1. Introduction

The most common energy storage systems are batteries whose storage capacity surpasses by far mechanical or latent-heat storage systems.¹ Batteries based on lithium were developed and optimized in the last decades² and are used widely in many modern applications. For large-scale grid application, however, their use may be restricted by limited geological reserves of lithium and earth-abundant alternatives are needed. Studies smoothly pass through the development of dual metal ion batteries and hybrid metal ion batteries.³ One of the possible solutions is the development and implementation of batteries based on sodium whose geological reserves are essentially limitless. Such a possibility is being extensively investigated.⁴⁻⁶ Some of the phases proposed for use in such batteries are isostructural with the minerals blödite [nominally Na₂-Mg(SO₄)₂·4H₂O] and kröhnkite [nominally Na₂Cu(SO₄)₂·2H₂O].

Thermodynamic stability is one of the criteria for a successful development of commercial batteries. The phases that make up the anodes and cathodes must retain their properties over many redox cycles. Natrochalcite [Na₃Cu₃(OH)(H₂O)(SO₄)₂], as an example, turns amorphous when operating as an anode, but recrystallizes back during the subsequent charge.⁶ H₂O as a component in the batteries may be problematic because sulfates tend to be soluble and reactive towards water.⁷ Hence, anhydrous sulfates may be preferred but hydrous sulfates are being tested as well.⁸ Thermodynamic data suggest which phase assemblage is located energetically downhill and predict if, and with what driving force, the phases of interest for the battery development may tend to convert to other ones.

In this work, we address the question of thermodynamic properties and thermodynamic stability of a series of binary sodium-transition metal sulfates isostructural with blödite or kröhnkite. Some of them were previously tested as precursors for possible use in sodium-based batteries. The thermodynamic data were derived by a combination of acid-solution and relaxation calorimetry. Of particular interest is then the question is the title compounds have a tendency to decompose to simple sulfates.

Thermodynamics of the double sulfates
Na₂M²⁺(SO₄)₂·nH₂O (M = Mg, Mn, Co, Ni, Cu, Zn, n = 2 or 4) of the blödite–kröhnkite family†

Juraj Majzlan, Delyana Marinova and Edgar Dachs

The double sulfates with the general formula Na₂M²⁺(SO₄)₂·nH₂O (M = Mg, Mn, Co, Ni, Cu, Zn, n = 2 or 4) are being considered as materials for electrodes in sodium-based batteries or as precursors for such materials. These sulfates belong structurally to the blödite (n = 4) and kröhnkite (n = 2) family and the M cations considered in this work were Mg, Mn, Co, Ni, Cu, Zn. Using a combination of calorimetric methods, we have measured enthalpies of formation and entropies of these phases, calculated their Gibbs free energies (ΔG°) of formation and evaluated their stability with respect to Na₂SO₄, simple sulfates MSO₄·xH₂O, and liquid water, if appropriate. The ΔG° values (all data in kJ mol⁻¹) are: Na₂Ni(SO₄)₂·4H₂O: -3032.4 ± 1.9, Na₂Mg(SO₄)₂·4H₂O: -3432.3 ± 1.7, Na₂Co(SO₄)₂·4H₂O: -3034.4 ± 1.9, Na₂Zn(SO₄)₂·4H₂O: -3312.6 ± 1.9, Na₂Mn(SO₄)₂·2H₂O: -2727.3 ± 1.8. The data allow the stability of these phases to be assessed with respect to Na₂SO₄. MSO₄·mH₂O and H₂O(l). Na₂Ni(SO₄)₂·4H₂O is stable with respect to Na₂SO₄, NiSO₄ and H₂O(l) by a significant amount of ≈50 kJ mol⁻¹ whereas Na₂Mn(SO₄)₂·2H₂O is stable with respect to Na₂SO₄, MnSO₄ and H₂O(l) only by ≈25 kJ mol⁻¹. The values for the other blödite–kröhnkite phases lie in between. When considering the stability with respect to higher hydrates, the stability margin decreases; for example, Na₂Ni(SO₄)₂·4H₂O is still stable with respect to Na₂SO₄, NiSO₄, 4H₂O and H₂O(l), but only by ≈20 kJ mol⁻¹. Among the phases studied and chemical reactions considered, the Na–Ni phase is the most stable one, and the Na–Mn, Na–Co, and Na–Cu phases show lower stability.

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¹Institute of Geosciences, Friedrich-Schiller University, Burgweg 11, 07749 Jena, Germany. E-mail: Juraj.Majzlan@uni-jena.de
²Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria
³Department of Chemistry and Physics of Materials, University of Salzburg, Jakob-Haringer-Strasse 2a, 5020 Salzburg, Austria
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2. Crystal structures of blödite and kröhnkite

The crystal structure of blödite [Fig. 1a, nominally Na$_2$Mg(SO$_4$)$_2$·4H$_2$O]$^{11,12}$ consists of [Mg(SO$_4$)$_2$(H$_2$O)$_4$]$^{2-}$ clusters that are interlinked by Na-centered polyhedra and hydrogen bonds. The ionic conductivity of these phases is facilitated by Na ions positioned in channels running along the [100] direction. Apart from Mg$^{2+}$, the structures of this type could also incorporate divalent Fe, Co, Ni, Cu, Zn. The crystal structure of kröhnkite [Fig. 1b, nominally Na$_2$Cu(SO$_4$)$_2$·2H$_2$O]$^{13}$ is more condensed than that of blödite. It consists of heteropolyhedral chains composed of CuO$_4$(H$_2$O)$_2$ octahedra and sulfate tetrahedra.$^{14,15}$ In kröhnkite itself, the octahedra are strongly distorted owing to the Jahn–Teller effect but these structures accept other cations that do not have the tendency to distort the octahedra.

3. Experimental section

3.1. Synthesis

Syntheses of the phases investigated in this work were extensively described.$^{16–20}$ The double salts Na$_2$M$^{2+}$(SO$_4$)$_2$·nH$_2$O (M = Mg, Mn, Co, Ni, Cu, Zn n = 2 or 4) were obtained by crystallization from ternary solutions according to the solubility diagrams of the three-component Na$_2$SO$_4$–M$^{2+}$SO$_4$–H$_2$O systems at 25 °C. Essentially, saturated high-temperature solutions at about 60–70 °C, were cooled subsequently to 25 °C, thereby forming a solid phase. The suspensions were stirred vigorously for 2 days until complete homogenization and then filtered. The concentration of M$^{2+}$ ions was determined by different titrimetric methods of analysis and by calculations using the method of algebraic indirect identification of solid-phase compositions.

3.2. Characterization

After the syntheses, but also prior to each calorimetric experiment, phase purity of the samples was tested by powder X-ray diffraction (XRD). The data were collected with a Bruker D8 ADVANCE with DAVINCI design, and with Cu Kα radiation, Ni filter, and a Lynxeye 1D detector. A step size of 0.02° 2θ and a 0.25 s time per step of were used. Lattice parameters were refined using the JANA2006 program.$^{21}$

3.3. Calorimetric methods

For the solution calorimetric experiments at $T = 25$ °C, we used a commercial IMC-4400 isothermal microcalorimeter (Calorimetry Sciences Corporation) which we modified for the purposes of acid-solution calorimetry.$^{22}$ The liquid bath of the calorimeter was held at a constant temperature of 298.15 K with fluctuations smaller than 0.005 K. The calorimetric solvent was 25 g of deionized water or 25 g of 5 N HCl contained in a polyetheretherketone (PEEK) cup with a total volume of 60 mL. The cup was then closed with a PEEK screw lid and inserted into the calorimeter well. The calorimeter stabilized after ≈ 8 hours. During the stabilization and the experiment, the solvent was stirred by a SiO$_2$ glass stirrer by a motor positioned about 40 cm from the active zone of the instrument. The samples were pressed into a pellet and weighed on a micro-balance with a precision of 0.002 mg (as stated by the manufacturer). The pellets were then dropped through an SiO$_2$ glass tube into the solvent and the heat produced or consumed during the

![Fig. 1](image-url) Crystal structure of (a) blödite (projection onto 001) and (b) kröhnkite (projection onto 100). Cyan octahedra are Cu-centered, deep-green octahedra Mg-centered. Yellow are sulfate tetrahedra, gray balls represent Na, small white balls the H atoms. Red balls represent O atoms, their size reduced when they a part of a coordination polyhedron. Note the octahedral–tetrahedral chains (parallel to [001]) in the structure of kröhnkite and the cluster of two tetrahedra and an octahedron in the structure of blödite.
dissolution was measured. The heat flow between the reaction cup and the constant temperature reservoir was then integrated to calculate the caloric effect. A typical experiment lasted 50–60 minutes and the end of the experiment was judged from the return of the baseline to the pre-experiment position. The pellet mass of each measured phase was calculated according to the stoichiometry of the thermochemical cycle. Further details on operation, calibration, and accuracy checks can be found in.

Heat capacity was measured by relaxation calorimetry using a commercial Physical Properties Measurement System (PPMS, from Quantum Design, San Diego, California) at the University of Salzburg, Austria. With due care, accuracy can be within 1% for 5 K to 300 K, and 5% for 0.7 K to 5 K. Powdered samples were wrapped in a thin Al foil and compressed to produce 0.5 mm thick pellets, which were then placed onto the sample platform of the calorimeter for measurement.

4. Results

All samples used in this study were crystalline, with sharp peaks in their powder XRD patterns. The refined lattice parameters are summarized in Table 1. The structures corresponded to the structures previously determined for the minerals biödite$^{22}$ and kröhnkite.$^{23}$ The starting models for the full-profile fits were taken from these publications.

Enthalpies of dissolution in 5 N HCl, measured by acid-solution calorimetry, were converted to enthalpies of formation via the appropriate thermochemical cycles (Table 2). A suite of simple metal sulfates, metal oxides, and Na$_2$SO$_4$ were used as reference phases in this process.$^{22}$ The dissolution of all samples was rapid and no problems were encountered during the calorimetric experiments.

| Table 2 | Thermochemical cycles for the studied phases with the enthalpy values measured or used in these cycles. All values in kJ mol$^{-1}$ |
|-----------------|-----------------|
| Na$_2$M(SO$_4$)$_2$·nH$_2$O = 2Na$^+$ + M$^{2+}$ + 2SO$_4$$^{2-}$ + nH$_2$O | (1) |
| Na$_2$SO$_4$ = 2Na$^+$ + SO$_4$$^{2-}$ | (2) |
| MSO$_4$·mH$_2$O = M$^{2+}$ + SO$_4$$^{2-}$ + mH$_2$O | (3) |
| MO + 2H$^+$ = M$^{2+}$ + H$_2$O | (4) |
| H$_2$O(l) = H$_2$O [aq.] | (5) |
| 2Na + S + 2O$_2$ = Na$_2$SO$_4$ | (6) |
| M + S + (2 + m/2)O$_2$ + mH$_2$ = MSO$_4$·mH$_2$O | (7) |
| M + (1/2)O$_2$ = MO | (8) |
| H$_2$ + (1/2)O$_2$ = H$_2$O | (9) |
| 2Na + M + 2S + (4 + n/2)O$_2$ + nH$_2$ = Na$_2$M(SO$_4$)$_2$·nH$_2$O | (10) |

For a thermodynamic cycle closed with the simple metal sulfate (MSO$_4$·mH$_2$O, M = Mg, Ni, Co, Cu): $\Delta H_{\text{f,0}}$ = $\Delta H_{\text{f}}$ = $\Delta H_1$ + $\Delta H_2$ + $\Delta H_3$ + (n-m)$\Delta H_3$ for Na$_2$M(SO$_4$)$_2$·nH$_2$O. For a thermodynamic cycle closed with the metal oxide (MO, M = Mn, Zn, MgSO$_4$, and MgO): $\Delta H_{\text{f,0}}$ = $\Delta H_{\text{f}}$ = $\Delta H_4$ + $\Delta H_5$ + $\Delta H_6$ + $\Delta H_{\text{f,MgSO}_4}$ + $\Delta H_{\text{f,MgO}}$ + n$\Delta H_{\text{f,Mn}}$ - $\Delta H_{\text{f,MO}}$ + $\Delta H_{\text{f,SO}_4}$ for Na$_2$M(SO$_4$)$_2$·nH$_2$O.

Dissolution/dilution enthalpies

$\Delta H_{\text{f,CO}}$ = $\Delta H_{\text{f}}$(Na$_2$Co(SO$_4$)$_2$·4H$_2$O) = 51.62 ± 0.31(6) kJ mol$^{-1}$

$\Delta H_{\text{f,Cu}}$ = $\Delta H_{\text{f}}$(Na$_2$Cu(SO$_4$)$_2$·2H$_2$O) = 54.18 ± 0.38(4) kJ mol$^{-1}$

$\Delta H_{\text{f,Mg}}$ = $\Delta H_{\text{f}}$(Na$_2$Mg(SO$_4$)$_2$·4H$_2$O) = 42.21 ± 0.21(5) kJ mol$^{-1}$

$\Delta H_{\text{f,Mn}}$ = $\Delta H_{\text{f}}$(Na$_2$Mn(SO$_4$)$_2$·2H$_2$O) = 37.97 ± 0.17(5) kJ mol$^{-1}$

$\Delta H_{\text{f,Ni}}$ = $\Delta H_{\text{f}}$(Na$_2$Ni(SO$_4$)$_2$·4H$_2$O) = 49.27 ± 0.15(6) kJ mol$^{-1}$

$\Delta H_{\text{f,Zn}}$ = $\Delta H_{\text{f}}$(Na$_2$Zn(SO$_4$)$_2$·4H$_2$O) = 65.22 ± 0.17(5) kJ mol$^{-1}$

$\Delta H_3$ = $\Delta H_{\text{f}}$(Na$_2$SO$_4$) = 21.08 ± 0.14(6) kJ mol$^{-1}$

$\Delta H_{\text{f,CO}}$ = $\Delta H_{\text{f}}$(CoSO$_4$·7H$_2$O) = 44.66 ± 0.31(6) kJ mol$^{-1}$

$\Delta H_{\text{f,Cu}}$ = $\Delta H_{\text{f}}$(CuSO$_4$·5H$_2$O) = 49.71 ± 0.19(17) kJ mol$^{-1}$

$\Delta H_{\text{f,Mg}}$ = $\Delta H_{\text{f}}$(MgSO$_4$·7H$_2$O) = -53.50 ± 0.48(7) kJ mol$^{-1}$

$\Delta H_{\text{f,Ni}}$ = $\Delta H_{\text{f}}$(NiSO$_4$·7H$_2$O) = 41.26 ± 0.58(9) kJ mol$^{-1}$

$\Delta H_{\text{f,Mg}}$ = $\Delta H_{\text{f}}$(MgO) = -149.68 ± 0.69(6) kJ mol$^{-1}$

$\Delta H_{\text{f,Mn}}$ = $\Delta H_{\text{f}}$(MnO) = -113.35 ± 0.05(3) kJ mol$^{-1}$

$\Delta H_{\text{f,Zn}}$ = $\Delta H_{\text{f}}$(ZnO) = -70.24 ± 0.11(4) kJ mol$^{-1}$

$\Delta H_5$ = $\Delta H_{\text{f,SO}_4}$ = -0.54 kJ mol$^{-1}$

$\Delta H_6$ = $\Delta H_{\text{f}}$(Na$_2$SO$_4$) = -1387.8 ± 0.4 kJ mol$^{-1}$

$\Delta H_7$ = $\Delta H_{\text{f}}$(CuSO$_4$·5H$_2$O) = -2279.3 ± 1.5 kJ mol$^{-1}$

$\Delta H_8$ = $\Delta H_{\text{f}}$(NiSO$_4$·7H$_2$O) = -2976.8 ± 1.5 kJ mol$^{-1}$

$\Delta H_9$ = $\Delta H_{\text{f}}$(MgSO$_4$·7H$_2$O) = -1288.64 ± 1.28 kJ mol$^{-1}$

$\Delta H_{\text{f,Mn}}$ = $\Delta H_{\text{f}}$(MnO) = -385.2 ± 0.5 kJ mol$^{-1}$

$\Delta H_{\text{f,Zn}}$ = $\Delta H_{\text{f}}$(ZnO) = -350.5 ± 0.3 kJ mol$^{-1}$

$\Delta H_9$ = $\Delta H_{\text{f}}$(H$_2$O) = -285.8 ± 0.1 kJ mol$^{-1}$
\[ \sum_{p} T^p \] (with \( p = 0 \)–8 or 0–9) were used. The polynomials were joined and used for the determination of thermodynamic functions between 0–300 K. The results, including values of smoothed \( C_p \) and entropy at evenly spaced temperature intervals, are listed in Tables S1–S10.†

The enthalpies of formation and entropies of formation (Table 3) were used to calculate Gibbs free energies of formation. Auxiliary data needed for these calculations (entropies of elements in their standard state) were taken from ref. 26.

5. Discussion

The enthalpies of dissolution of the title compounds in 5 N HCl are endothermic, with small magnitude (Table 2), as expected for hydrated sulfates. They show no linear correlation between the ionic radii (IR) of the divalent metals (Fig. 3), as reported for similar Li phases.²⁸ With the exception of Mn²⁺ (IR = 0.83 Å), the ionic radii of the divalent metals considered here are fairly similar to each other. We assume that a simple relationship is obscured by the structural variations between the blödlite- and kröhnkite-like sulfates. In addition, the introduction of \( \text{H}_2\text{O} \) molecules in these structures induces structural depolymerization, as opposed to the anhydrous phases. Such depolymerization can allow relaxation of the structures and flexibility in the uptake of various divalent cations to a certain extent. Detailed studies²⁶–²⁹ showed that mixing is severely limited in many solid solutions of these phases and, therefore, the flexibility is also limited.

There is no simple (i.e., linear) relationship between the chemical composition and formation enthalpies or Gibbs free energies. To decipher such relationship, detailed studies of the electronic structure of the title compounds, using \textit{ab initio} calculations, may be needed. Such calculations are, however, beyond the scope of this contribution. Even though the question of interplay of crystal structures and thermodynamic properties is intriguing and recurring, this study cannot provide satisfactory answers to it.

Gibbs free energies of formation (Table 3) allow to evaluate the stability of the title phases quantitatively with respect to the simple sulfates. Considering the reaction

\[
\text{Na}_2\text{M(SO}_4\text{)}_2\cdot n\text{H}_2\text{O(cr)} = \text{Na}_2\text{SO}_4\cdot x\text{H}_2\text{O(cr)} + \text{MSO}_4\cdot m\text{H}_2\text{O(cr)} + (n - m - x)\text{H}_2\text{O(l)}
\]

A set of equilibria can be evaluated. If the batteries should be operated with such phases, the presence of additional free water (aqueous solution) is unlikely. The implication for this reaction is that \( m < n \), and hence higher hydrates are not considered in

| Table 3 | Summary of thermodynamic data for the \( \text{Na}_2\text{M(SO}_4\text{)}_2\cdot n\text{H}_2\text{O} \) phases from this study |
|---------|-------------------------------------------------|
| \( \Delta_d\overrightarrow{H} \) kJ mol\(^{-1} \) | \( \Delta_d\overrightarrow{S} \) J mol\(^{-1} \) K\(^{-1} \) | \( \Delta_d\overrightarrow{G} \) kJ mol\(^{-1} \) |
| \( \text{Na}_2\text{Ni(SO}_4\text{)}_2\cdot 4\text{H}_2\text{O} \) | \(-3492.5 \pm 1.7 \) | \(407.3 \pm 2.9 \) | \(-1543.2 \pm 2.9 \) | \(-3032.4 \pm 1.9 \) |
| \( \text{Na}_2\text{Mg(SO}_4\text{)}_2\cdot 4\text{H}_2\text{O} \) | \(-3896.4 \pm 1.5 \) | \(396.7 \pm 2.8 \) | \(-1556.6 \pm 2.8 \) | \(-3432.3 \pm 1.7 \) |
| \( \text{Na}_2\text{Co(SO}_4\text{)}_2\cdot 4\text{H}_2\text{O} \) | \(-3494.0 \pm 1.6 \) | \(409.3 \pm 2.9 \) | \(-1541.4 \pm 2.9 \) | \(-3034.4 \pm 1.9 \) |
| \( \text{Na}_2\text{Zn(SO}_4\text{)}_2\cdot 4\text{H}_2\text{O} \) | \(-3588.9 \pm 1.7 \) | \(431.8 \pm 3.0 \) | \(-1530.5 \pm 3.1 \) | \(-3132.6 \pm 1.9 \) |
| \( \text{Na}_2\text{Cu(SO}_4\text{)}_2\cdot 2\text{H}_2\text{O} \) | \(-2791.7 \pm 3.5 \) | \(315.5 \pm 3.8 \) | \(-1171.8 \pm 3.8 \) | \(-2442.3 \pm 3.6 \) |
| \( \text{Na}_2\text{Mn(SO}_4\text{)}_2\cdot 2\text{H}_2\text{O} \) | \(-3066.8 \pm 1.7 \) | \(347.4 \pm 2.4 \) | \(-1138.7 \pm 2.5 \) | \(-2727.3 \pm 1.8 \) |
these calculations. For consistency, all Gibbs free energies of formation ($\Delta_f G^\circ$) for the transition-metal sulfates were taken from ref. 30, even though the thermodynamic data for some systems have been updated since then, e.g.,$^{27}$ The $\Delta_f G^\circ$ value for CoSO$_4$·H$_2$O was corrected because the values of formation enthalpy and entropy, listed by$^{28}$ do not add up to her $\Delta_f G^\circ$ for this phase. The $\Delta_f G^\circ$ values for magnesium sulfates were adopted from ref. 31 that for Na$_2$SO$_4$ from ref. 26. The $\Delta_f G^\circ$ values for this reaction are graphically shown for all Na$_2$M(SO$_4$)$_2$·nH$_2$O(cr) phases in Fig. 4. We note that these values are approximate as only pure H$_2$O(l) is considered. As mentioned above, the Na–M sulfates are highly soluble and aqueous solutions, if present, would likely have high ionic strength and affect the equilibria. Because of the uncertainties regarding the composition of such solutions and the appropriate activity-molality models, calculations involving aqueous solutions with Na, M, and sulfate as solutes were not performed here.

6. Conclusions

All Na$_2$M(SO$_4$)$_2$·nH$_2$O phases are stable with respect to the assemblages of Na$_2$SO$_4$, MSO$_4$·mH$_2$O, and H$_2$O(l). However, the differences among the Na$_2$M(SO$_4$)$_2$·nH$_2$O phases with different M$^{2+}$ cations are significant. When considering their stability with respect to Na$_2$SO$_4$, MSO$_4$, and H$_2$O(l), the Gibbs free energies vary from $\approx$ 25 kJ mol$^{-1}$ for M = Mn up to $\approx$ 50 kJ mol$^{-1}$ for M = Ni. The differences, although smaller in magnitude, remain also for higher sulfates (MSO$_4$·mH$_2$O). For the tetrahydrates (MSO$_4$·4H$_2$O), the difference between M = Ni and M = Mg is only $\approx$ 7 kJ mol$^{-1}$ (Fig. 4). Hence, the thermodynamic calculations document the stability of the Na$_2$M(SO$_4$)$_2$·nH$_2$O phases. They also show that the stability margin is relatively small. Should the Na$_2$M(SO$_4$)$_2$·nH$_2$O phases be decomposed during desodiation cycles, the driving force for the re-assembling of their structures is small and their recrystallization, similar to that observed for natrochalcite,$^9$ could be problematic. From the set investigated here, the Na$_2$Ni(SO$_4$)$_2$·4H$_2$O phase is the most stable one with respect to the simple sulfates. If Na$_2$Fe(SO$_4$)$_2$·2H$_2$O should turn out as a promising candidate for the sodium batteries,$^{10}$ the stability of the dihydrate with M = Ni should be also explored with respect to the stabilization of the materials in the batteries.

Conflicts of interest

The authors declare no conflict of interest.

References

1 M. A. Hannan, M. M. Hoque, A. Mohamed and A. Ayob, *Renewable Sustainable Energy Rev.*, 2017, 69, 771.
2 M. Li, J. Lu, Z. Chen and K. Amine, *Adv. Mater.*, 2018, 30, 1800561.
3 R. Stoyanova, V. Koleva and A. Stoyanova, *Chem. Rec.*, 2019, 19, 474.
4 M. Reynaud, M. Ati, S. Boulineau, M. T. Sougrati, B. C. Melot, G. Rousse, J. N. Chotard and J. M. Tarascon, *ECS Trans.*, 2013, 50, 11.
5 C. Masquelier and L. Crouguennec, *Chem. Rev.*, 2013, 113, 6552.
6 Z. Liu, H. J. Zhou, S. S. Ang and J. J. Zhang, *Electrochim. Acta*, 2016, 211, 619.
7 T. Watcharatharapong, J. T. Thienprasert, S. Chakraborty and R. Ahuja, *Nano Energy*, 2019, 55, 123.
8 T. Jin, H. Li, K. Zhu, P.-F. Wang, P. Liu and L. Jiao, *Chem. Soc. Rev.*, 2020, 49, 2342.
9 P. Barpanda, G. Oyama, S. Nishimura, S.-C. Chung and A. Yamada, *Nat. Commun.*, 2014, 5, 4358.
10 P. Barpanda, G. Oyama, C. D. Ling and A. Yamada, *Chem. Mater.*, 2014, 26, 1297.
11 M. Giglio, *Acta Crystallogr.*, 1958, 11, 789.
12 F. C. Hawthorne, *Can. Mineral.*, 1985, 23, 669.
13 B. Dahlman, *Ark. Mineral. Geol.*, 1952, 1, 339–366.
14 M. Fleck, U. Kolitsch and B. Hertweck, *Z. Kristallogr.*, 2002, 217, 435.
15 U. Kolitsch and M. Fleck, *Eur. J. Mineral.*, 2006, 18, 471.
16 M. Georgiev, T. Bancheva, D. Marinova, R. Stoyanova and D. Stoilova, *International Journal of Scientific Research in Science and Technology*, 2016, 2, 279.
17 M. Georgiev, D. Marinova, T. Bancheva and D. Stoilova, *J. Chem. Technol. Metall.*, 2017, 52, 902.
18 D. Marinova, M. Georgiev, T. Bancheva and D. Stoilova, *International Journal of Scientific Research in Science and Technology*, 2016, 2, 283.
19 D. Marinova, M. Georgiev, T. Bancheva, R. Stoyanova and D. Stoilova, *J. Therm. Anal. Calorim.*, 2017, 130, 1925.
20 D. Marinova, M. Wildner, T. Bancheva, R. Stoyanova, M. Georgiev and D. G. Stoilova, *Phys. Chem. Miner.*, 2018, 45, 801.
21 V. Petříček, M. Dušek and L. Palatinus, *Z. Kristallogr.*, 2014, **229**, 345.
22 J. Majzlan, *Acta geol. Slovaca*, 2017, **9**, 171.
23 C. A. Kennedy, M. Stancescu, R. A. Marriott and M. A. White, *Cryogenics*, 2007, **47**, 107.
24 J. Majzlan, A. Zittlau, K. D. Grevel, J. Schliesser, B. F. Woodfield, E. Dachs, M. Števko, J. Plášil and S. Milovská, *Can. Mineral.*, 2015, **53**, 937.
25 F. C. Hawthorne and R. B. Ferguson, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1975, **31**, 1753.
26 R. A. Robie and B. S. Hemingway, *United States Geol. Surv. Bull.*, 1995, **2131**, 461.
27 K. D. Grevel and J. Majzlan, *Chem. Geol.*, 2011, **286**, 301.
28 R. J. Lemire, D. A. Palmer, P. Taylor and H. Schlenz, *Chemical Thermodynamics of Iron, Part 2*. OECD Nuclear Energy Agency, 2020, p. 921.
29 A. V. Radha, L. Lander, G. Rousse, J. M. Tarascon and A. Navrotsky, *J. Mater. Chem. A*, 2015, **3**, 2601.
30 C. W. DeKock, *Information Circular*, Bureau of Mines, 1982, 8910, p. 45.
31 K. D. Grevel and J. Majzlan, *Geochim. Cosmochim. Acta*, 2009, **73**, 6805.