$ with the unit cell parameters a = 11.071(5) Å, c = 21.156(8) Å and a =

23   11.066(1) Å, c = 22.420(1) Å respectively. These new phases show the versatility of

24   the ettringite family of structures to tolerate a large range of cation sizes on the

25   octahedral M site and highlights the preference of tetravalent cations to crystallise

26   with the thaumasite structure over the ettringite structure.

27

28

29   *Keywords*: Ettringite; Thaumasite; X-ray Diffraction, Synchrotron.

30

31   **1. Introduction**

32

33

34   Ettringite, Ca$_6$[Al(OH)$_6$.12H$_2$O]$_2$(SO$_4$)$_3$.2(H$_2$O) and thaumasite,

35   Ca$_3$[Si(OH)$_6$.12H$_2$O](SO$_4$)(CO$_3$), are minerals that occur as secondary alteration

36   phases in mafic, igneous and metamorphic rocks [1,2]. They also form in cement

37   pastes, mortars and concretes, in field structures and when made in the laboratory.

38   Ettringite forms as a hydration product of tricalcium aluminate in the presence of

39   sulphate ions in Portland cements. Thaumasite forms in ordinary and sulphate-

40   resisting Portland cements, when stored at low temperatures, in damp conditions, in

41   the presence of carbonate ions and an external supply of sulphate ions [3]. However,

42   there is one report of thaumasite forming in Portland cements in warm climates [4].

43

44   The chemistry of ettringite can be altered to produce thaumasite through

45   replacement of aluminium with silicon as well as replacing one of the sulphate

46   groups and two molecules of water with two carbonate groups. This allows for the

47   more positively charged Si^{4+} replacing Al^{3+} [3]. Thaumasite and ettringite are also

48   structurally related; both adopt hexagonal structures, but with different space groups.

49   Ettringite crystallises in space group P31c with a = 11.224 Å, c = 21.108 Å [5,6] and

50   thaumasite crystallises in space group $P6_3$ with a = 11.04 Å, c = 10.39 Å. [7,8] Solid

51   solutions exist between these two phases, however, there are reported

52   discontinuities in the unit cell parameters attributed to the different space groups

53   each of the phases crystallise in [9].

54

55   The structures of ettringite and thaumasite can be described as consisting of cation

56   and anion columns. Ettringite consists of cation columns with composition

57    $Ca_3[Al(OH)_6.12H_2O]^{3+}$, that run parallel to the c axis, with the sulphate anions and

58   remaining water molecules in channels running parallel to these columns (Fig. 1).

59   Thaumasite has a cylindrical column of composition $Ca_3[Si(OH)_6.12H_2O]^{3+}$ that runs

60   parallel to the c axis, with the sulphate and carbonate anions ordered in the channels

61   between the columns, which also contain water molecules [3,7]. Thaumasite is

62   especially unusual as the tetravalent silicon ion is octahedrally co-ordinated by (OH^-)

63   [1]; only one other phase is known, $Si_2P_2O_7$, that can form at ambient pressures with

64   Si^{4+} octahedrally co-ordinated [10].

65

66   Ettringite has been shown to accommodate a wide range of both cations and anions

67   [11-13]. Mineral samples of ettringite can contain trace amounts of Fe^{3+} and Si^{4+},

3

68   substituting for the Al^{3+} on the octahedral site [14]. The existence of minerals which

69   contain significant amounts of Fe^{3+} or Si^{4+} are distinct, but related, mineral species,

70   known as sturmanite, $Ca_6[(Fe_{0.6}Al_{0.2}Mn_{0.2})(OH)_6.12H_2O]_2(SO_4)_{2.7}[B(OH)_3]_{0.3}[B(OH)_4]$

71   and charlesite, $Ca_6[(Al,Si)(OH)_6.12H_2O]_2(SO_4)_2[B(OH)_4]_2.H_2O$ [15,16]. They also

72   exhibit substitution of some of the sulphate groups with borate polyanions.

73

74   There are two reported thaumasite-type minerals, jouravskite

75      $Ca_3[Mn(OH)_6.12H_2O](SO_4)(CO_3)$ [17] and carraraite $Ca_3[Ge(OH)_6.12H_2O](SO_4)(CO_3)$

76   [18], which have the octahedral site, occupied by Si^{4+} in thaumasite, replaced by the

77   tetravalent cations Mn^{4+} and Ge^{4+}.

78

79   Synthetic studies to date have focused mainly on sulphate anion replacement in

80   ettringite, with reports of ettringite-type phases forming with many anions, e.g. NO_3^-,

81      $B(OH)_4^-$, OH^-, SO_3^{2-}, CrO_4^{2-}, CO_3^{2-}, Cl^- [11,12]. Investigations into the solid solution

82   formation between ettringite and its carbonate analogue have been carried out [19].

83   The lattice parameter trends indicate the two end members form partial solid

84   solutions and there is no continuous solid solution between the end members.

85   These results are similar to the discontinuities in the lattice parameters found

86   between ettringite and thaumasite end members [3,9].

87

88   Our investigations here have focused on substitution of the Al^{3+} site by trivalent and

89   tetravalent cations. We have successfully synthesised one new ettringite-type phase,

90      $Ca_6[Ga(OH)_6.12H_2O](SO_4)_3.2(H_2O)$ and two new thaumasite-type phases,

4

91    $Ca_6[M(OH)_6.12H_2O](SO_4)_2(CO_3)_2$, M=Mn and Sn. During this study, ettringite, and

92   the reported iron analogue, $Ca_6[Fe(OH)_6.12H_2O](SO_4)_3.2H_2O$ [20,21] were also

93   synthesised under the same conditions. Here we report the characterisation of the

94   ettringite and thaumasite type phases using both in-house techniques (powder X-ray

95   Diffraction and infrared spectroscopy) as well as high resolution synchrotron powder

96   X-Ray Diffraction, on beamline I11 at The Diamond Light Source.

97

98   **2. Experimental**

99

100

101   The ettringite-type phases were prepared using a variation on the saccharate

102   method, [21] whereby a solution of $M_2(SO_4)_3$, M= Al^{3+}, Fe^{3+}, Ga^{3+} or MSO_4, M= Mn^{2+},

103   Sn^{2+} (Sigma-Aldrich 99.9% pure), was added to a solution of CaO (Sigma-Aldrich

104   99.9% pure) in a 6:1 (Ca:M) ratio. The CaO was heated overnight at 1000 °C, to

105   ensure the removal of water and decarbonation of any calcium carbonate, then

106   dissolved in a 10 % sugar solution (10 g of sugar in 100 ml distilled water) and mixed

107   using a magnetic stirrer. In a second beaker, the appropriate metal sulphate was

108   dissolved in 100 ml of distilled water and then added to the CaO solution. The

109   beaker was covered with parafilm and left on a stirrer plate at room temperature

110   overnight. After 24 h the solution was vacuum filtered and left in a desiccator to dry.

111   The precipitates were analysed by powder X-ray Diffraction (PXRD) and infrared

112   spectroscopy (IR).

113

114 PXRD data were collected on a Bruker D8 Advance diffractometer in reflection

115 geometry, Cu Kα_1 radiation and a Braun linear position sensitive detector. Data were

116 collected over the 2θ range 5-90˚ with a step size of 0.007˚ 2θ and a count time of

117 1.8 s per step. NIST SRM640c silicon was added as an internal standard. Lattice

118 parameters were determined using a least squares refinement procedure, part of the

119 Stoe WinXPow software suite. IR spectra were collected on neat powders using a

120 Shimadzu FTIR 8400S Spectrophotometer with a Specac Golden Gate attachment

121 between 400-4000 cm^{-1}.

122

123 Synchrotron Radiation PXRD data were collected at room temperature on the

124 ettringite and thaumasite type phases at The Diamond Light Source (Didcot, UK), I11

125 beamline, High Resolution Powder Diffractometer [23]. The samples were mounted

126 in 0.5 mm Lindemann capilliaries and measured in Debye-Scherrer (tramsmission)

127 geometry. The data were collected over the 2 θ range 5°-150° 2 θ for 30 minutes.

128 The X-ray wavelength (0.826262 Å) and 2θ zero offset were calibrated by refinement

129 of the diffraction pattern of a silicon standard (NIST SRM640c). Data were refined

130 using the refinement package Topas Academic v4 [24]. Rietveld refinement was

131 carried out for each dataset to investigate whether the samples crystallised with

132 either the ettringite or thaumasitetype structure.

133

134

135

136 **3. Results**

137

138

3.1 X-ray Diffraction

140

Fig. 2 shows the laboratory PXRD patterns of the phases formed from the above

synthetic procedure. Comparison to the International Center for Diffraction Data

Powder Diffraction File (ICDD PDF) confirmed the phases to be ettringite type (ICDD

No 41-1451) [5]. Synthesis of ettringite under the same experimental conditions was

carried out and is included on Fig. 2 for comparison purposes. Many synthetic

studies of the formation of ettringite are carried out under CO_2-free conditions due to

the reported formation of $CaCO_3$ [9,11,12]. Analysis of the PXRD data showed that

only the Fe ettringite-type phase had a trace amount of $CaCO_3$ present, whereas all

other samples were found to contain only ettringite-type crystalline phases (within

the detection limits of the PXRD technique). This suggests that the addition of CaO

to a sucrose solution, to improve the solubility of CaO had also reduced and in some

cases prevented, the formation of $CaCO_3$. It should be noted that the broad

background feature around 10° 2θ may be due to the presence of amorphous gel-

like phases that often form as pre-cursors in synthetic cement-type systems [25].

Results of the lattice parameter refinements carried out on the laboratory PXRD data,

are shown in Table 1.

157

158

3.2 Infrared Spectroscopy

7

160

161   IR data were also used to confirm the phases present were ettringite type and to

162   investigate the presence of functional groups in the structures. Comparison of the IR

163   spectra of the new phases to the IR spectrum of pure ettringite shows similarities

164   suggesting the phases formed are ettringite (Fig. 3). The broad band at 3400 cm^{-1} is

165   indicative of the water vibrations in the channel of the structure (Fig.1), the stretch in

166   the region 1100 cm^{-1} is characteristic of the presence of sulphate groups and the

167   band in the region 1400 cm^{-1} would indicate the presence of the CO_3^{2-} group [26,27].

168   The IR spectrum of $CaCO_3$ is included for comparison.

169

170   **3.3 Rietveld refinement of synchrotron PXRD data**

171

172   Initial analysis of the high resolution PXRD data collected on beamline I11 showed

173   that the Al and Fe substituted ettringite samples and the thaumasite-type samples

174   contained impurity phases, not detected on analysis of the laboratory PXRD data.

175   Table 2 gives details of the phases identified to be present in each sample.

176

177   Refinement strategy

178

179   Full structural refinements were carried out using the Rietveld refinement method in

180   the refinement programme Topas Academic [24]. The initial strategy used for each

181   refinement was the same, whereby the background was modelled using a

182   Chebychev function and the peak shape modelled using the modified Thomson-Cox-

183   Hasting pseudo Voigt function with the asymmetry of low angle peaks modelled

184   using a simple axial model.

185

186   The ettringite-type phases $Ca_6[M(OH)_6.12H_2O]_2(SO_4)_3.2H_2O$, M=Al, Fe, Ga were

187   refined using a published ettringite structural model as a starting point, with the

188   occupancy of the O19 site, the oxygen atom of the unbound water molecule in the

189   anion column (Fig. 1b), fixed at 2/3 as in the published model [6]. After refinement of

190   the background, lattice parameters and profile parameters had converged the

191   thermal parameters (beq) were then refined. Although it is more normal to refine the

192   atomic positions before the thermal parameters, after testing many different

193   strategies, this chosen one was found to produce the most stable refinements. The

194   thermal parameters of the O sites were then constrained in sets to give stable

195   refinements; O1-O4 (O sites co-ordinated to the M cation), O5-O12 (O sites co-

196   ordinated to just the Ca sites) and O13-O18, (O sites co-ordinated to the S sites),

197   and the thermal parameters of the S sites were also constrained. The atomic

198   positions were then refined and finally all variable parameters were allowed to refine

199   until the least squares refinement converged. In the case of the Ga sample, all

200   constraints on the thermal parameters could be removed, but for the Al and Fe

201   samples this was not possible. The sulphate anions in both the Al and Fe

202   substituted samples were especially problematic to refine and give reasonable

203   calculated S-O bond lengths and beq. Therefore the positional parameters were

204   fixed to those of the structural model [6].

205

206   Refinement of the thaumasite phases, $Ca_6[M(OH)_6.12H_2O]_2(SO_4)_2(CO_3)_2$, M = Mn,

207   Sn, were carried out using a published structural model as a starting point [8]. The

208   initial refinement strategy was the same as for the ettringite phases and constraints

209   were placed on the O thermal parameters. In general, for both thaumasite phases, a

210   stable refinement of the carbonate and sulphate anions was not acheived and in

211   both cases, the C and S thermal parameters were fixed at 1. More reasonable C-O

212   and S-O bond lengths were produced using this strategy.

213

214   Refinement of $Ca_6[Al(OH)_6.12H_2O]_2(SO_4)_3.2H_2O$

215   The ettringite sample, $Ca_6[Al(OH)_6.12H_2O]_2(SO_4)_3.2H_2O$ was found to be multiphase,

216   (Table 2), therefore a multiphase Rietveld refinement was carried out. The final

217   observed-calculated and difference profiles (Fig. ESI 1) and the refined atomic

218   positions and thermal parameters (Table ESI 1) are provided as electronic

219   supplementary information and the calculated bond lengths are shown in Table 3.

220

221   Refinement of $Ca_6[Fe(OH)_6.12H_2O]_2(SO_4)_3.2H_2O$

222   The Fe substituted ettringite phase $Ca_6[Fe(OH)_6.12H_2O]_2(SO_4)_3.2H_2O$ was also

223   found to have impurity phases present (Table 2) and therefore a multiphase Rietveld

224   refinement of these data was carried out. To allow a stable refinement, the

225   constraints on the thermal parameters, as indicated in the refinement strategy, were

226   introduced as well as fixing the atomic co-ordinates of the position O19. The final

227   observed, calculated and difference profile (Fig. ESI 2) and the refined atomic

228 positions and thermal parameters (Table ESI 2) are provided as electronic

229 supplementary information and the calculated bond lengths are given in Table 3.

230

231

232 Refinement of $Ca_6[Ga(OH)_6.12H_2O]_2(SO_4)_3.2H_2O$

233 The Ga substituted ettringite phase, $Ca_6[Ga(OH)_6.12H_2O]_2(SO_4)_3.2H_2O$ was found to

234 be phase pure and refinement of this dataset produced a very stable refinement,

235 whereby all parameters could be refined and no constraints were required. The final

236 observed, calculated and difference plots (Figure ESI 3) and the refined atomic

237 positions and thermal parameters (Table ESI 3) are provided as electronic

238 supplementary information and the calculated bond lengths are presented in Table 3.

239

240 Refinement of $Ca_6[M(OH)_6.12H_2O]_2(SO_4)_2(CO_3)_2$, M=Mn, Sn

241 The Sn and Mn compounds had the targeted compositions

242 $Ca_6[M(OH)_6.12H_2O]_2(SO_4)_3.2H_2O$,M = Mn, Sn. However, both were determined to

243 contain carbonate units as shown by IR (Fig. 3, band at ~1400 cm^{-1}) and the PXRD

244 data could be refined on a smaller unit cell, related to that of thaumasite (Table 1).

245 The composition is therefore proposed to be similar to that of thaumasite

246 $Ca_6[M(OH)_6.12H_2O]_2(SO_4)_2(CO_3)_2$, M=Mn, Sn. The Sn and Mn thaumasite-type

247 phases were shown to contain an impurity phase, that has yet to be identified and

248 therefore single phase Rietveld refinements were carried out. In both refinements it

249 was difficult to achieve a stable refinement of the sulphate and carbonate anions and

250 constraints on the O sites were introduced, which included fixing the thermal

11

251 parameter of the O5 site at 1 during refinement of the Sn phase. The thermal

252 parameter of the C1 site was fixed at 1 during the refinement of both the thaumasite

253 phases and the thermal parameter of the S1 site was fixed at 1 during refinement of

254 the Sn phase. To produce a stable refinement of the Mn-thaumasite phase, the

255 atomic positions of the S1 and C1 sites were fixed at the values given in the starting

256 model [8].

257

258 The final observed, calculated and difference profiles for the Mn-substituted

259 thaumasite phase $Ca_6[Mn(OH)_6.12H_2O]_2(SO_4)_2(CO_3)_2$, (Fig. ESI 4) and the refined

260 atomic positions and thermal parameters (Table ESI 4) are provided as

261 supplementary electronic information and the calculated bond lengths are presented

262 in Table 4. The observed, calculated and difference profiles from refinement of the

263 data collected on the Sn-thaumasite phase $Ca_6[Sn(OH)_6.12H_2O]_2(SO_4)_2(CO_3)_2$, are

264 shown (Fig. ESI 5) and the refined atomic position and thermal parameters (Table

265 ESI 5) are presented as electronic supplementary information and the calculated

266 bond lengths are shown in Table 4.

267

268 Bond Valence Analysis

269 Using the calculated bond lengths for each of the ettringite and thaumasite phases,

270 bond valence analysis was carried out [28]. Table 5 presents the valences

271 determined for each of the cations in all of the investigated phases.

272

273

274

4. Discussion

276

277   Laboratory PXRD data, IR data and refinement of the synchrotron PXRD data

278   confirmed the compositions $Ca_6[M(OH)_6.12H_2O]_2(SO_4)_3.2H_2O$, M=Al, Fe, Ga

279   crystallised with an ettringite-type structure. Only the Ga substituted compound was

280   found to be single phase whereas the Al and Fe substituted phases had impurities

281   present (Table 2). The IR spectrum of the Fe substituted phase has a strong band at

282   1415 cm^{-1} indicating the presence of a CO_3^{2-} ion (Fig. 3); this confirms the result from

283   analysis of the PXRD datasets (both laboratory and synchrotron) which show a trace

284   amount of $CaCO_3$ to be present. The other impurity phases identified on analysis of

285   the synchrotron PXRD data may be due to the degradation of the samples, given the

286   time period between synthesis of the samples and data collection on beamline I11 (2

287   months).

288

289   The Mn and Sn substituted compounds were synthesised under the same conditions

290   as the ettringite-type phases. The PXRD data when compared to the standard

291   ettringite pattern exhibited shifts in 2 θ positions, as expected due to the different

292   ionic radii of the cations occupying the octahedral site. However, there were notable

293   missing key reflections associated with an ettringite-type diffraction pattern. Fig. 4

294   highlights an expanded range of PXRD data with the hkl indices marked on the

295   reflections for ettringite; the 002, 101, 103 and 104 are absent. This, along with

296   other absent reflections for an ettringite-type structure at higher 2θ values (not

297 shown here) suggested that the Mn and Sn phases were thaumasite-type structures.

298 The IR spectra for the Mn and Sn compounds clearly showed the presence of a

299 carbonate group at ~1375 cm^{-1} (Fig. 3). Analysis of the PXRD data (both lab and

300 synchrotron) found no evidence for the presence of $CaCO_3$ in quantities detectable

301 by PXRD. As the syntheses were carried out in air, we propose that CO_2 from the

302 atmosphere has dissolved into the solutions during synthesis and suggest this is the

303 source of the carbonate ions. We therefore conclude the carbonate is likely to be

304 structurally incorporated in the Sn and Mn compounds, rather than present as a

305 separate impurity phase. Structural refinement of the synchrotron PXRD data using

306 a thaumasite model confirmed both the Sn and Mn substituted compounds

307 crystallise with a thaumasite-type structure.

308

309 The Mn-substituted phase is a synthetic analogue of the mineral jouravskite and the

310 oxidation state of the Mn in jouravskite is suggested to be 4+ [17]. We therefore

311 suggest the Mn in the synthetic jouravskite phase is also tetravalent. This study

312 suggests that when sources of Ca ions and sulphate anions are in the presence of

313 tetravalent metal cations, thaumasite rather than ettringite-type phases are formed

314 incorporating carbonate into the structure to balance the extra positive charge of the

315 octahedral cation (tetravalent versus trivalent in ettringite).

316

317 The refined unit cell parameters for all the ettringite and thaumasite type phases are

318 plotted against the ionic radii for the octahedral cations and presented in Fig. 5.

319 Included for comparison are the published lattice parameters for ettringite and

320 thaumasite [5,7]. The c parameters for all the thaumasite type-phases have been

14

321 doubled for comparison. This plot shows that as the ionic radii of the octahedral

322 cations increase, the *c* parameter also increases. The refined *a* unit cell parameter

323 shows two trends depending on whether the structure is ettringite or thaumasite-type.

324 The ettringite-type structures (M=Al, Ga, Fe) show a decrease in *a* as the ionic radii

325 increase. Whereas the refined *a* unit cell parameters for the thaumasite-type phases

326 are clustered and are shorter than those of the ettringite-type compounds. This is

327 further evidence that the Mn and Sn phases have a thaumasite-type structure and

328 fits well with previous work on thaumasite-ettringite solid solutions where the *a*

329 parameters of thaumasite members are in the range 11.054-11.11 Å [3,9].

330

331 Structural refinements of the synchrotron PXRD data were only possible through

332 introduction of constraints on the thermal parameters and, in some cases, the atomic

333 positions, as highlighted in the results section. Refinement of the ettringite sample

334 proved to be rather problematic, which was partly due to the data quality, asthe

335 sample was found to be multiphase containing three crystalline impurity phases

336 (Table 2) and a suspected amorphous phase, present as a hump in the dataset

337 around 11° 2θ. Gypsum ($CaSO_4.2H_2O$) is a common degradation product of natural

338 ettringite minerals and this phase was found to be present in the sample. It is likely

339 the sample has degraded between being synthesised and data collection on I11 as

340 the impurity phases were not observed on analysis of the laboratory PXRD data.

341

342 Analysis of the bond lengths shows the Al-O and Ca-O to be within acceptable

343 ranges for such polyhedra, which is confirmed by the bond valence analysis (Table

344 5). The fixed sulphate units have good bond lengths, but the thermal parameters

345 refine to rather high values. This suggests there are issues with the sulphate anions

346 in this structure and it is thought to be due to disorder within the anion column.

347 Further analysis of low temperature data is required to resolve this.

348

349 Refinement of data collected on the Fe substituted sample also produced high

350 thermal parameters of the O atoms which bond to the sulphur atoms, again

351 indicating that there is possible disorder in the anion column. The other issue with

352 this refinement is the highly disordered nature of the Fe1 octahedra, with very short

353 Fe1-O2 bond lengths. Initially it was assumed the Fe^{3+} may be in the high spin state

354 introducing a Jahn-Teller distortion of the Fe1 octahedra; this was not replicated by

355 the Fe2 octahedra, which is much more regular. Again, further analysis of low

356 temperature synchrotron data is required to try and resolve these issues.

357

358 The Ga substituted sample was shown to be single phase and highly crystalline.

359 Refinement of the data collected on this sample was very stable and all constraints

360 could be lifted. The thermal parameters of certain O sites have large errors and this

361 is especially the case for the sulphate anions. Bond valence analysis shows that the

362 Ga and Ca valences are close to their ideal values, but the sulphur ions deviate a lot

363 from the expected 6+. The bond lengths between the S and O atoms of the sulphate

364 anions are somewhat longer than the reported bond lengths for ettringite, but the unit

365 cell is larger and again it is likely that the anion columns are highly disordered.

366

367 Refinement of the datasets collected on the thaumasite-type phases,

368 $Ca_6[M(OH)_6.12H_2O]_2(SO_4)_2(CO_3)_2$, M=Mn, Sn, were carried out using the constraints

369 as detailed in the results section. The Mn-substituted phase has calculated Mn-O

370 and Ca-O bond lengths that are acceptable, which is reinforced by the bond valence

371 analysis (Table 5). Refined parameters from the thaumasite composition

372 $Ca_6[Sn(OH)_6.12H_2O]_2(SO_4)_2(CO_3)_2$ gave calculated C-O bond lengths shorter than

373 those for carbonate in the thaumasite structure and the S-O bond lengths in the

374 basal plane of the sulphate anion are longer than those calculated from the atomic

375 positions for thaumasite as given by Jacobsen et al [8]. Bond valence analysis

376 carried out from the calculated bond lengths show that the carbon atom is slightly

377 over bonded, due the short bond length but the sulphur atom is very underbonded

378 due to these long bond lengths. It is suggested that the anion columns in the

379 thaumasite-type phases are also very disordered and refinement of low temperature

380 data may allow a more stable refinement.

381

382 Table 6 shows details of the range of cation bond lengths and average values

383 determined for each of the phases investigated here. The average cation-oxygen

384 bond lengths are plotted as a function of M cation radius and presented in Fig. 6.

385 The Ca-O bond lengths show very little change as a function of M cation radius,

386 whereas the M-O bond lengths increase as the M cation radius increases, the S-O

387 and C-O bond lengths show no obvious trend as a function of M cation radius.

388

389

390

391

392

5. Conclusions

394

395

Investigations into the formation of new substituted ettringite-type phases, replacing

the octahedral Al cation with other trivalent as well as tetravalent cations has been

carried out. We have successfully synthesised ettringite, Fe-substituted ettringite

and a new Ga-substituted ettringite using a simple precipitation method, whereby a

sucrose solution was used to improve the solubility of CaO and attempt to inhibit the

formation of $CaCO_3$. This method was only partially successful, reducing the amount

of calcite formed, in the case of ettringite and Fe-ettringite and inhibiting its formation

in the case of the Ga, Mn and Sn substituted phases. However, it is evident that

some CO_2 did dissolve into the solutions as, in the presence of tetravalent cations

(Mn^{4+} and Sn^{4+}), the phases formed were thaumasite-type, which have CO_3^{2-} anions

structurally incorporated. . This was confirmed through the presence of a carbonate

stretch in the IR spectra, not observed for the ettringite-type phases. The

incorporation of carbonate into the structure allows for the more positively charged

tetravalent cations to replace Al^{3+} in the ettringite structure, whereby two carbonate

anions replace one sulphate anion and two water molecules. The PXRD data were

also indexed with a thaumasite-type unit cell.

412

18

413   Structural refinements of all the phases were carried out through refinement of high

414   resolution synchrotron powder XRD data. This confirmed that the compositions

415    $Ca_6[M(OH)_6.12H_2O]_2(SO_4)_3.2H_2O$, M= Al, Fe and Ga crystallised with the ettringite

416   structure type and the compositions $Ca_6[M(OH)_6.12H_2O]_2(SO_4)_2(CO_3)_2$, M = Mn, Sn

417   crystallised with the thaumasite type structure.

418

419   Under laboratory conditions, the synthesis of thaumasite is a lengthy process and

420   requires low temperatures (0-5°C) [29]. However, the formation of the Mn and Sn

421   substituted thaumasite phases occurs at room temperature and within 24 hours. It is

422   likely that the Mn and Sn thaumasite phases form more readily than pure thaumasite

423   as these tetravalent cations have large ionic radii and adopt octahedral co-ordination

424   more readily than Si^{4+}, which is more commonly tetrahedrally co-ordinated under

425   ambient pressures.

426

427   As there are still issues with the phase purity of some of the samples and to confirm

428   the thaumasite-type phases will only form in the presence of CO_2, synthesis of all the

429   targeted compositions under N_2 will be attempted. Also, to resolve the issues with

430   some of the structural refinements, low temperature synchrotron powder XRD data

431   has now been collected and refinement of these datasets will be used to test the

432   hypothesis that the anion columns are highly disordered.

433

434   **Acknowledgements**

435

436

444

445

446 **References**

447

448

449 [1] D. McConnel and J. Murdoch, Min. Mag., 33 (1962), pp. 59-64

450 [2] R.A. Edge, H.F.W Taylor, Nature, 224 (1969), pp363-364

451 [3] S.M. Torres, C.A. Kirk, C.J. Lynsdale, R.N. Swamy and J.H. Sharp, Cem. Concr.
452 Res., 34 (2004), pp. 1297-1305

453 [4] S. Diamond, Cem. Concr. Res., 25(8) (2003), pp. 1161-1164

454 [5] A.E. Moore and H.F.W. Taylor, Acta Cryst., B26 (1970), pp. 386-393

455 [6] F. Goetz-Neunhoeffer and J. Neubauer, Powder Diffraction, 21 (2006), pp 4-11

456 [7] R.A. Edge and H.F.W. Taylor, Acta Cryst., B27 (1971), pp. 594-601

457 [8] S.D. Jacobsen, J.R. Smythe and R.J. Swope, Phys. Chem, Mineral., 30 (2003),

458   pp. 321-329

459 [9] S.J. Barnett, C.D. Adam and A.R.W. Jackson, J. Mater. Sci., 35 (2000), pp. 4109-

460   4114

461 [10] E. Tillmanns, W. Gebert and W.H. Baur, J. Solid State Chem., 7 (1973), pp. 69-

462   84

463 [11] H. Poellmann and H.J. Kuzel, Cem. Concr. Res., Cem. Conr. Res., 20 (1990),

464   pp. 941-947

465 [12] H. Poellmann and R. Wenda, Cem. Concr. Res., 23 (1993), pp. 422-430

466 [13] M.L.D. Gougar, B.E. Scheetz and D.M. Roy, Waste Manage., 16(4) (1996), pp.

467   295-303

468 [14] S. Cairns, C.C. Wilson and C.A. Kirk, Structural studies of ettringite-type

469   minerals in the collections of the Natural History Museum, London, unpublished

470   results

471 [15] D.Y.Puschhcarovsky, Y.S. Lebedeva, N.V. Zubovka, M. Pasero, M. Bellezza, S.

472   Merlino and N.V. Chukanov, Can. Mineral., 42 (2004), pp. 723-729

473 [16] P.J. Dunn, D.R. Peacor, P.B. Leavens and J.L. Baum, Am. Mineral., 68 (1983),

474   pp. 1033-1037

475 [17] C. Gaudefroy and F. Permingeat, Soc. Franc. Mineral. Crist, Bull., 88 (1965), pp.

476   254-262

477 [18] S. Merlino and P. Orlandi, Am. Min., 86 (2001), pp. 1293-1301

478   [19] S.J. Barnett, C.D. Adams and A.R.W. Jackson, Cem, Concr. Res., 31 (2001), pp.

479   13-17

480   [20] R. Buhlert and H.-J. Kuzel, ZKG Int., 24 (1971), pp. 83-85

481   [21] H. McMurdie, M. Morris, E. Evans, B. Paretzkin, W. Wong-Ng and Y. Zhang,

482   Powder Diffraction, 2 (1987), p. 44

483   [22] H. Poellmann, H.J. Kuzel and R.Wenda, N. Jb. Miner. Abh., 160 (1989), pp.

484   133-158

485   [23] S.P. Thompson, J.E. Parker, J. Potter, T.P. Hill, A. Birt, T.M. Cobb, F. Yuan, C.C.

486   Tang,Rev. Sci. Instrum., 80 (2009), pp. 075107–075109

487   [24] Topas Academic reference

488   [25] H.F.W. Taylor, Cement Chemistry, Second Edition, Thomas Telford Publishing,

489   London, 1997

490   [26] J. Coates, Interpretation of IR spectra, a practicle approach, Encyclopedia of

491   Chemistry, J. Wiley and Sons Ltd, Chichester, 2000, pp 10815-10837

492   [27] H. Kollmann and G. Strübl, Chem. Erde., 40 (1981), pp. 110-120

493

494   [28] D. Altermatt and I.D. Brown, Acta Cryst. B41 (1985(, pp240-244

495   [29] J. Aguilera, M.T. Blanco-Valera and T. Vazquez, Cem. Concr. Res., 31 (2001),

496   pp. 1163-1168

1 Table Captions

2

3

4 Table 1 Refined unit cell parameters.

5

6 Table 2 Identification of phases present from analysis of synchrotron powder XRD

7 data and weighted R value from Rietveld refinement of data.

8

9 Table 3 Calculated Bond Lengths from Rietveld refinement of data collected on

10 ettringite-type phases; $Ca_6[M(OH)_6.12H_2O]_2(SO_4)_3.2H_2O$, M = Al, Fe, Ga.

11

12 Table 4 Calculated Bond Lengths from Rietveld refinement of data collected on

13 thaumasite-type phases; $Ca_6[M(OH)_6.12H_2O]_2(SO_4)_2(CO_3)_2$, M = Mn, Sn.

14

15 Table 5 Cation valences determined using Bond Valence Analysis [28].

16

17 Table 6 Cation-oxygen bond lengths presented as a range of values (top values) and

18 average value (bottom value) for each ettringite and thaumasite type phase.

19

20   Table ESI1 Refined atomic positions and thermal parameters of

21    $Ca_6[Al(OH)_6.12H_2O]_2(SO_4)_3.2H_2O$, * parameters fixed at values from cif file.

22

23   Table ESI2 Refined atomic positions and thermal parameters of

24    $Ca_6[Fe(OH)_6.12H_2O]_2(SO_4)_3.2H_2O$, * parameters fixed at values from cif file.

25

26   Table ESI3 Refined atomic positions and thermal parameters of

27    $Ca_6[Ga(OH)_6.12H_2O]_2(SO_4)_3.2H_2O$, * parameters fixed at values from cif file.

28

29   Table ESR4 Refined atomic positions and thermal parameters of

30    $Ca_6[Mn(OH)_6.12H_2O]_2(SO_4)_2(CO_3)_2$, * parameters fixed at values from cif file.

31

32   Table ESR5 Refined atomic positions and thermal parameters of

33    $Ca_6[Sn(OH)_6.12H_2O]_2(SO_4)_2(CO_3)_2$, * parameters fixed at values from cif file.

34

35

36   Figure Captions

37

38

39   Fig.1 (a) ab projection of ettringite: $Al(OH)_6$ purple, SO_4^{2-} yellow, Ca blue, O pink (b).

40   Projection of ettringite down [11-20].

41

42   Fig.2 Powder XRD patterns of ettringite-type phases.

43

44   Fig.3 IR spectra of ettringite-type phases, red Al, yellow Fe, purple Ga, green Mn,

45   blue Sn and grey $CaCO_3$.

46

47   Fig. 4 Comparison of ettringite PXRD data with PXRD data collected on thaumasite-

48   type phases.

49

50   Fig. 5 Refined lattice parameters against octahedral cation radii. (a)refined *a*

51   parameter, ■, published ettringite *a* parameter,◇, [5] published thaumasite *a*

52   parameter,◆,[7] (b) refined *c* parameter, ▲, published ettringite *c* parameter, , [5],

53   published thaumasite *c* parameter,● , [7].

54

55   Fig. 6 Average Cation – Oxygen Bond Lengths as a function of cation radius of

56   octahedral site ion. ◇Ca-O,▲M-O,● S-O, **X** C-O.

57

58

59

60   Fig. ESI 1 Final observed (blue), calculated (red) and difference (green) profiles from

61   multiphase Rietveld refinement of $Ca_6[Al(OH)_6.12H_2O]_2(SO_4)_3.2H_2O$.

62

63   Fig. ESI 2 Final observed (blue), calculated (red) and difference (green) profiles from

64   multiphase Rietveld refinement of $Ca_6[Fe(OH)_6.12H_2O]_2(SO_4)_3.2H_2O$.

65

66   Fig. ESI 3 Final observed (blue), calculated (red) and difference (green) profiles from

67   multiphase Rietveld refinement of $Ca_6[Ga(OH)_6.12H_2O]_2(SO_4)_3.2H_2O$.

68

69   Fig. ESI 4 Final observed (blue), calculated (red) and difference (green) profiles

70   from multiphase Rietveld refinement of $Ca_6[Mn(OH)_6.12H_2O]_2(SO_4)_2(CO_3)_2$.

71

72   Fig. ESI 5 Final observed (blue), calculated (red) and difference (green) profiles from

73   multiphase Rietveld refinement of $Ca_6[Sn(OH)_6.12H_2O]_2(SO_4)_2(CO_3)_2$.

74

Table 1.docx

Analogue	Cation radius (Å)	a (Å)	c (Å)
Al	0.535	11.227(3)	21.466(4)
Mn [a]	0.53	11.071(5)	21.156(8)
Ga	0.62	11.202(2)	21.797(3)
Fe	0.645	11.162(3)	22.04(1)
Sn [a]	0.69	11.066(1)	22.420(1)

[a] Refined on thaumasite-type cell in space group . c parameter doubled for comparison to ettringite cell.

Table 2.docx

Composition	Phases present	Rwp
$Ca_6[Al(OH)_6.12H_2O]_2(SO_4)_3.2H_2O$	$Ca_6[Al(OH)_6.12H_2O]_2(SO_4)_3.2H_2O$ + $CaSO_4.2H_2O$ + $Al_2(SO_4)_3.8H_2O$ + $CaCO_3$	8.060
$Ca_6[Fe(OH)_6.12H_2O]_2(SO_4)_3.2H_2O$	$Ca_6[Fe(OH)_6.12H_2O]_2(SO_4)_3.2H_2O$ + $CaSO_4.2H_2O$ + $CaSO_4.0.5H_2O$ + $CaCO_3$	11.724
$Ca_6[Ga(OH)_6.12H_2O]_2(SO_4)_3.2H_2O$	$Ca_6[Ga(OH)_6.12H_2O]_2(SO_4)_3.2H_2O$	10.197
$Ca_6[Mn(OH)_6.12H_2O]_2(SO_4)_2(CO_3)_2$	$Ca_6[Mn(OH)_6.12H_2O]_2(SO_4)_2(CO_3)_2$ + unknown impurity phase	7.005
$Ca_6[Sn(OH)_6.12H_2O]_2(SO_4)_2(CO_3)_2$	$Ca_6[Sn(OH)_6.12H_2O]_2(SO_4)_2(CO_3)_2$ + unknown impurity phase	10.195

Table 3.docx

Cation	O site	Al	Fe	Ga
M1	O1	1.95(4) x3	2.10(6) x3	1.98(5) x3
	O2	1.85(4) x3	1.67(7) x3	1.95(5) x3
M2	O3	2.02(3) x3	1.90(6) x3	1.97(5) x3
	O4	1.81(4) x3	2.43(6) x3	1.96(5) x3
Ca2	O1	2.40(4)	2.42(6)	2.41(5)
	O1	2.50(4)	2.59(6)	2.50(5)
	O3	2.34(4)	2.49(6)	2.42(5)
	O3	2.54(4)	2.54(6)	2.49(5)
	O6	2.51(5)	2.09(7)	2.43(5)
	O8	2.38(5)	2.6(7)	2.52(5)
	O10	2.58(3)	2.27(4)	2.46(4)
	O12	2.51(3)	2.85(3)	2.69(4)
Ca2	O2	2.46(4)	2.20(6)	2.36(5)
	O2	2.49(5)	2.45(5)	2.47(4)
	O4	2.45(4)	2.42(7)	2.47(6)
	O4	2.46(4)	2.66(6)	2.51(5)
	O5	2.60(5)	2.49(7)	2.28(5)
	O7	2.45(6)	2.67(7)	2.63(5)
	O9	2.71(3)	2.72(3)	2.75(2)
	O11	2.76(3)	2.87(2)	2.71(3)
S1	O13	1.72(7)	1.55(1)	1.49(11)
	O16	1.58(2) x3	1.48(6) x3	1.54(5) x3
S2	O14	1.42(8)	1.18(1)	1.42(7)
	O17	1.86(4)x3	1.51(5) x3	1.67(3) x3

| S3 | O15 | 1.59(7) | 1.58(1) | 1.58(9) |
| | O18 | 1.41(2) x3 | 1.80(6) x3 | 1.51(3) x3 |

Table 4.docx

Cation	O site	Mn	Sn
M1	O7	1.94(3) x3	2.16(2) x3
	O8	1.91(3) x3	1.89(2) x3
Ca1	O1	2.49(3)	2.48(2)
	O2	2.53(3)	2.56(2)
	O3	2.32(3)	2.42(3)
	O4	2.48(3)	2.51(3)
	O7	2.68(4)	2.57(3)
	O7	2.73(4)	2.66(3)
	O8	2.22(4)	2.40(3)
	O8	2.23(4)	2.45(3)
S1	O6	1.70(2) x3	1.72(2) x3
	O9	1.47(3)	1.45(4)
C1	O5	1.29 x3 (fixed)	1.24(2) x3

Cation	O site	Mn	Sn
M1	O7	1.94(3) x3	2.16(2) x3
	O8	1.91(3) x3	1.89(2) x3
Ca1	O1	2.49(3)	2.48(2)

Table 5.docx

Octahedral cation	M1	M2	Ca1	Ca2	S1	S2	S3	C1
Al [5]	3.23	3.33	2.34	2.01	5.82	5.92	5.9	
Al	2.69	3.24	1.82	2.13	5.84	5.87	5.84	
Fe	4.15	2.81	2.17	2.07	5.71	5.83	5.67	
Ga	3.18	3.18	1.99	1.94	5.2	4.39	5.2	
Mn	3.77		2.36		3.96			3.93
Sn	4.63		1.91		3.9			4.5

Table 6.docx

	Al	Fe	Ga	Mn	Sn
Ca1-O	2.38-2.78	2.31-2.92	2.41-2.69	2.22-2.73	2.40-2.66
	2.54	2.52	2.49	2.46	2.51
Ca2-O	2.33-2.62	2.32-2.79	2.36-2.75		
	2.47	2.51	2.52		
M1-O	1.82-2.05	1.73-2.2	1.95-1.98	1.91-1.94	1.89-2.16
	1.94	1.97	1.97	1.93	2.03
M2-O	1.74-2.00	2.01-2.07	1.96-1.97		
	1.87	2.04	1.97		
S1-O	1.44-1.50	1.47-1.50	1.49-1.54	1.47-1.70	1.45-1.72
	1.49	1.49	1.53	1.64	1.65
S2-O	1.46-1.49	1.48-1.50	1.42-1.67		
	1.48	1.5	1.61		
S3-O	1.44-1.50	1.28-1.50	1.51-1.58		
	1.49	1.5	1.53		
C1-O				1.29	1.24
				1.29	1.24

site	x	y	z	occupancy	beq
Al1	0	0	0	1	1.4(4)
Al2	0	0	0.25	1	0.9(4)
Ca1	0.002(1)	0.812(1)	0.8697(8)	1	1.6(2)
Ca2	0.997(1)	0.191(1)	0.1195(8)	1	1.5(2)
O1	1.004(3)	0.153(2)	0.938(1)	1	1.67(8)
O2	0.001(4)	0.862(3)	0.050(1)	1	1.67(8)
O3	1.001(2)	0.133(2)	0.793(1)	1	1.67(8)
O4	-0.001(3)	0.876(2)	0.186(2)	1	1.67(8)
O5	1.008(3)	0.345(3)	0.044(2)	1	1.67(8)
O6	0.006(2)	0.645(2)	0.950(1)	1	1.67(8)
O7	0.012(2)	0.360(2)	0.197(1)	1	1.67(8)
O8	0.988(2)	0.644(2)	0.778(1)	1	1.67(8)
O9	0.236(2)	0.394(2)	0.621(1)	1	1.67(8)
O10	0.726(2)	0.620(2)	0.369(1)	1	1.67(8)
O11	0.248(2)	0.400(2)	0.134(1)	1	1.67(8)
O12	0.751(2)	0.589(2)	0.852(1)	1	1.67(8)
O13	0.33333	0.66667	0.425*	1	8.5(2)
O14	0.33333	0.66667	0.819*	1	8.5(2)
O15	0.33333	0.66667	0.076	1	8.5(2)
O16	0.195	0.628	0.519	1	8.5(2)
O17	0.195*	0.620*	0.724*	1	8.5(2)
O18	0.192*	0.585*	0.982*	1	8.5(2)
O19	0.227*	0.685*	0.243*	0.667	1.6(1)
S1	0.33333	0.66667	0.492*	1	2.5(1)
S2	0.33333	0.66667	0.751*	1	2.5(1)
S3	0.33333	0.66667	0.009*	1	2.5(1)

site	x	y	z	occupancy	beq
Fe1	0	0	0.007(2)	1	1.7(4)
Fe2	0	0	0.249(1)	1	1.0(4)
Ca1	0.017(1)	0.818(1)	0.877(1)	1	1.1(4)
Ca2	0.990(2)	0.190(2)	0.122(1)	1	1.2(4)
O1	0.999(4)	0.156(3)	0.946(2)	1	1.1(2)
O2	0.012(5)	0.888(4)	0.057(2)	1	1.1(2)
O3	0.983(4)	0.132(4)	0.805(2)	1	1.1(2)
O4	0.001(4)	0.854(4)	0.191(2)	1	1.1(2)
O5	0.994(5)	0.335(5)	0.038(3)	1	2.5(2)
O6	0.004(4)	0.666(4)	0.953(2)	1	2.5(2)
O7	-0.004(5)	0.353(4)	0.197(2)	1	2.5(2)
O8	0.995(4)	0.650(4)	0.789(2)	1	2.5(2)
O9	0.284(3)	0.414(3)	0.620(2)	1	2.5(2)
O10	0.767(3)	0.605(3)	0.370(2)	1	2.5(2)
O11	0.239(3)	0.411(5)	0.135(2)	1	2.5(2)
O12	0.739(4)	0.583(5)	0.860(2)	1	2.5(2)
O13	0.33333	0.66667	0.425*	1	7.9(5)
O14	0.33333	0.66667	0.819*	1	7.9(5)
O15	0.33333	0.66667	0.076	1	7.9(5)
O16	0.195	0.628	0.519	1	7.9(5)
O17	0.195*	0.620*	0.724*	1	7.9(5)
O18	0.192*	0.585*	0.982*	1	7.9(5)
O19	0.209(3)	0.661(4)	0.240(2)	0.667	1.0*
S1	0.33333	0.66667	0.492*	1	2.0(2)
S2	0.33333	0.66667	0.751*	1	2.0(2)
S3	0.33333	0.66667	0.009*	1	2.0(2)

site	x	y	z	occupancy	beq
Ga1	0	0	0	1	1.4(2)
Ga2	0	0	0.25	1	1.0(2)
Ca1	0.006(2)	0.811(2)	0.876(1)	1	2.6(3)
Ca2	0.989(1)	0.189(1)	0.1228(8)	1	1.0(2)
O1	1.001(4)	0.142(5)	0.946(2)	1	1.9(9)
O2	0.000(5)	0.864(4)	0.056(2)	1	0.9(9)
O3	0.999(4)	0.138(5)	0.806(2)	1	1.4(9)
O4	0.004(5)	0.864(4)	0.195(2)	1	1.9(9)
O5	0.992(5)	0.332(5)	0.048(2)	1	2.6(9)
O6	0.003(5)	0.670(3)	0.961(2)	1	2.0(8)
O7	0.013(4)	0.353(4)	0.214(2)	1	3.3(9)
O8	0.991(4)	0.634(3)	0.801(2)	1	2.4(7)
O9	0.279(2)	0.412(2)	0.628(2)	1	3.0(7)
O10	0.763(3)	0.599(3)	0.376(2)	1	1.6(8)
O11	0.253(3)	0.397(3)	0.135(2)	1	3.6(1.0)
O12	0.756(4)	0.585(3)	0.861(2)	1	2.3(1.0)
O13	0.33333	0.66667	0.423(5)	1	6.5(3.2)
O14	0.33333	0.66667	0.814(2)	1	5.2(1.8)
O15	0.33333	0.66667	0.077(4)	1	4.6(2.4)
O16	0.195(4)	0.637(5)	0.520(2)	1	5.1(1.2)
O17	0.177(2)	0.634(4)	0.725(2)	1	6.9(1.2)
O18	0.185(3)	0.588(4)	0.983(2)	1	4.8(1.0)
O19	0.230(3)	0.647(5)	0.247(3)	0.667	5.7(1.2)
S1	0.33333	0.66667	0.491(1)	1	1.8(1.0)
S2	0.33333	0.66667	0.749(2)	1	1.5(5)
S3	0.33333	0.66667	0.005(2)	1	2.4(9)

site	x	y	z	occupancy	beq
Ca1	0.197(1)	0.996(2)	0.267(2)	1	3.2(2)
Mn1	0	0	0.004(2)	1	4.6(3)
C1	0.33333	0.66667	0.4623*	1	1*
S1	0.33333	0.66667	0.98382*	1	0.2(4)
O1	0.398(3)	0.234(4)	0.227(3)	1	1.4(2)
O2	0.248(3)	0.406(3)	0.252(4)	1	1.4(2)
O3	-0.014(3)	0.299(2)	0.079(2)	1	1.4(2)
O4	0.022(3)	0.361(2)	0.439(3)	1	1.4(2)
O5	0.20088	0.623	0.45809	1	1.4(2)
O6	0.174(2)	0.624(2)	0.041(2)	1	1.4(2)
O7	0.152(3)	0.152(3)	0.096(3)	1	1.4(2)
O8	0.120(3)	0.118(3)	0.374(2)	1	1.4(2)
O9	0.33333	0.66667	0.845(3)	1	1.4(2)

site	x	y	z	occupancy	beq
Ca1	0.2104(7)	1.006(1)	0.209(2)	1	1.83(9)
Sn1	0	0	-0.044(2)	1	1.61(5)
C1	0.33333	0.66667	0.485(2)	1	1*
S1	0.33333	0.66667	0.945(2)	1	1*
O1	0.420(2)	0.240(2)	0.184(2)	1	1.4(2)
O2	0.246(2)	0.407(2)	0.208(3)	1	1.4(2)
O3	-0.024(2)	0.336(2)	0.044(2)	1	1.4(2)
O4	0.009(2)	0.345(2)	0.389(2)	1	1.4(2)
O5	0.2394(8)	0.641(2)	0.413(1)	1	1*
O6	0.172(1)	0.625(2)	0.0003(8)	1	5.6(5)
O7	0.159(2)	0.158(2)	0.068(2)	1	0.7(2)
O8	0.113(2)	0.120(2)	0.333(2)	1	0.7(2)
O9	0.33333	0.66667	0.816(3)	1	5.6(5)

Transmittance

CaCO₃
Sn-ett
Mn-ett
Ga-ett
Fe-ett
Al-ett

cm⁻¹

Key:
black sticks: [41-1451] Ettringite
* Si internal standard

Mn *

Sn

Ga

Fe

$Ca_6[Al(OH)_6 \cdot 12H_2O]_2(SO_4)_3 \cdot 2H_2O$

Transmittance

Highlights

- A new ettringite-type phase, $Ca_6[Ga(OH)_6.12H_2O]_2(SO_4)_3.2H_2O$ is reported.

- Two new thaumasite phases, $Ca_6[M(OH)_6.12H_2O]_2(SO_4)_2(CO_3)_2$, M = Mn, Sn are reported.

- We highlight the preference of tetravalent cations to form thaumasite-type phases.