Selective metathesis synthesis of MgCr$_2$S$_4$ by control of thermodynamic driving forces†

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MgCr$_2$S$_4$ thiospinel is predicted to be a compelling Mg-cathode material, but its preparation via traditional solid-state synthesis methods has proven challenging. Wustrow et al. [Inorg. Chem., 2018, 57, 14] found that the formation of MgCr$_2$S$_4$ from MgS + Cr$_2$S$_3$ binaries requires weeks of annealing at 800 °C with numerous intermediate regrinds. The slow reaction kinetics of MgS + Cr$_2$S$_3$ → MgCr$_2$S$_4$ can be attributed to a miniscule thermodynamic driving force of ΔH = −2 kJ mol$^{-1}$. Here, we demonstrate that the double ion-exchange metathesis reaction, MgCl$_2$ + 2NaCrS$_2$ → MgCr$_2$S$_4$ + 2NaCl has a reaction enthalpy of ΔH = −47 kJ mol$^{-1}$, which is thermodynamically driven by the large exothermicity of NaCl formation. Using this metathesis reaction, we successfully synthesized MgCr$_2$S$_4$ nanoparticles (<200 nm) from MgCl$_2$ and NaCrS$_2$ precursors in a KCl flux at 500 °C in only 30 minutes. NaCl and other metathesis byproducts are then easily washed away by water. We rationalize the selectivity of MgCr$_2$S$_4$ in the metathesis reaction from the topology of the DFT-calculated pseudo-ternary MgCl$_2$–CrCl$_3$–Na$_2$S phase diagram. Our work helps to establish metathesis reactions as a powerful alternative synthesis route to inorganic materials that have otherwise small reaction energies from conventional precursors.

Introduction

Synthesis is the bedrock of inorganic materials chemistry, serving as the first step to any further investigation into the structure–property relationships of materials. For ceramic materials, the traditional approach to solid-state synthesis involves grinding or milling precursors into powder form, followed by the firing of these precursors at high temperatures to form more complex materials. While this approach has led to the synthesis of many inorganic materials, it remains limited by a number of thermodynamic and kinetic constraints. For example, the synthesis temperature should be high enough to facilitate fast diffusion and reaction kinetics, but low enough that the target compound does not melt or decompose. However, high temperatures also lead to the ripening of large particles, which eliminates interfaces and thereby reduces reaction kinetics. Because of these often conflicting constraints, solid-state synthesis occasionally proceeds with slow reaction kinetics, non-equilibrium intermediates, or impurities, which hinder the phase-pure synthesis of a desired target material.

One such material that has proven difficult to synthesize via traditional solid-state synthesis is MgCr$_2$S$_4$ thiospinel. In the search for Mg-ion cathode materials beyond the dominant Chevrel Mo$_6$S$_8$ phase, Mg-thiospinels emerged as a promising...
class of compounds. Thiospinels benefit from a soft sulfur anion sublattice, which enhances Mg-ion mobility compared to oxides, and a spinel framework, which provides a favorable tetrahedral $\rightarrow$ octahedral $\rightarrow$ tetrahedral Mg$^{2+}$ migration path with a low diffusion barrier.$^{5,9}$ MgTi$_2$S$_4$ was the first demonstrated Mg-thiospinel cathode material, successfully cycled at a C/5 rate at 60 °C and achieving a specific energy density of 230 Wh kg$^{-1}$. Our computational search for other candidate Mg-thiospinels found MgCr$_2$S$_4$ to possess compelling properties, including a high specific capacity (209 mAh g$^{-1}$) and energy density (244 Wh kg$^{-1}$), as well as a relatively low Mg-ion diffusion barrier of 540 meV. Notably, MgCr$_2$S$_4$ was calculated with a density functional theory (DFT) to fall upon the Mg–Cr–S convex hull, meaning it is thermodynamically stable with respect to competing compounds and should therefore be synthesizable.

Following this prediction, Wustrow et al. successfully synthesized MgCr$_2$S$_4$ through a traditional solid-state synthesis approach—although it was found to be a laborious reaction.$^{12}$ Starting from elemental (Mg + Cr + S) precursors, the binary sulfides, MgS and Cr$_2$S$_3$, formed rapidly upon heating. However, the subsequent reaction from MgS + Cr$_2$S$_3$ to ternary MgCr$_2$S$_4$ required holding at 800 °C for two weeks, with numerous intermediate regrinds. Notably, the reaction could not be accelerated by carrying out the synthesis at higher temperatures as MgCr$_2$S$_4$ decomposes into MgS and Cr$_2$S$_3$ above 900 °C. Although MgCr$_2$S$_4$ is indeed a thermodynamically stable compound, we calculate the driving force (reaction enthalpy, $\Delta H_r$) for its formation from MgS + Cr$_2$S$_3$ to be extremely small (−2 kJ mol$^{-1}$, eqn (1)).

$$\text{MgS} + \text{Cr}_2\text{S}_3 \rightarrow \text{MgCr}_2\text{S}_4; \Delta H_r = -2 \text{ kJ mol}^{-1}$$ (1)

All reaction energies in this work utilize the publicly available DFT-calculated thermochemical data in the Materials Project database (Methods). The slow reaction kinetics observed by Wustrow et al. can be attributed to this miniscule thermodynamic driving force. Moreover, long synthesis times can lead to the ripening of large MgCr$_2$S$_4$ particles, which reduces the interfacial area needed to activate Mg-ion intercalation and further slows down the reaction kinetics.

Metathesis reactions offer an intriguing synthesis route to solid-state materials with otherwise small reaction energies. In a metathesis reaction, an alkali or alkaline earth metal compound is combined with a metal halide, which drives a highly exothermic double ion-exchange reaction. For example, a compelling metathesis reaction for MgCr$_2$S$_4$ can be written as:

$$2\text{NaCr}_2\text{S}_4 + \text{MgCl}_2 \rightarrow \text{MgCr}_2\text{S}_4 + 2\text{NaCl}; \Delta H_r = -47 \text{ kJ mol}^{-1}$$ (2)

The $> 20 \times$ increase in thermodynamic driving force from $\Delta H_r = -2 \text{ kJ mol}^{-1}$ to $-47 \text{ kJ mol}^{-1}$ is because Na$^+$ and Cl$^-$ are separated in the precursors but rejoined to form the very stable NaCl salt on the product side. Along with a dramatic increase in reaction enthalpy, other advantages afforded by metathesis reactions include faster reaction kinetics and the potential to form nanocrystals and porous materials.$^{13}$ Not only can metathesis reactions be used to synthesize stable materials with otherwise small reaction energies, the increased thermodynamic driving force and fast reaction kinetics also affords the synthesis of metastable materials,$^{14}$ as were previously demonstrated on nitrides,$^{13,15–17}$ sulfides,$^{13,16,19}$ and oxides.$^{20–22}$ Motivated by the metathesis reaction shown in eqn (2), we designed a two-step sequential metathesis reaction to synthesize MgCr$_2$S$_4$, as visualized in Scheme 1.

### Results

In the first reaction, we ball milled CrCl$_3$ and Na$_2$S to form NaCrS$_2$ (eqn (3)). This reaction is highly exothermic ($\Delta H_r = -359 \text{ kJ mol}^{-1}$) and proceeds even without external heating.

$$\text{CrCl}_3 + 2\text{Na}_2\text{S} \rightarrow \text{NaCrS}_2 + 3\text{NaCl}; \Delta H_r = -359 \text{ kJ mol}^{-1}$$ (3)

To conduct the metathesis reaction described in eqn (2), we next heated the byproducts from eqn (3) in a KCl–MgCl$_2$ flux at 500 °C in nitrogen atmosphere. We prepared the KCl–MgCl$_2$ flux at the eutectic composition of KCl: MgCl$_2$ $\sim 2:1$, which has a melting point of ~430 °C.$^{23}$

We chose to conduct the reaction in a mixed chloride flux media because the eutectic temperature of a mixed chloride flux can be relatively low, which provides a liquid reaction media to facilitate fast diffusion kinetics. Here, we considered LiCl, NaCl, and KCl as candidate flux chemistries to mix with MgCl$_2$. We disqualified a LiCl–MgCl$_2$ flux because the ion-exchange reaction of NaCrS$_2$ with LiCl has a favorable driving force to form LiCrS$_2$, which could compete with the formation of MgCr$_2$S$_4$ (eqn (4)). We also disqualified NaCl–MgCl$_2$ as a potential flux media because NaCl is a byproduct of the metathesis reaction, meaning the NaCl composition of the flux would change as the metathesis reaction proceeds. Any deviation away from the eutectic composition would increase the melting temperature of the NaCl–MgCl$_2$ flux; which, if increased too much, could cause the flux to solidify and thereby disrupt the reaction. KCl–MgCl$_2$ emerges as the ideal flux media, because the formation of KCrS$_2$ from NaCrS$_2$ + KCl is not thermodynamically

![Scheme 1 Two-step metathesis flux synthesis of MgCr$_2$S$_4$.](image-url)
favorable (eqn (5)), and the eutectic point of KCl–MgCl₂ (~430 °C)²³ is lower than that of NaCl–MgCl₂ (~445 °C)²³ Furthermore, the formation of NaCl byproduct in a KCl–MgCl₂ flux would actually lower the KCl–MgCl₂ eutectic temperature,²⁴ and thereby would not impede the flux-mediated reaction kinetics.

\[
\text{NaCrS}_2 + \text{LiCl} \rightarrow \text{LiCrS}_2 + \text{NaCl}; \Delta H_r = -16 \text{ kJ mol}^{-1} \tag{4}
\]

\[
\text{NaCrS}_2 + \text{KCl} \rightarrow \text{KCrS}_2 + \text{NaCl}; \Delta H_r = +33 \text{ kJ mol}^{-1} \tag{5}
\]

These reaction thermodynamics are also straightforward to evaluate using the Materials Project Reaction Calculator app, which can help guide the rational design of flux chemistries.

We synthesized NaCrS₂ in a reaction between CrCl₃ and Na₂S by ball-milling at 450 rpm in a zirconia jar with zirconia milling media. We tried three molar ratios for CrCl₃ : Na₂S—1 : 2 (stoichiometric), 1 : 2.05 (2.5% Na₂S excess), and 1 : 2.5 (25% KBr flux, with excess MgBr₂ and Na₂S, and subsequently removed placed in a carbon crucible together with the MgCl₂–KCl flux for 30 min. In the second step, the ball-milled mixture of NaCrS₂ and NaCl were placed in a carbon crucible together with the MgCl₂–KCl flux at a molar ratio of NaCrS₂ : MgCl₂ = 1 : 5. The reaction was performed at 500 °C for 30 minutes in an inert nitrogen atmosphere. After cooling, the synthesized products were washed with distilled water and centrifuged in air to remove the flux and excess MgCl₂ and Na₂S. Fig. 1 shows the XRD characterization of the synthesis products. The ball-milling of Na₂S and CrCl₃ indeed produced NaCrS₂ with NaCl byproduct, as anticipated from eqn (3). The reaction of NaCrS₂ + NaCl in a MgCl₂–KCl flux resulted in MgCr₂S₄, Cr₂S₃ and MgO, where the ratios of these products varied with the Na₂S excess in the precursor (Fig. 1).

For a stoichiometric ratio of CrCl₃ : Na₂S = 1 : 2, we observe a coexistence of Cr₂S₃ and MgCr₂S₄. When we include Na₂S excess in the synthesis of NaCrS₂ (eqn (3)), the Cr₂S₃ impurity from the flux reaction is diminished. With 25% Na₂S excess, the reaction yields nearly phase-pure MgCr₂S₄.

All metathesis byproducts and flux media (KCl, NaCl, MgCl₂, Na₂S) and any possibly synthesized MgS are soluble in water and were removed from the system by washing with distilled water. Although our final product yields MgCr₂S₄ as the dominant phase, it contains MgO as a minor impurity. These reactions were conducted in inert nitrogen atmosphere, suggesting the incorporation of oxygen in MgO may have arisen from washing with water. To examine the effect of washing with water, we performed the same synthesis reaction of NaCrS₂ with MgBr₂–KBr flux, with excess MgBr₂ and Na₂S, and subsequently removed metathesis products by washing with anhydrous methanol. In the MgBr₂ synthesis, MgO still forms as an impurity phase, in fact with even larger phase fraction than when synthesized in the MgCl₂–KCl flux (Fig. S1, ESI†). This suggests that the oxygen does not originate from the water. Oxygen impurities may have therefore already existed in the MgCl₂ or MgBr₂ precursors, or from a low but nonzero pO₂ or pH₂O in the nitrogen atmosphere.

We performed three control experiments to validate the importance of the designed synthesis parameters for the metathesis reaction of MgCr₂S₄. In our first control experiment, we reacted the traditional precursors MgS + Cr₂S₃ in a MgCl₂–KCl flux at 500 °C for 30 min, and in the second control experiment, we reacted NaCrS₂ + MgCl₂ without the flux at 500 °C for 30 min. Neither of these two control experiments were found to form MgCr₂S₄ (Fig. S2 and S3, ESI†). The former reaction supports the importance of metathesis precursors, NaCrS₂ + MgCl₂, while the latter reaction supports the need for a liquid phase (i.e., MgCl₂–KCl flux). For the third control experiment, we reacted NaCrS₂ with MgCl₂ at 800 °C, where MgCl₂ becomes liquid even without KCl (the melting point of MgCl₂ is 714 °C).²⁵ This reaction did form MgCr₂S₄ along with Cr₂S₃ impurity (Fig. S3, ESI†). This final control reaction shows that MgCl₂ liquid is important for this reaction, and the presence of KCl enables this liquid phase to form well below the MgCl₂ melting point, decreasing the required temperature from 714 °C to 430 °C. Together, these experiments show that the rapid synthesis of MgCr₂S₄ at 500 °C requires the metathesis precursors (NaCrS₂ + MgCl₂) and the MgCl₂–KCl flux.

Rietveld refinement of MgCr₂S₄ synthesized from Na₂S and MgCl₂ excess (Fig. 2a) shows that the lattice parameter of MgCr₂S₄ is 1.01426(12) nm, agreeing with the previously reported MgCr₂S₄ synthesized by high-temperature solid-state synthesis (1.01415(2) nm).¹² Rietveld refinement shows no inversion between Mg and Cr sites in the spinel structure. Fig. 2b shows the STEM images and corresponding EDX mapping of MgCr₂S₄ particles synthesized via metathesis reactions with Na₂S and MgCl₂ excess. The as-synthesized particles are 50–200 nm in size and 20–50 nm in thickness. The relative surface area of powder
by N₂ absorption is found to be 55 m² g⁻¹. These small MgCr₂S₄ particle sizes result from the low temperatures and short reaction times of metathesis synthesis, which quench the nanoparticles shortly after nucleation and before significant crystal growth occurs.14 This can be contrasted against conventional solid-state synthesis, where high reaction temperatures and long anneal times tend to yield large particle sizes due to Ostwald ripening and particle coarsening during crystal growth.5,26 The molar ratio of Mg/Cr/S determined by EDX of the product is 1/2.4/4.1, which is close to the stoichiometric ratio of MgCr₂S₄. EDX mapping showed homogeneously distributed Mg and Cr, further supporting the formation of MgCr₂S₄.

The electronic properties of MgCr₂S₄ are an important consideration for Mg-ion battery performance and photochemical applications because Cr₂S₃ has been reported as an n- and p-type semiconductor (band gap, E₉ = 0.8 eV).27 We measured the optical band gap of MgCr₂S₄ using diffuse reflectance spectroscopy (ESI†), which we estimate from the Tauc-plot to be 2.2 eV (Fig. S4, ESI†). By means of Mott–Schottky plot analysis (Fig. S5, ESI†), MgCr₂S₄ is shown to be an n-type semiconductor with a flat-band potential of ca. −0.6 V vs. Ag/AgCl at pH 7.0, indicating it is also a candidate H₂ evolution photocatalyst under visible light radiation.28

Discussion

The accelerated formation of MgCr₂S₄ during metathesis (~30 minutes) compared with solid-state synthesis (~2 weeks) can be rationalized from the thermodynamic topology of each synthesis space. Fig. 3a shows the ternary convex hull phase diagram for Mg–Cr–S, and Fig. 3b shows a pseudo-ternary convex hull phase diagram for MgCl₂–CrCl₃–Na₂S, which is a slice of the larger 5-component Mg–Cr–S–Na–Cl phase diagram. The colorbar illustrates the ‘depth’ of the convex hull, corresponding to the reaction energy at each composition relative to the precursor endpoints. Even though MgCr₂S₄ has a very favorable formation enthalpy of −1.289 eV atom⁻¹, MgS and Cr₂S₃ also have very negative formation enthalpies of −1.76 and −1.097 eV atom⁻¹, respectively. In the Mg–Cr–S phase diagram, the deepest point is at the MgS composition, meaning MgS acts as a thermodynamic ‘sink’ in the traditional ceramic synthesis and explains why MgS tends to persist during the traditional ceramic synthesis. Fig. 3c depicts the tiny energy gain to form MgCr₂S₄ along the MgS–Cr₂S₃ reaction tie-line, which further underlies the slow reaction kinetics.

On the other hand, the MgCl₂–CrCl₃–Na₂S metathesis phase diagram exhibits a qualitatively different thermodynamic topology. Here, each Mg–Cr–S composition must also be accompanied by a stoichiometrically balanced amount of NaCl, which modifies the reaction energies at each composition in the pseudo-ternary space. MgCr₂S₄ is balanced by 8NaCl, whereas MgS is balanced by 2NaCl, NaCrS₂ by 3NaCl, and Cr₂S₃ by 6NaCl. In the MgCl₂–CrCl₃–Na₂S phase diagram, the inclusion of NaCl shifts the deepest thermodynamic point from MgS to MgCr₂S₄ + Cr₂S₃, which are indeed the observed reaction products in Fig. 1 when synthesized without Na₂S excess. The metathesis route therefore enhances the selective synthesis of MgCr₂S₄ by relocating the thermodynamic sink in composition space. Furthermore, because S is tied up with Cr in the NaCrS₂ precursor, MgS is unlikely to form in the metathesis reaction, as this would require NaCrS₂ decomposition and subsequent reaction of S with the MgCl₂ flux.

By increasing the amount of Na₂S excess in the precursor, the diffraction peaks of MgCr₂S₄ became dominant and the Cr₂S₃ impurity is eliminated (Fig. 1). This can be rationalized from Le Chatlier’s principle, as illustrated in Fig. 3c, where Cr₂S₃ impurities react with excess Na₂S as well as excess MgCl₂ from the flux, which further drives the reaction towards the MgCr₂S₄ product side. The reaction between Cr₂S₃, MgCl₂ and Na₂S (Fig. 3c, orange line) has larger thermodynamic driving force than that between NaCrS₂ and MgCl₂ (Fig. 3c, blue line). Operating with excess Na₂S and MgCl₂ therefore encourages the formation of MgCr₂S₄ at the expense of the Cr₂S₃ impurity. Wustrow et al. used a similar strategy in the traditional solid-state synthesis route, providing excess MgS to react with Cr₂S₃ impurities in order to achieve high-purity MgCr₂S₄.

Fig. 3  (a) Rietveld profile of MgCr₂S₄ synthesized with excess Na₂S. Residual is shown as the blue line. (b) STEM image of MgCr₂S₄ platelet particles. Right side is STEM and EDX mapping: red and green signals represent Mg and Cr signals, respectively.
Conclusions

In summary, we demonstrated metathesis reactions as a powerful synthesis route to inorganic materials with otherwise small thermodynamic driving forces. The formation of NaCl as a byproduct not only increases the reaction enthalpy of forming the target phase, but shifts the topology of the phase diagram, changing the composition of the deepest point of the convex hull and thereby enhancing structure-selectivity. Here, we demonstrated the metathesis synthesis of MgCr$_2$S$_4$ in only 30 minutes at 500 $^\circ$C, in contrast to a two-week traditional ceramic synthesis at 800 $^\circ$C with multiple intermediate regrinds. Furthermore, the synthesized MgCr$_2$S$_4$ particles were 100–200 nm in size, which is a smaller particle size than would be realized in a direct solid-state ceramic synthesis. Our metathesis synthesis of MgCr$_2$S$_4$ enables future studies of its electrochemical performance for Mg-battery and photocatalytic applications.

From a more general perspective, the concept of the metathesis reaction broadens how we evaluate synthesis and synthesizability. Traditionally, we take an ‘addition’ approach to materials synthesis, where one mixes together simple precursors to form a more complex multicomponent material. In the metathesis route, the reactions are driven by stable but removable byproducts, which include but are not limited to alkali metal halides. For example, the reaction of chlorides/oxides with H$_2$S or NH$_3$ gas could also be used to synthesize sulfides, oxysulfides, nitrides and oxynitrides by generating HCl/H$_2$O gas as a byproduct.$^{29-31}$ Inclusion of these extra species into the phase diagram provides new degrees of freedom for synthesis design, opening up a vast and promising design space for clever metathesis reactions, which can be rapidly screened and evaluated using publicly available DFT thermochemical data. Creative new precursor combinations are still waiting to be exploited within a metathesis synthesis paradigm, which may currently be overlooked due to preconceived notions about precursor selection.$^{32}$

Methods

The thermodynamics for all reactions discussed in this work are obtained from density functional theory calculations of the
reaction enthalpy, $\Delta H_r$, as calculated using the Reaction Calculator app on the Materials Project database. The deviation between calculated and experimentally obtained $\Delta H_r$ for solid-state reactions, such as those discussed in this work, is expected to be on the order of $\pm 5$–$10 \text{ kJ mol}^{-1}$. We note that $\Delta H$ calculations do not account for the effects of temperature and entropy on the reaction free energies. For solid-state reactions, the TAS contribution to the free energy is generally negligible when all products and reactants are solids. We demonstrated this by calculating the Gibbs energies of reaction, $\Delta G_r$, at 1000 K for each of the reactions in this work using the model described in ref. 36 (Table S1, ESI†). $\Delta H_r$ and $\Delta G_r$ (1000 K) are $\pm 2$ and $\pm 9 \text{ kJ mol}^{-1}$, respectively, for eqn (1), and $\pm 47$ and $\pm 50 \text{ kJ mol}^{-1}$ for eqn (2).

The syntheses were performed by two-step metathesis reactions. First, the reaction between CrCl$_3$ (99%, Sigma-Aldrich) and Na$_2$S (Nagao & Co., Ltd) with the molar ratio of 1:2, 1:2.05 (2.5% Na$_2$S excess), and 1:2.5 (25% Na$_2$S excess) were performed to produce NaCrS$_2$ and NaCl. This reaction was performed by ball-milling at 450 rpm with zirconia pot and ball. The second step was the reaction of NaCrS$_2$ with MgCl$_2$. This reaction was performed at 500 °C for 30 minutes in an inert atmosphere. The ball-milled mixture of NaCrS$_2$ and NaCl was placed in a carbon crucible together with an MgCl$_2$–KCl flux: MgCl$_2$ (99.9%, Kojundo Chemical Laboratory), KC1 (99.5%, Wako Chemicals). The molar ratio of NaCrS$_2$ to MgCl$_2$ was 1:5. After cooling, the synthesized products were washed with distilled water and centrifuged in ambient atmosphere to remove flux and excess MgCl$_2$ and Na$_2$S. XRD diffraction was measured by MiniFlex 600 (Rigaku). Composition ratio was determined by EDX equipped with scanning electron microscopy (SEM: TM3030). Morphology was observed by scanning transmission electron microscopy (STEM: Hitachi HD-2000). The diffuse reflectance spectra of MgCr$_2$S$_4$ were measured using a UV-vis spectrophotometer (JASCO V-750) at room temperature. Moth-Schottky plot measurements were conducted using an ALS760Es electrochemical analyzer (BAS) at room temperature. The electrochemical cell was made of Pyrex glass and was a three-electrode-type system using Pt wire and an Ag/AgCl electrode (in saturated KCl aqueous solution) as the counter and reference electrodes, respectively. The pH of the electrolyte solution was adjusted to be 7.0 by mixing NaH$_2$PO$_4$·2H$_2$O (99.0–102.0%, Kanto Chemical) and Na$_2$HPO$_4$·12H$_2$O (>99.0%, Kanto Chemical), while keeping the total phosphate concentration of 0.1 M.

Conflicts of interest
There are no conflicts to declare.

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