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$620^\circ C$

$2\text{MnSO}_4 + \text{Na}_6\text{[Al}_6\text{Si}_6\text{O}_{24}] \rightarrow \text{Na}_6\text{Mn}_2\text{[Al}_6\text{Si}_6\text{O}_{24]}(\text{SO}_4)_2$

Versus: $2\text{MnSO}_4(s) \rightleftharpoons \text{Mn}_2\text{O}_3(s) + \text{SO}_3(g) + \text{SO}_2(g)$
On the thermal stability of manganese(II) sulfate and its reaction with zeolite A to form the sodalite Na$_6$Mn$_2$[Al$_6$Si$_6$O$_{24}$](SO$_4$)$_2$

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ABSTRACT

Thermal gravimetric analysis and in situ high-temperature powder X-ray diffraction (HT-PXRD) revealed that MnSO$_4$ begins to thermally decompose under air at $\sim$625 °C, which is significantly lower than the values reported in the literature. The reaction is kinetically sluggish and yields bixbyite, Mn$_2$O$_3$, $\geq$625 °C and hausmannite, Mn$_3$O$_4$, $\geq$850 °C. Na$_6$Mn$_2$[Al$_6$Si$_6$O$_{24}$](SO$_4$)$_2$ was prepared as a novel sodalite-type phase by reacting zeolite A, Na$_6$[Al$_6$Si$_6$O$_{24}$], with MnSO$_4$ as a compacted mixed-powder monolith at 650 °C under air. In situ HT-PXRD indicated that this reaction commenced at about 620 °C. Rietveld refinement of the PXRD data recorded at 20 °C showed that Na$_6$Mn$_2$[Al$_6$Si$_6$O$_{24}$](SO$_4$)$_2$ crystallizes with a cubic cell, $a = 0.89780(2)$ nm, and is isostructural (I43m) with the mineral haüyne, Na$_6$Ca$_2$[Al$_6$Si$_6$O$_{24}$](SO$_4$)$_2$. The product material contained traces of Mn$_2$O$_3$ which imparts a purplish-brown coloration; highlighting the problem of preparing Na$_6$Mn$_2$[Al$_6$Si$_6$O$_{24}$](SO$_4$)$_2$ as a monophasic material within the narrow temperature ‘window’ available for this reaction.

Highlights:
• Na$_6$Mn$_2$[Al$_6$Si$_6$O$_{24}$](SO$_4$)$_2$ was prepared as a novel manganese(II) analogue of haüyne.
• Na$_6$Mn$_2$[Al$_6$Si$_6$O$_{24}$][SO$_4$]$_2$ has a cubic unit cell parameter $a = 0.89780(2)$ nm.
• Thermal decomposition of MnSO$_4$ in air occurs $\geq$ 625 °C and is kinetically sluggish.
• Optimal temperature for reacting zeolite A with MnSO$_4$ under air is about 620 °C.

Keywords: zeolite A; manganese sulfate; sodalite; synthesis; thermal stability; crystal structure
1. Introduction

Sodalite, Na$_8$[Al$_6$Si$_6$O$_{24}$]Cl$_2$, is a rock forming tectosilicate mineral which in its pure and idealised form is colourless and photo-inactive. It crystallizes in a cubic system and has a characteristic aluminosilicate cage-like structure that is also a feature of certain zeolites, such as, zeolites A, X and Y [1–3]. In the case of sodalite, ordering among the Al and Si atoms generates a primitive cubic cell (space group P$\overline{4}3n$) [4], whereas the disordered analogue can be described by a body-centred cubic cell (space group I$\overline{4}3m$) [5].

The sodalite structure can accommodate a wide variety of chemical substitutions involving both intra- and extra-framework anions and cations, including complex ions, in addition to various Al/Si ratios within the framework structure [5–7]. Certain extra-framework substitutions result in coloured or photoactive materials that are of technological interest. For example, the rare mineral lazurite, (Na,Ca)$_8$[Al$_6$Si$_6$O$_{24}$](Cl,SO$_4$,S)$_{2-\delta}$, and its artificial analogue, ultramarine, exhibit an intense blue coloration due to a high concentration of the S$_3^-$ radical anion chromophore and are thus used as pigments [8]. Hackmanite, with a typical composition Na$_8$[Al$_6$Si$_6$O$_{24}$]Cl$_{1.8}$S$_{0.1}$, is the popular name given to a photochromic variety of sodalite that changes reversibly from colourless to magenta under 254 nm UV irradiation and is bleached under visible light, in which divalent monosulfide S$^{2-}$ ions partially substitute for pairs of Cl$^-$ ions [9–11]. The partially oxidized derivative, Na$_8$[Al$_6$Si$_6$O$_{24}$]Cl$_{2-2(\alpha+\gamma)}$S$_x$(SO$_4$)$_y$, can be viewed as a solid-solution between sodalite, Na$_8$[Al$_6$Si$_6$O$_{24}$]Cl$_2$, sulfosodalite, Na$_8$[Al$_6$Si$_6$O$_{24}$]S, and nosean, Na$_8$[Al$_6$Si$_6$O$_{24}$]SO$_4$, in which the S$^{2-}$ and SO$_4^{2-}$ ions, together with the respective anion vacancies, are randomly distributed among the chloride sites, that enables this form of sodalite to emit a bright orange-yellow luminescence under violet light (i.e., 400 nm irradiation) [10]. The promise of modifying or discovering further photoactive properties is our driving force for exploring substitutional chemistry in these sodalite materials.
Many sodalites can be considered as pseudo-binary phases. For example, sodalite, nosean and haüyne can be expressed by the formulae, 2NaCl·6NaAlSiO₄, Na₂SO₄·6NaAlSiO₄ and 2CaSO₄·6NaAlSiO₄, respectively; and more complex varieties, such as, hackmanite can be expressed as the pseudo-ternary phase, 1.8NaCl·0.1Na₂S·6NaAlSiO₄. This aspect offers the possibility of preparing them by simple additive reactions at high temperature; e.g., 6NaAlSiO₄ + 2NaCl → Na₈[Al₆Si₆O₂₄]Cl₂. In some syntheses, nepheline can serve as a convenient source of the NaAlSiO₄ component, or alternatively, a calcined equimolar mixture of Na₂CO₃ and kaolinite, Al₂Si₂O₅(OH)₄. However, the use of zeolite A, Na₆[Al₆Si₆O₂₄], has one definite advantage in that it has an open-framework structure that closely resembles the product sodalite [6–7], [11–14]. Thus, during the reaction, zeolite A needs to undergo only a comparatively minor structural conversion in which some of the structural building blocks (e.g., β-cages or half-cages) are maintained and reconnected, as guided by the ions from the added salt (NaCl, Na₂SO₄ etc.), to form the sodalite framework. Therefore, the use of zeolite A allows the synthesis to be performed at a lower temperature than that demanded by other educts, thus enabling the preparation of certain sodalites that would otherwise be unstable under the refractory conditions imposed by conventional solid-state routes. For example, Na₆Zn₂[Al₆Si₆O₂₄](SO₄)₂, which can be considered as a zinc analogue of haüyne, is unstable above 700 °C, but can be prepared by reacting zeolite A with ZnSO₄ at 700 °C, as reported by one of us (Warner) elsewhere [15].

The recent discovery of Na₆Zn₂[Al₆Si₆O₂₄](SO₄)₂ led us to consider whether the manganese(II) analogue Na₆Mn₂[Al₆Si₆O₂₄](SO₄)₂ might exist. Inspiration was drawn from the occurrence of a solid-solution between helvite, Mn₈[Be₆Si₆O₂₄]S₂, and genthelvite, Zn₈[Be₆Si₆O₂₄]S₂ (minerals in the sodalite group), in which the Mn²⁺ and Zn²⁺ ions occupy all the sodium-sites in the sodalite structure [16]; and from the fact that Mn²⁺ ions are known to partially substitute for tetrahedrally coordinated Zn²⁺ ions in willemite, Zn₂SiO₄. However, the fully substituted end-member, Mn₆SiO₄,
adopts the olivine structure in which the Mn\textsuperscript{2+} ions are \textit{octahedrally} coordinated, indicating that
the incorporation of tetrahedrally coordinated Mn\textsuperscript{2+} ions in \textquotedblright Na\textsubscript{6}Mn\textsubscript{2}[Al\textsubscript{6}Si\textsubscript{6}O\textsubscript{24}](SO\textsubscript{4})\textsubscript{2} \textquotedblright cannot be
presumed; and so we conducted experiments to verify that Mn\textsuperscript{2+} ions can fully substitute for the
Ca\textsuperscript{2+} ions in haüyne.

Our initial attempts at preparing Na\textsubscript{6}Mn\textsubscript{2}[Al\textsubscript{6}Si\textsubscript{6}O\textsubscript{24}](SO\textsubscript{4})\textsubscript{2} by reacting zeolite A,
Na\textsubscript{6}[Al\textsubscript{6}Si\textsubscript{6}O\textsubscript{24}].2.2H\textsubscript{2}O, with MnSO\textsubscript{4}.H\textsubscript{2}O at 700 °C resulted in a mixture of Mn\textsubscript{2}O\textsubscript{3} and unreacted
zeolite A, with only minor amounts of Na\textsubscript{6}Mn\textsubscript{2}[Al\textsubscript{6}Si\textsubscript{6}O\textsubscript{24}](SO\textsubscript{4})\textsubscript{2}, identified retrospectively; thus
indicating that MnSO\textsubscript{4}.H\textsubscript{2}O had preferentially decomposed into Mn\textsubscript{2}O\textsubscript{3} rather than reacting with
zeolite A to form the desired sodalite. Since MnSO\textsubscript{4} is reported to be stable under air at 750 °C
[17–19], we had not anticipated its decomposition under our synthesis conditions at 700 °C.
Therefore, we conducted a systematic study of the thermal stability of manganese(II) sulfate
monohydrate, MnSO\textsubscript{4}.H\textsubscript{2}O, using thermal gravimetric analysis (TGA) and \textit{in situ} high-temperature
powder X-ray diffraction (HT-PXRD). We also performed \textit{in situ} HT-PXRD on a sample of zeolite A
up to 800 °C, since similar measurements by Musyoko \textit{et al.} [20] were recorded to only 440 °C. We
also recorded the reaction profile for a mixture of MnSO\textsubscript{4}.H\textsubscript{2}O and zeolite A using \textit{in situ} HT-PXRD,
to find the optimal temperature to conduct the synthesis of Na\textsubscript{6}Mn\textsubscript{2}[Al\textsubscript{6}Si\textsubscript{6}O\textsubscript{24}](SO\textsubscript{4})\textsubscript{2}. These
results, together with our attempts at preparing Na\textsubscript{6}Mn\textsubscript{2}[Al\textsubscript{6}Si\textsubscript{6}O\textsubscript{24}](SO\textsubscript{4})\textsubscript{2} as a monophasic
material, are presented in this present paper.

2. Experimental

2.1. Thermogravimetric analysis

Thermogravimetric analysis (TGA) were performed on samples of MnSO\textsubscript{4}.H\textsubscript{2}O (Sigma Aldrich,
\textsubscript{\geq} 99\%) with a typical mass of about 15–20 mg using a NETZSCH STA 449F3 analyser. The samples
were held inside an alumina crucible under an atmosphere of artificial air (P\textsubscript{O\textsubscript{2}} = 0.2 bar and P\textsubscript{N\textsubscript{2}} =
0.8 bar) with a total flow rate = 50 mL/min and heated from room temperature to 1100 °C at the various rates: 0.25 °C/min; 0.5 °C/min; 1 °C/min; 2 °C/min; 5 °C/min; and 10 °C/min.

2.2. Powder X-ray diffractometry

The product materials were analysed by PXRD using a Panalytical X’pert PRO MPD diffractometer with Cu-\(K_{\alpha}\) radiation. High-score Plus software was used to strip reflections attributed to Cu-\(K_{\alpha2}\) radiation. Polycrystalline silicon was used as an external standard for aligning the instrument.

In situ HT-PXRD was performed on samples of manganese(II) sulfate monohydrate, MnSO\(_4\)·H\(_2\)O (Sigma Aldrich, ≥ 99.9%); zeolite A, Na\(_6\)Al\(_6\)Si\(_6\)O\(_{24}\)·2.2H\(_2\)O (molecular sieves 4A, Sigma Aldrich, 325 mesh) used as supplied; and a powder mixture of MnSO\(_4\)·H\(_2\)O and zeolite A, Na\(_6\)Al\(_6\)Si\(_6\)O\(_{24}\)·2.2H\(_2\)O, in the molar ratio 2:1, respectively, using an Anton Paar HTK1200 high-temperature stage in flat powder bed mode. The heating and data-collection profile involved recording the initial pattern at 30 °C, followed by heating at a rate of 5°C/min to the next temperature step with a dwell time of 55 minutes, whereupon the PXRD pattern was recorded during the final 10 minutes, before heating the sample to the next temperature step, etc.

2.3. Synthesis of Na\(_6\)Mn\(_2\)[Al\(_6\)Si\(_6\)O\(_{24}\)](SO\(_4\))\(_2\)

Taking into consideration the results of the TGA and HT-PXRD as reported further below, the following procedure was found to be a reliable and effective method for producing a 20-g sample of Na\(_6\)Mn\(_2\)[Al\(_6\)Si\(_6\)O\(_{24}\)](SO\(_4\))\(_2\). Firstly, the zeolitic water content of the zeolite A (Sigma Aldrich, 325 mesh) was determined by TGA as Na\(_6\)Al\(_6\)Si\(_6\)O\(_{24}\)·2.2H\(_2\)O. Appropriate amounts of MnSO\(_4\)·H\(_2\)O (Sigma-Aldrich ≥ 99.9%) and zeolite A, Na\(_6\)Al\(_6\)Si\(_6\)O\(_{24}\)·2.2H\(_2\)O in the molar ratio 2:1, respectively, were ground together using a Fritsch planetary monomill Pulverisette 6 with 50 x 10 mm diameter
zirconia balls in a 250-mL zirconia vial at a rotation of 400 rpm for 30 min, with cyclohexane as the
counterpart. The resulting slurry was placed in a Petri-dish and left to evaporate in a fume
cupboard overnight before dehydrating the contents in an electric oven at 250 °C for 20 h. This
procedure was adopted here since preliminary experiments indicated that a higher yield of the
target compound was achieved through reacting the reagents in their anhydrous form. PXRD
confirmed the presence of anhydrous MnSO₄ and zeolite A. This anhydrous powder mixture was
compacted into monoliths using a 32-mm diameter Specac stainless steel die and a uniaxial press
under a load of 10 tonnes. The monoliths were then placed on top of a sacrificial powder bed of
anhydrous MnSO₄ in a small alumina crucible (CC47 Almath Ltd) with a matching lid. Recrystallized
alumina crucibles were considered inert under these conditions, thus avoiding the need for a
platinum crucible. This procedure was devised to create a stagnant atmosphere to limit the loss of
SO₂ from the system. This crucible was in turn placed on top of a powder bed of anhydrous CuSO₄
inside a slightly larger alumina crucible (CC62 Almath Ltd) with its matching lid secured. CuSO₄ is
reported to thermally decompose at 600 °C yielding CuO and SO₃(g) [17], [21], and so was used
here to create an atmosphere sufficiently rich in SO₂/SO₃ to help retard the thermal
decomposition of the MnSO₄ in the inner crucible. This was then placed in a preheated chamber
furnace (Lenton UAF15/10) at 650 °C, and held there for 24 h before cooling to room temperature
at a rate of 200°C/h. The product material was removed from the alumina crucible and analysed
by PXRD.

2.4 Rietveld refinement

Rietveld refinement of the PXRD data was performed using the software package, FullProf
Suite [22]. The structure of Na₆Ca₂[Al₆Si₆O₂₄](SO₄)₂ (space group I₄ 3m, ICSD data base No. 28479)
[5] was used as the starting model with Ca exchanged for Mn, i.e., Na₆Mn₂[Al₆Si₆O₂₄](SO₄)₂. The
following parameters were refined: Scale factor, cell parameter, profile parameters (W, X, U, V and
shape), atomic positions, isotropic atomic displacement parameters, background, and zero-shift. The atomic positions and displacement parameters were kept identical for Na and Mn as well as for Al and Si. The atomic displacement of the sulfate was refined as one rigid unit. Note that occupancies were fixed to the stoichiometry of Na₆Mn₂[Al₆Si₆O₂₄](SO₄)₂. The background was described using linear interpolation between manually selected background points, and the peak shapes were fitted using a Pseudo-Voigt profile function. The resulting agreement parameters (not corrected for background) are $R_p = 8.77\%$, $R_{wp} = 12.0\%$, $R_{Bragg} = 15.3\%$, $R_{exp} = 4.14\%$ and $\chi^2 = 10.8$.

3. Results and discussion

The thermogravimetric analysis of MnSO₄·H₂O under artificial air for various heating rates is shown in Fig. 1. The loss in mass of 9.0% over the temperature range 200–300 °C is attributed to the removal of 1 mole of H₂O of crystallization, with the formation of anhydrous MnSO₄. The further loss in mass of 49.8% (w.r.t. anhydrous MnSO₄) over the temperature range 625–1000 °C, is attributed to the thermal decomposition of MnSO₄ with the eventual formation of Mn₃O₄ as the final solid residue at 1000 °C; see reaction (1). The TGA profiles for the low heating rates (0.25 °C/min and 0.5 °C/min) show a slightly lower loss in mass of 48.2% (w.r.t. anhydrous MnSO₄) at about 840 °C, which is attributed to the formation of Mn₂O₃ as an intermediate phase before it undergoes further reduction to Mn₃O₄ at temperatures $\geq$850 °C as concluded above. The phase changes attributed to these mass losses are consistent with the conclusions of Hammerschmidt and Wrobel [18] and Su et al. [19] regarding this system, although the temperatures for these phase transitions differ for the reasons discussed further below.

$$3\text{MnSO}_4(s) \rightleftharpoons \text{Mn}_3\text{O}_4(s) + 2\text{SO}_3(g) + \text{SO}_2(g)$$ (1)
Note that the equilibrium partial pressures, $P_{SO_2}$ and $P_{SO_3}$ in reaction (1) are interrelated to $P_{O_2}$ through the equilibrium reaction, $SO_3(g) \rightleftharpoons SO_2(g) + \frac{1}{2}O_2(g)$, in which the forward reaction is favoured at high temperature; see Stern and Weise [23] for further details regarding this matter.

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**Fig. 1.** Thermogravimetric analysis of MnSO$_4$·H$_2$O under artificial air ($P_{O_2} = 0.2$ bar, $P_{N_2} = 0.8$ bar) for various heating rates: (a) 0.25 °C/min; (b) 0.5 °C/min; (c) 1 °C/min; (d) 2 °C/min; (e) 5 °C/min; (f) 10 °C/min.

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**Fig. 2.** Correlation of the on-set temperature (as defined in the text) for the thermal decomposition of anhydrous MnSO$_4$ under artificial air as a function of heating rate.
The on-set temperature for reaction (1) was defined here as the temperature in the TGA profile at which a loss in mass of 0.5% of the anhydrous MnSO$_4$ occurred. The on-set temperature was found to be dependent on the heating rate (see Figs. 1 and 2), indicating that this reaction is kinetically sluggish under these conditions. Ostroff and Sanderson [17] performed TGA on a sample of MnSO$_4$ using a heating rate of 9 °C/min with a nitrogen gas flow rate of 84 mL/min, and obtained a decomposition temperature of 755 °C which fits well with our data in Fig. 2. Hammerschmidt and Wrobel [18] obtained a similar temperature of 750 °C using a heating rate of 10 °C/min with a nitrogen gas flow rate of 200 mL/min. Fig. 2 reveals a progressive decrease in the onset-temperature with decreasing heating rate, which appears to accelerate at lower heating rates. Extrapolating the data in the lower range (1−0.25 °C/min) to an infinitely low heating rate (0 °C/min), yields a limiting or minimal decomposition temperature of about 625 °C.

The HT-PXRD patterns in Fig. 3 show that MnSO$_4$·H$_2$O dehydrated during the early stage of the heating process, and was transformed into the high-temperature polymorph, β-MnSO$_4$ by 650 °C. Upon further heating, β-MnSO$_4$ began to decompose into bixbyite, Mn$_2$O$_3$, at about 660 °C, as described by reaction (2). However, under the conditions of this experiment, this reaction is apparently complete only at 710 °C; which is consistent with the slow kinetics inferred by the above TGA results. These measurements were terminated at 750 °C, whereby the reduction of Mn$_2$O$_3$ to Mn$_3$O$_4$ had not yet occurred; which is in agreement with the findings by Su et al. [19].

$$2\text{MnSO}_4(s) \rightleftharpoons \text{Mn}_2\text{O}_3(s) + \text{SO}_3(g) + \text{SO}_2(g)$$

Although the $P_{O_2}$ in the prevailing atmosphere surrounding the sample of MnSO$_4$ is assumed to be 0.2 bar, the $P_{SO_3}$ and $P_{SO_2}$ are unspecified, and, therefore, likely to vary during the reaction, as governed by the rate of their evolution and subsequent expulsion by the carrier gas in the
In an instrument. Nevertheless, adopting the thermodynamic data from the *HSC Chemistry*® software (Version 4.1, Outokumpo Research Oy, Finland), the minimal on-set decomposition temperature of 625 °C would correspond to a $P_{SO_3}$ of $1.5 \times 10^{-4}$ bar and a $P_{SO_2}$ of $5 \times 10^{-5}$ bar, in which the $P_{O_2}$ is fixed at 0.21 bar (see Supplementary data), if our MnSO$_4$/air system were to be regarded as being in a state of pseudo-equilibrium. However, since the reactor inside the TGA instrument is essentially an open system, any condition that facilitates the expulsion of SO$_3$/SO$_2$, such as a high flow rate of the carrier gas, should tend to lower the decomposition temperature for reactions (1) and (2). The value of 625 °C is therefore a kinetically derived parameter with a practical significance in that MnSO$_4$ should be preserved below this temperature, so long as a $P_{SO_3}$ greater than $1.4 \times 10^{-4}$ bar and a $P_{SO_2}$ greater than $5 \times 10^{-5}$ bar can be maintained in the surrounding atmosphere in which the $P_{O_2}$ is 0.21 bar (viz. air).

**Fig. 3.** In situ HT-PXRD patterns (Cu-K$_{\alpha1}$) of MnSO$_4$·H$_2$O heated step-wise under air from 30 °C to 720 °C with temperature intervals as shown. Patterns at 730 °C, 740 °C and 750 °C were essentially the same as at 720 °C and therefore not shown. JCPDS 33-906 for MnSO$_4$·H$_2$O (filled circles); JCPDS 29-898 for β-MnSO$_4$ (open squares); and JCPDS 78-390 for Mn$_2$O$_3$ (filled squares).

--- 2 column fitting image ---
Fig. 4. *In situ* HT-PXRD patterns (Cu-Kα) of zeolite A, Na₆[Al₆Si₆O₂₄]·2.2H₂O, heated step-wise under air from 30 °C to 800 °C with temperature intervals as shown. JCPDS 76-6495 for zeolite A (open squares); and JCPDS 52-1342 for low-carnegieite, NaAl₂SiO₄ (filled diamonds).

Fig. 5. *In situ* HT-PXRD patterns (Cu-Kα) of a mixture of manganese(II) sulfate monohydrate, MnSO₄·H₂O, and partially hydrtaed zeolite A, Na₆[Al₆Si₆O₂₄]·2.2H₂O in the molar ratio 2:1 heated step-wise under air from 30 °C to 650 °C with temperature intervals as shown (see Section 2.2). Then held at 650 °C with patterns a–g recorded sequentially at 1 h intervals. Na₆Mn₂[Al₆Si₆O₂₄](SO₄)₂ (filled circles); JCPDS 75-6495 for zeolite A (open squares); and JCPDS 78-390 for Mn₂O₃ (filled squares).
Fig. 4 shows that zeolite A is thermally stable up to at least 700 °C, but undergoes a structural transformation to low-carnegieite above 700 °C which is almost complete by 800 °C. This is consistent with the work by Mala et al. [24] in which their PXRD pattern for a calcined sample of zeolite A showed a significant reduction in peak intensities for zeolite A at 800 °C. This indicates that zeolite A should be capable of acting as an educt for the intended synthesis up to at least 700 °C.

$$\text{Na}_6[\text{Al}_{16}\text{Si}_{16}\text{O}_{24}] + 2\text{MnSO}_4 \rightarrow \text{Na}_6\text{Mn}_2[\text{Al}_{16}\text{Si}_{16}\text{O}_{24}](\text{SO}_4)_2 \quad \ldots \quad (3)$$

Fig 5. shows that the reaction between zeolite A and MnSO$_4$ (in the form of a loosely compacted powder bed) to produce Na$_6$Mn$_2$[Al$_{16}$Si$_{16}$O$_{24}$](SO$_4$)$_2$ commences at about 620 °C and has progressed significantly by 650 °C (see reaction 3). Although the product material after a further 6 h at 650 °C comprises Na$_6$Mn$_2$[Al$_{16}$Si$_{16}$O$_{24}$](SO$_4$)$_2$ as the major phase, it is accompanied by considerable amounts of Mn$_2$O$_3$ and zeolite A as minor phases. It is very likely that the Mn$_2$O$_3$ produced here is a consequence of the open system deployed in the HT-PXRD analysis, which has been shown above to accelerate the decomposition of MnSO$_4$, and a less than optimal compaction of the starting reagents.

The above results reveal that there are essentially two competing reactions involving MnSO$_4$: its reaction with zeolite A to form Na$_6$Mn$_2$[Al$_{16}$Si$_{16}$O$_{24}$](SO$_4$)$_2$ (reaction 3); and its thermal decomposition to Mn$_2$O$_3$ (reaction 2). We exploited differences in their kinetics to devise a preparative procedure to optimise the synthesis of Na$_6$Mn$_2$[Al$_{16}$Si$_{16}$O$_{24}$](SO$_4$)$_2$. We found that there is a benefit in applying a rapid heating rate, by placing the charge in a pre-heated furnace at 650 °C, with the intention to get the reactants to the desired temperature as quick as possible, so that MnSO$_4$ can react with zeolite A before it has time to decompose to Mn$_2$O$_3$ under these conditions.
Once the MnSO$_4$ component has reacted with zeolite A, and is inside the sodalite-cage, it is protected from thermal decomposition, at least at 650 °C.

![PXRD pattern](image)

**Fig. 6.** Rietveld refinement of Na$_6$Mn$_2$[Al$_6$Si$_6$O$_{24}$](SO$_4$)$_2$ (I$\bar{4}$ 3m, $a = 0.89780(2)$ nm) against the PXRD data (Cu-K$_{\alpha 1}$) at 20 °C for the sample as prepared here (colour online).

The PXRD pattern (recorded at 20 °C) for the product material as prepared by the method described in the *Experimental Section* is shown in Fig. 6. Na$_6$Mn$_2$[Al$_6$Si$_6$O$_{24}$](SO$_4$)$_2$ was found to be isostructural with the cubic sodalite mineral haüyne, Na$_6$Ca$_2$[Al$_6$Si$_6$O$_{24}$](SO$_4$)$_2$ (space group I$\bar{4}$ 3m), and the unit cell parameter for Na$_6$Mn$_2$[Al$_6$Si$_6$O$_{24}$](SO$_4$)$_2$ refined to $a = 0.89780(2)$ nm, see Table 1; (for interatomic distances and indexing see Tables S1 and S2, respectively, in the Supplementary data). In the structure, Na and Mn occupy the same 8c atomic position, while Si and Al occupy the same 12d position. In both cases, the occupancy was fixed to the stoichiometry of Na$_6$Mn$_2$[Al$_6$Si$_6$O$_{24}$](SO$_4$)$_2$. The isotropic displacement factors refine to relatively large values, i.e. about 8 times larger than those of the atoms in the [SO$_4$] and [(Al,Si)O$_4$] tetrahedra. Given the high coordination number of the Na/Mn-site and thereby the large size of this site, it is reasonable to expect that the Na/Mn-atom rattles around the equilibrium position. No signs of Na-Mn ordering,
i.e. no signs of super structure reflections were observed in the PXRD data; however, the large atomic vibrations would likely smear the effect of the potential cation ordering. The nearly identical X-ray scattering power of Si and Al renders these elements indistinguishable by PXRD, and therefore potential Si-Al ordering cannot be ruled out. We note that refinement of the PXRD data for Na₆Mn₂(Al₆Si₆O₂₄)(SO₄)₂ was also attempted in a primitive unit cell as suggested by Saalfeld [4] for haüyne (space group P̅4 3n). However, this did not yield a satisfactory fit as the relative intensities do not match the data, despite various attempts to refine the structure, peak profiles and preferred orientation (see Supplementary data). Furthermore, removing the I-centering makes the (210)-reflection at about 22.12 degrees 2θ allowed. In the PXRD pattern (Fig. 6) no reflection is observed at this angle, which indicates that the body-centered cell is correct.

Table 1.
Structural information for Na₆Mn₂(Al₆Si₆O₂₄)(SO₄)₂ at 20 °C obtained from Rietveld refinement of PXRD data shown in Figure 6.

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>U_iso (Å²)</th>
<th>Wyckoff site multiplicity and letter</th>
<th>Occupancy*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>0.2191(5)</td>
<td>0.2191(5)</td>
<td>0.2191(5)</td>
<td>0.083(4)</td>
<td>8c</td>
<td>0.75</td>
</tr>
<tr>
<td>Mn</td>
<td>0.2191(5)</td>
<td>0.2191(5)</td>
<td>0.2191(5)</td>
<td>0.083(4)</td>
<td>8c</td>
<td>0.25</td>
</tr>
<tr>
<td>Al</td>
<td>0.25</td>
<td>0</td>
<td>0</td>
<td>0.010(2)</td>
<td>12d</td>
<td>0.5</td>
</tr>
<tr>
<td>Si</td>
<td>0.1442(3)</td>
<td>0.4772(3)</td>
<td>0.007(3)</td>
<td>24g</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.007(3)</td>
<td>24g</td>
<td>1</td>
</tr>
<tr>
<td>O</td>
<td>0.9021(3)</td>
<td>0.9021(3)</td>
<td>0.9021(3)</td>
<td>0.007(3)</td>
<td>8c</td>
<td>1</td>
</tr>
</tbody>
</table>

*) not refined
The unit cell parameter for Na$_6$Mn$_2$(Al$_6$Si$_6$O$_{24}$)(SO$_4$)$_2$ ($a = 0.89780(2)$ nm, space group $I43m$) lies in between that for Na$_6$Zn$_2$(Al$_6$Si$_6$O$_{24}$)(SO$_4$)$_2$ ($a = 0.8923(1)$ nm) [15] and haüyne, Na$_6$Ca$_2$(Al$_6$Si$_6$O$_{24}$)(SO$_4$)$_2$ ($a = 0.909$ nm) [5]; which is consistent with a slightly larger ionic radius of 80 pm for tetrahedrally coordinated (high-spin) Mn$^{2+}$ compared with 73 pm for Zn$^{2+}$ as reported by Shannon [25]. To the best of our knowledge a value for the ionic radius of tetrahedrally coordinated Ca$^{2+}$ is not reported in the literature since this is a very unusual coordination for Ca$^{2+}$. However, by assuming a linear correlation between the above cell constants and the respective ionic radii for the divalent cations, Zn$^{2+}$, Mn$^{2+}$ and Ca$^{2+}$, yields an estimated value of 93 pm for Ca$^{2+}$. This value is consistent with being smaller than the ionic radius of 114 pm for octahedrally coordinated Ca$^{2+}$ [25].

Note that the small Bragg peaks at approximately 23 and 33 degrees 2θ in Figure 6, which are not explained by the Na$_6$Mn$_2$(Al$_6$Si$_6$O$_{24}$)(SO$_4$)$_2$ structure, fit well with the peak positions of bixbyite, Mn$_2$O$_3$ (cf. JCPDS 41-1442). The pale purplish-brown coloration of the product material is attributed to traces of Mn$_2$O$_3$, since the actual Na$_6$Mn$_2$(Al$_6$Si$_6$O$_{24}$)(SO$_4$)$_2$ crystallites appear colourless under the microscope. The formation of Mn$_2$O$_3$ as a side product is consistent with the synthesis being performed at 650 °C; i.e., just above the decomposition temperature of 625 °C for MnSO$_4$ under air as inferred by the results of the TGA (see above).

4. Conclusion

This work has shown that the thermal decomposition of β-MnSO$_4$ under air is a slow process that commences at about 625 °C, which is significantly lower than the values reported in the literature. β-MnSO$_4$ decomposes to bixbyite, Mn$_2$O$_3$, at ~625 °C, and to the reduced phase, hausmannite, Mn$_3$O$_4$, at ~850 °C. We regard the slow rate of reaction to be one of the reasons why the temperatures quoted in the literature for its thermal decomposition differ so widely,
since dissimilarities in the heating rate can lead to erroneous interpretations of the measurements. Another important reason is that in an open-system with poorly defined partial pressures of SO\textsubscript{2}/SO\textsubscript{3}, the stability of the system will be affected by the removal of SO\textsubscript{2}/SO\textsubscript{3} from the atmosphere surrounding the sample. Therefore, any expulsion of the effluent gas will tend to favour the decomposition of \(\beta\)-MnSO\textsubscript{4}, irrespective of the actual temperature. Furthermore, most of the studies reported in the literature involved finding the favourable conditions for the full conversion of MnSO\textsubscript{4} to Mn\textsubscript{3}O\textsubscript{4}, whereas we sought the maximum temperature at which MnSO\textsubscript{4} can be preserved under air.

\(\text{Na}_6\text{Mn}_2[\text{Al}_6\text{Si}_6\text{O}_{24}](\text{SO}_4)_2\) was prepared by the solid-state reaction between anhydrous MnSO\textsubscript{4} and dehydrated zeolite A at 650 °C, and was shown to crystallize with the sodalite-type structure. The product material contained traces of bixbyite, Mn\textsubscript{2}O\textsubscript{3}, due to the thermal decomposition of a certain fraction of the MnSO\textsubscript{4} under these preparative conditions involving an open system. Experiments are under preparation to explore the possibility of using an evacuated quartz-glass ampoule — infilled with a glass rod to limit the vapour space — with the objective of preparing \(\text{Na}_6\text{Mn}_2[\text{Al}_6\text{Si}_6\text{O}_{24}](\text{SO}_4)_2\) as a monophasic material through the reaction between anhydrous MnSO\textsubscript{4} and zeolite A at 620 °C in a closed system. Furthermore, it should be informative to analyse pristine \(\text{Na}_6\text{Mn}_2[\text{Al}_6\text{Si}_6\text{O}_{24}](\text{SO}_4)_2\) using \(^{29}\text{Si}\) MAS NMR to help resolve the issue of Si-Al ordering, since this has been applied by certain workers to other sodalites [26].

Our results suggest it should be possible to substitute other divalent tetrahedrally coordinated cations with ionic radii between 73–93 pm, for example Cd\textsuperscript{2+} and Fe\textsuperscript{2+}, for Ca\textsuperscript{2+} in haüyne, \(\text{Na}_6\text{Ca}_2[\text{Al}_6\text{Si}_6\text{O}_{24}](\text{SO}_4)_2\) by the method described in this paper, so long as the divalent metal sulfate is thermally stable under stagnant air at the temperature that is high enough for it to react with zeolite A.
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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://

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https://pubs.geoscienceworld.org/msa/ammin/article-abstract/40/1-2/22/539444


of artificial `hackmanite', Na₈[Al₆Si₆O₂₄]Cl₁.₅S₀.₁; `sulfosodalite', Na₈[Al₆Si₆O₂₄]S; and natural 

https://doi.org/10.1007/s00269-011-0471-y

https://doi.org/10.1016/j.micromeso.2012.05.020

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(Mn,Fe,Zn)₈(Be₆Si₆O₂₄)S₂, Am. Mineral 70 (1985) 186–192.


Graphical Abstract Legend:

We report the temperature for the thermal decomposition of MnSO$_4$ under air, and on the reaction between MnSO$_4$ and zeolite A for the synthesis of a novel sodalite, Na$_6$Mn$_2$[Al$_6$Si$_6$O$_{24}$](SO$_4$)$_2$. 