



# Selective metathesis synthesis of $\text{MgCr}_2\text{S}_4$ by control of thermodynamic driving forces†

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$\text{MgCr}_2\text{S}_4$  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  $\text{MgCr}_2\text{S}_4$  from  $\text{MgS} + \text{Cr}_2\text{S}_3$  binaries requires weeks of annealing at 800 °C with numerous intermediate regrinds. The slow reaction kinetics of  $\text{MgS} + \text{Cr}_2\text{S}_3 \rightarrow \text{MgCr}_2\text{S}_4$  can be attributed to a miniscule thermodynamic driving force of  $\Delta H = -2 \text{ kJ mol}^{-1}$ . Here, we demonstrate that the double ion-exchange metathesis reaction,  $\text{MgCl}_2 + 2\text{NaCrS}_2 \rightarrow \text{MgCr}_2\text{S}_4 + 2\text{NaCl}$ , has a reaction enthalpy of  $\Delta H = -47 \text{ kJ mol}^{-1}$ , which is thermodynamically driven by the large exothermicity of NaCl formation. Using this metathesis reaction, we successfully synthesized  $\text{MgCr}_2\text{S}_4$  nanoparticles (<200 nm) from  $\text{MgCl}_2$  and  $\text{NaCrS}_2$  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  $\text{MgCr}_2\text{S}_4$  in the metathesis reaction from the topology of the DFT-calculated pseudo-ternary  $\text{MgCl}_2\text{--CrCl}_3\text{--Na}_2\text{S}$  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,<sup>1</sup> serving as the first step to any further investigation into the

### New concepts

Complex inorganic materials are usually synthesized by an ‘addition’ approach, whereby simple precursors are reacted to form a target multicomponent phase. However, if the simple precursors are already very stable themselves, then there may be little free energy left to drive a chemical reaction to a higher-component phase, which often results in slow kinetics and long-lived reaction impurities. Here, we demonstrate that metathesis reactions operate in a fundamentally different synthesis paradigm. During double ion-exchange metathesis, the inclusion of extra chemical species, such as  $\text{Na}^+$  and  $\text{Cl}^-$ , dramatically changes the thermodynamic topology of the phase diagram. This shifting energy landscape modifies the relevant chemical reactions, intensifies reaction thermodynamics, and can relocate the ‘thermodynamic sink’ of the phase diagram to a new composition—enhancing structure-selectivity towards a target multicomponent phase. We further demonstrate that candidate metathesis reactions can be rapidly screened and evaluated using publicly available DFT thermochemical data. The additional degrees of freedom afforded by including extra elements into the phase diagram opens up a vast and promising design space for creative new metathesis reactions.

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.<sup>2</sup> 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.<sup>3</sup> Because of these often conflicting constraints, solid-state synthesis occasionally proceeds with slow reaction kinetics, non-equilibrium intermediates, or impurities,<sup>4–6</sup> 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  $\text{MgCr}_2\text{S}_4$  thiospinel. In the search for Mg-ion cathode materials beyond the dominant Chevrel  $\text{Mo}_6\text{S}_8$  phase,<sup>7</sup> Mg-thiospinels emerged as a promising

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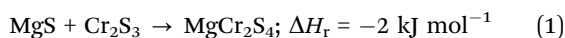
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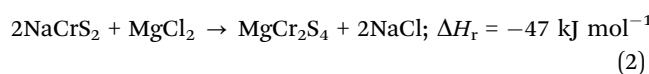
class of compounds. Thiospinels benefit from a soft sulfur anion sublattice, which enhances Mg-ion mobility compared to oxides, and a spinel framework, which provides a favorable tetrahedral  $\rightarrow$  octahedral  $\rightarrow$  tetrahedral  $\text{Mg}^{2+}$  migration path with a low diffusion barrier.<sup>8,9</sup>  $\text{MgTi}_2\text{S}_4$  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 W h  $\text{kg}^{-1}$ .<sup>10,11</sup> Our computational search for other candidate Mg-thiospinels found  $\text{MgCr}_2\text{S}_4$  to possess compelling properties, including a high specific capacity (209 mA h  $\text{g}^{-1}$ ) and energy density (244 W h  $\text{kg}^{-1}$ ), as well as a relatively low Mg-ion diffusion barrier of 540 meV.<sup>10</sup> Notably,  $\text{MgCr}_2\text{S}_4$  was calculated with 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  $\text{MgCr}_2\text{S}_4$  through a traditional solid-state synthesis approach—although it was found to be a laborious reaction.<sup>12</sup> Starting from elemental (Mg + Cr + S) precursors, the binary sulfides,  $\text{MgS}$  and  $\text{Cr}_2\text{S}_3$ , formed rapidly upon heating. However, the subsequent reaction from  $\text{MgS}$  +  $\text{Cr}_2\text{S}_3$  to ternary  $\text{MgCr}_2\text{S}_4$  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  $\text{MgCr}_2\text{S}_4$  decomposes into  $\text{MgS}$  and  $\text{Cr}_2\text{S}_3$  above 900 °C. Although  $\text{MgCr}_2\text{S}_4$  is indeed a thermodynamically stable compound, we calculate the driving force (reaction enthalpy,  $\Delta H_r$ ) for its formation from  $\text{MgS}$  +  $\text{Cr}_2\text{S}_3$  to be extremely small ( $-2$  kJ  $\text{mol}^{-1}$ , eqn (1)).

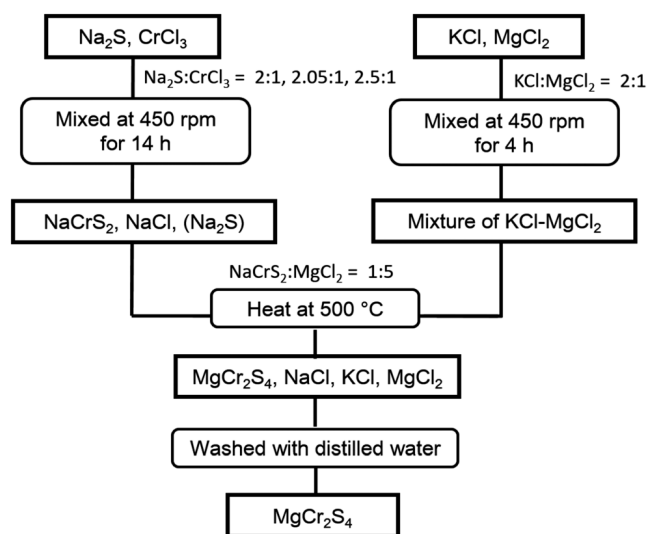


All reaction energies in this work utilize the publicly available DFT-calculated thermochemical data in the Materials Project database (Methods). The slow reaction kinetics observed by Wustrow *et al.* can be attributed to this miniscule thermodynamic driving force. Moreover, long synthesis times can lead to the ripening of large  $\text{MgCr}_2\text{S}_4$  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  $\text{MgCr}_2\text{S}_4$  can be written as:



The  $>20\times$  increase in thermodynamic driving force from  $\Delta H_r = -2$  kJ  $\text{mol}^{-1}$  to  $-47$  kJ  $\text{mol}^{-1}$  is because  $\text{Na}^+$  and  $\text{Cl}^-$  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.<sup>13</sup> Not only can metathesis reactions be used to synthesize stable materials with otherwise small reaction energies, the increased thermodynamic driving force and fast

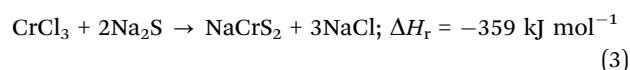


Scheme 1 Two-step metathesis flux synthesis of  $\text{MgCr}_2\text{S}_4$ .

reaction kinetics also affords the synthesis of metastable materials,<sup>14</sup> as were previously demonstrated on nitrides,<sup>13,15–17</sup> sulfides,<sup>13,18,19</sup> and oxides.<sup>20–22</sup> Motivated by the metathesis reaction shown in eqn (2), we designed a two-step sequential metathesis reaction to synthesize  $\text{MgCr}_2\text{S}_4$ , as visualized in Scheme 1.

## Results

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



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

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  $\text{MgCl}_2$ . We disqualified a LiCl– $\text{MgCl}_2$  flux because the ion-exchange reaction of  $\text{NaCrS}_2$  with LiCl has a favorable driving force to form  $\text{LiCrS}_2$ , which could compete with the formation of  $\text{MgCr}_2\text{S}_4$  (eqn (4)). We also disqualified NaCl– $\text{MgCl}_2$  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– $\text{MgCl}_2$  flux; which, if increased too much, could cause the flux to solidify and thereby disrupt the reaction. KCl– $\text{MgCl}_2$  emerges as the ideal flux media, because the formation of  $\text{KCrS}_2$  from  $\text{NaCrS}_2$  + KCl is not thermodynamically

favorable (eqn (5)), and the eutectic point of KCl–MgCl<sub>2</sub> (~430 °C)<sup>23</sup> is lower than that of NaCl–MgCl<sub>2</sub> (~445 °C)<sup>24</sup>. Furthermore, the formation of NaCl byproduct in a KCl–MgCl<sub>2</sub> flux would actually lower the KCl–MgCl<sub>2</sub> eutectic temperature,<sup>24</sup> and thereby would not impede the flux-mediated reaction kinetics.



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 NaCrS<sub>2</sub> in a reaction between CrCl<sub>3</sub> and Na<sub>2</sub>S by ball-milling at 450 rpm in a zirconia jar with zirconia milling media. We tried three molar ratios for CrCl<sub>3</sub>:Na<sub>2</sub>S—1:2 (stoichiometric), 1:2.05 (2.5% Na<sub>2</sub>S excess), and 1:2.5 (25% Na<sub>2</sub>S excess)—producing NaCrS<sub>2</sub> and NaCl (eqn (3)). In the second step, the ball-milled mixture of NaCrS<sub>2</sub> and NaCl were placed in a carbon crucible together with the MgCl<sub>2</sub>–KCl flux at a molar ratio of NaCrS<sub>2</sub>:MgCl<sub>2</sub> = 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 MgCl<sub>2</sub> and Na<sub>2</sub>S. Fig. 1 shows the XRD characterization of the synthesis products. The ball-milling of Na<sub>2</sub>S and CrCl<sub>3</sub> indeed produced NaCrS<sub>2</sub> with NaCl byproduct, as anticipated from eqn (3). The reaction of NaCrS<sub>2</sub> + NaCl in a MgCl<sub>2</sub>–KCl flux resulted in MgCr<sub>2</sub>S<sub>4</sub>, Cr<sub>2</sub>S<sub>3</sub> and MgO, where the ratios of these products varied with the Na<sub>2</sub>S excess in the precursor (Fig. 1). For a stoichiometric ratio of CrCl<sub>3</sub>:Na<sub>2</sub>S = 1:2, we observe a coexistence of Cr<sub>2</sub>S<sub>3</sub> and MgCr<sub>2</sub>S<sub>4</sub>. When we include Na<sub>2</sub>S excess in the synthesis of NaCrS<sub>2</sub> (eqn (3)), the Cr<sub>2</sub>S<sub>3</sub> impurity from the flux reaction is diminished. With 25% Na<sub>2</sub>S excess, the reaction yields nearly phase-pure MgCr<sub>2</sub>S<sub>4</sub>.

All metathesis byproducts and flux media (KCl, NaCl, MgCl<sub>2</sub>, Na<sub>2</sub>S) 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 MgCr<sub>2</sub>S<sub>4</sub> 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 NaCrS<sub>2</sub> with MgBr<sub>2</sub>–KBr flux, with excess MgBr<sub>2</sub> and Na<sub>2</sub>S, and subsequently removed metathesis products by washing with anhydrous methanol. In the MgBr<sub>2</sub> synthesis, MgO still forms as an impurity phase, in fact with even larger phase fraction than when synthesized in the MgCl<sub>2</sub>–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 MgCl<sub>2</sub> or MgBr<sub>2</sub> precursors, or from a low but nonzero *p*<sub>O<sub>2</sub></sub> and/or *p*<sub>H<sub>2</sub>O</sub> in the nitrogen atmosphere.

We performed three control experiments to validate the importance of the designed synthesis parameters for the metathesis reaction of MgCr<sub>2</sub>S<sub>4</sub>. In our first control experiment, we reacted the traditional precursors MgS + Cr<sub>2</sub>S<sub>3</sub> in a MgCl<sub>2</sub>–KCl flux at 500 °C for 30 min, and in the second control experiment,

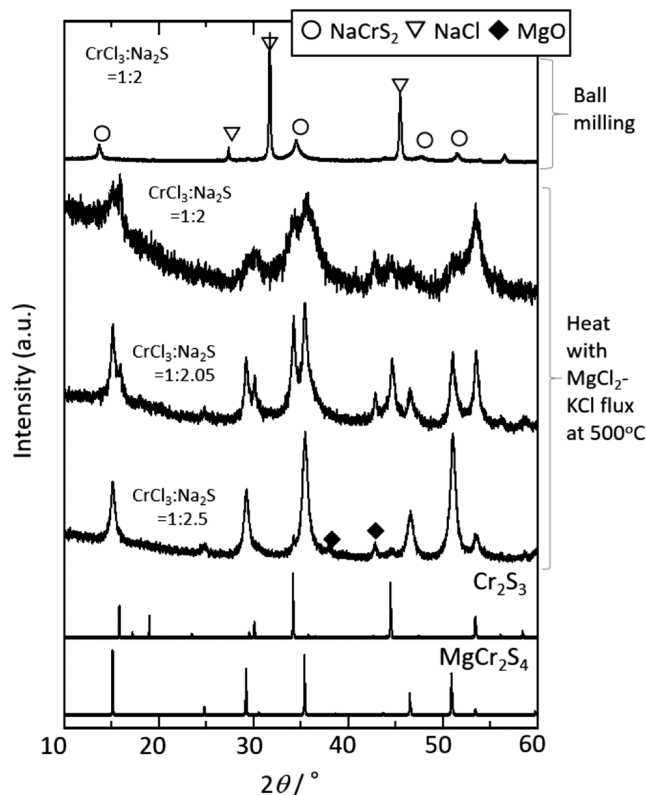


Fig. 1 XRD patterns of NaCrS<sub>2</sub> powder synthesized via ball milling from CrCl<sub>3</sub> and Na<sub>2</sub>S, and MgCr<sub>2</sub>S<sub>4</sub> powder synthesized by NaCrS<sub>2</sub> and MgCl<sub>2</sub>–KCl flux at 500 °C and subsequent wash with water. Different molar ratios of CrCl<sub>3</sub>:Na<sub>2</sub>S were utilized for producing MgCr<sub>2</sub>S<sub>4</sub>.

we reacted NaCrS<sub>2</sub> + MgCl<sub>2</sub> without the flux at 500 °C for 30 min. Neither of these two control experiments were found to form MgCr<sub>2</sub>S<sub>4</sub> (Fig. S2 and S3, ESI†). The former reaction supports the importance of metathesis precursors, NaCrS<sub>2</sub> + MgCl<sub>2</sub>, while the latter reaction supports the need for a liquid phase (*i.e.*, MgCl<sub>2</sub>–KCl flux). For the third control experiment, we reacted NaCrS<sub>2</sub> with MgCl<sub>2</sub> at 800 °C, where MgCl<sub>2</sub> becomes liquid even without KCl (the melting point of MgCl<sub>2</sub> is 714 °C).<sup>25</sup> This reaction did form MgCr<sub>2</sub>S<sub>4</sub>, along with Cr<sub>2</sub>S<sub>3</sub> impurity (Fig. S3, ESI†). This final control reaction shows that MgCl<sub>2</sub> liquid is important for this reaction, and the presence of KCl enables this liquid phase to form well below the MgCl<sub>2</sub> melting point, decreasing the required temperature from 714 °C to 430 °C. Together, these experiments show that the rapid synthesis of MgCr<sub>2</sub>S<sub>4</sub> at 500 °C requires the metathesis precursors (NaCrS<sub>2</sub> + MgCl<sub>2</sub>) and the MgCl<sub>2</sub>–KCl flux.

Rietveld refinement of MgCr<sub>2</sub>S<sub>4</sub> synthesized from Na<sub>2</sub>S and MgCl<sub>2</sub> excess (Fig. 2a) shows that the lattice parameter of MgCr<sub>2</sub>S<sub>4</sub> is 1.01426(12) nm, agreeing with the previously reported MgCr<sub>2</sub>S<sub>4</sub> synthesized by high-temperature solid-state synthesis (1.01415(2) nm).<sup>12</sup> 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 MgCr<sub>2</sub>S<sub>4</sub> particles synthesized via metathesis reactions with Na<sub>2</sub>S and MgCl<sub>2</sub> excess. The as-synthesized particles are 50–200 nm in size and 20–50 nm in thickness. The relative surface area of powder

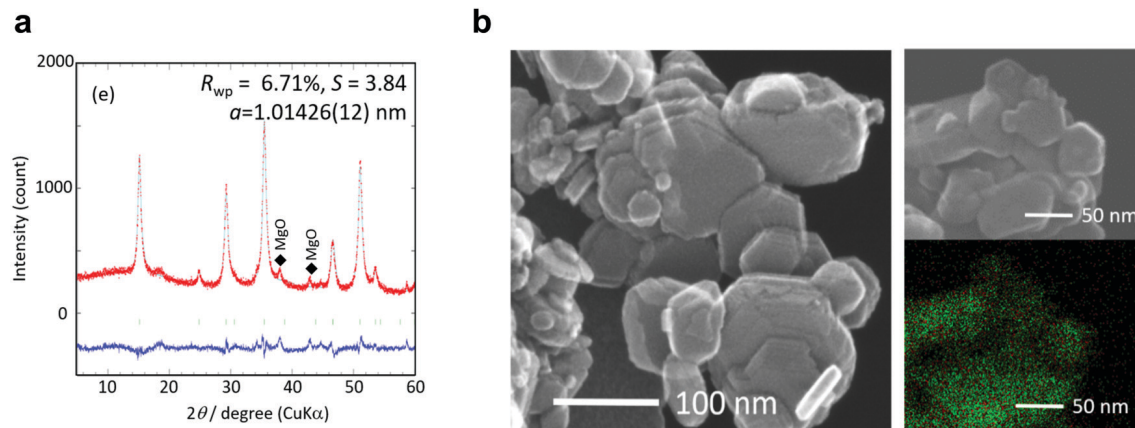


Fig. 2 (a) Rietveld profile of  $\text{MgCr}_2\text{S}_4$  synthesized with excess  $\text{Na}_2\text{S}$ . Residual is shown as the blue line. (b) STEM image of  $\text{MgCr}_2\text{S}_4$  platelet particles. Right side is STEM and EDX mapping: red and green signals represent Mg and Cr signals, respectively.

by  $\text{N}_2$  absorption is found to be  $55 \text{ m}^2 \text{ g}^{-1}$ . These small  $\text{MgCr}_2\text{S}_4$  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.<sup>13</sup> 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.<sup>3,26</sup> 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  $\text{MgCr}_2\text{S}_4$ . EDX mapping showed homogeneously distributed Mg and Cr, further supporting the formation of  $\text{MgCr}_2\text{S}_4$ .

The electronic properties of  $\text{MgCr}_2\text{S}_4$  are an important consideration for Mg-ion battery performance and photochemical applications because  $\text{Cr}_2\text{S}_3$  has been reported as an n- and p-type semiconductor (band gap,  $E_g = 0.8 \text{ eV}$ ).<sup>27</sup> We measured the optical band gap of  $\text{MgCr}_2\text{S}_4$  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†),  $\text{MgCr}_2\text{S}_4$  is shown to be an n-type semiconductor with a flat-band potential of ca.  $-0.6 \text{ V}$  vs. Ag/AgCl at pH 7.0, indicating it is also a candidate  $\text{H}_2$  evolution photocatalyst under visible light radiation.<sup>28</sup>

## Discussion

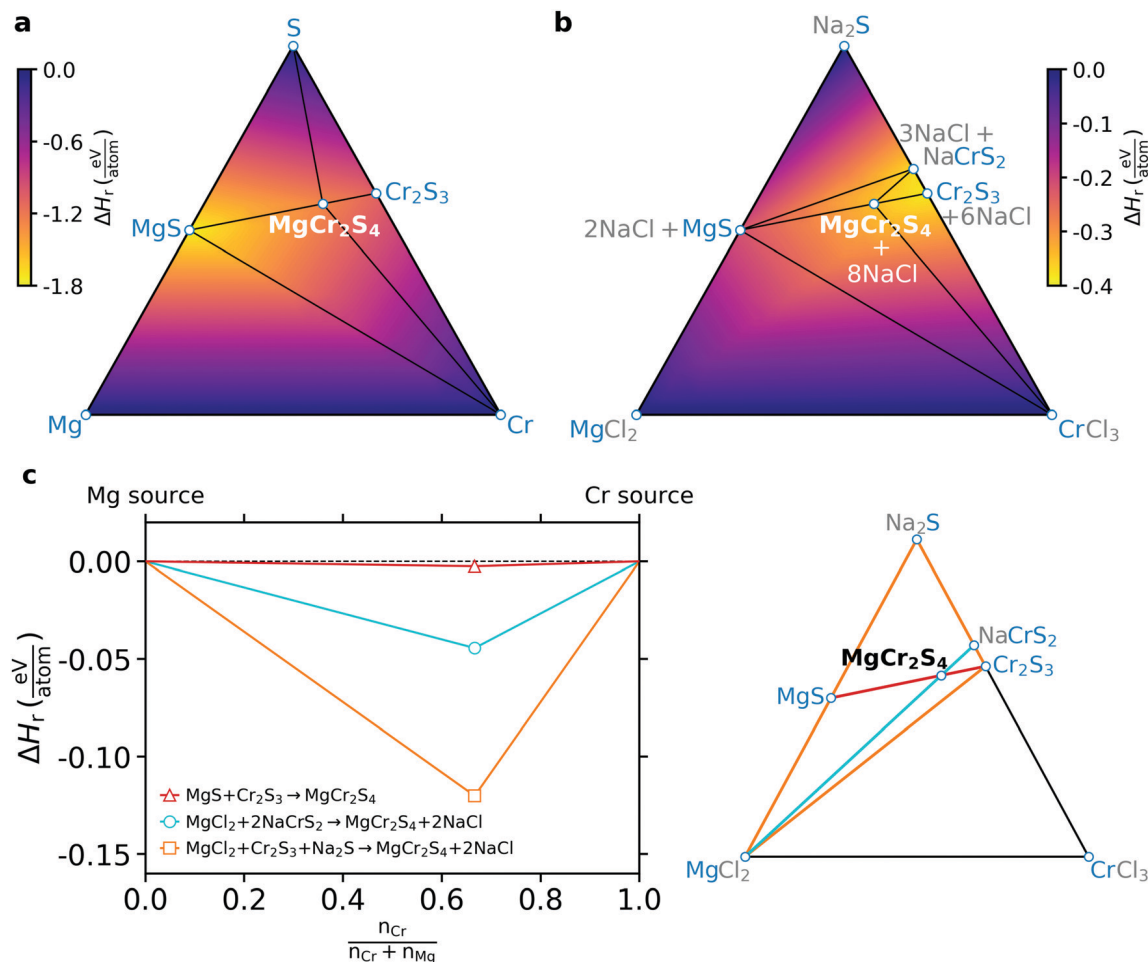
The accelerated formation of  $\text{MgCr}_2\text{S}_4$  during metathesis ( $\sim 30$  minutes) compared with solid-state synthesis ( $\sim 2$  weeks) can be rationalized from the thermodynamic topology of each synthesis space. Fig. 3a shows the ternary convex hull phase diagram for Mg–Cr–S, and Fig. 3b shows a pseudo-ternary convex hull phase diagram for  $\text{MgCl}_2$ – $\text{CrCl}_3$ – $\text{Na}_2\text{S}$ , 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  $\text{MgCr}_2\text{S}_4$  has a very favorable formation enthalpy of  $-1.289 \text{ eV atom}^{-1}$ , MgS and

$\text{Cr}_2\text{S}_3$  also have very negative formation enthalpies of  $-1.76$  and  $-1.097 \text{ eV atom}^{-1}$ , 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  $\text{MgCr}_2\text{S}_4$  along the  $\text{MgS}$ – $\text{Cr}_2\text{S}_3$  reaction tie-line, which further underlies the slow reaction kinetics.

On the other hand, the  $\text{MgCl}_2$ – $\text{CrCl}_3$ – $\text{Na}_2\text{S}$  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.  $\text{MgCr}_2\text{S}_4$  is balanced by 8NaCl, whereas MgS is balanced by 2NaCl,  $\text{NaCrS}_2$  by 3NaCl, and  $\text{Cr}_2\text{S}_3$  by 6NaCl. In the  $\text{MgCl}_2$ – $\text{CrCl}_3$ – $\text{Na}_2\text{S}$  phase diagram, the inclusion of NaCl shifts the deepest thermodynamic point from MgS to  $\text{MgCr}_2\text{S}_4 + \text{Cr}_2\text{S}_3$ , which are indeed the observed reaction products in Fig. 1 when synthesized without  $\text{Na}_2\text{S}$  excess. The metathesis route therefore enhances the selective synthesis of  $\text{MgCr}_2\text{S}_4$  by relocating the thermodynamic sink in composition space. Furthermore, because S is tied up with Cr in the  $\text{NaCrS}_2$  precursor, MgS is unlikely to form in the metathesis reaction, as this would require  $\text{NaCrS}_2$  decomposition and subsequent reaction of S with the  $\text{MgCl}_2$  flux.

By increasing the amount of  $\text{Na}_2\text{S}$  excess in the precursor, the diffraction peaks of  $\text{MgCr}_2\text{S}_4$  became dominant and the  $\text{Cr}_2\text{S}_3$  impurity is eliminated (Fig. 1). This can be rationalized from Le Chatelier’s principle, as illustrated in Fig. 3c, where  $\text{Cr}_2\text{S}_3$  impurities react with excess  $\text{Na}_2\text{S}$  as well as excess  $\text{MgCl}_2$  from the flux, which further drives the reaction towards the  $\text{MgCr}_2\text{S}_4$  product side. The reaction between  $\text{Cr}_2\text{S}_3$ ,  $\text{MgCl}_2$  and  $\text{Na}_2\text{S}$  (Fig. 3c, orange line) has larger thermodynamic driving force than that between  $\text{NaCrS}_2$  and  $\text{MgCl}_2$  (Fig. 3c, blue line). Operating with excess  $\text{Na}_2\text{S}$  and  $\text{MgCl}_2$  therefore encourages the formation of  $\text{MgCr}_2\text{S}_4$  at the expense of the  $\text{Cr}_2\text{S}_3$  impurity. Wustrow *et al.* used a similar strategy in the traditional solid-state synthesis route, providing excess MgS to react with  $\text{Cr}_2\text{S}_3$  impurities in order to achieve high-purity  $\text{MgCr}_2\text{S}_4$ .





**Fig. 3** Ternary phase diagrams for (a) Mg–Cr–S, corresponding to a traditional ceramic synthesis reaction and (b)  $\text{MgCl}_2$ – $\text{CrCl}_3$ – $\text{Na}_2\text{S}$ , corresponding to a metathesis reaction. The color bar indicates the reaction enthalpy between the corners of each triangle and the convex hull, which represents the minimum energy phase or mixture of phases at each composition. For (b),  $\Delta H_r$  is calculated by considering the formation of NaCl where appropriate and therefore is a pseudo-ternary representation of the quinary Mg–Cr–S–Na–Cl chemical space. (c) Driving force for  $\text{MgCr}_2\text{S}_4$  formation from three routes, highlighted by their color in the corresponding pseudo-ternary phase diagram. The reaction relevant to ceramic synthesis (eqn (1)) is shown in red, the metathesis reaction (eqn (3)) is shown in blue, and the reaction that proceeds with excess  $\text{Na}_2\text{S}$  +  $\text{MgCl}_2$ , and consumes impurity  $\text{Cr}_2\text{S}_3$ , is shown in orange.

## 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  $\text{MgCr}_2\text{S}_4$  in only 30 minutes at 500 °C, in contrast to a two-week traditional ceramic synthesis at 800 °C with multiple intermediate regrinds. Furthermore, the synthesized  $\text{MgCr}_2\text{S}_4$  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  $\text{MgCr}_2\text{S}_4$  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  $\text{H}_2\text{S}$  or  $\text{NH}_3$  gas could also be used to synthesize sulfides, oxysulfides, nitrides and oxynitrides by generating  $\text{HCl}/\text{H}_2\text{O}$  gas as a byproduct.<sup>29–31</sup> 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.<sup>32</sup>

## 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.<sup>33</sup> 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  $\sim 5\text{--}10\text{ kJ mol}^{-1}$ .<sup>34,35</sup> 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  $T\Delta S$  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  $-2$  and  $-9\text{ kJ mol}^{-1}$ , respectively, for eqn (1), and  $-47$  and  $-50\text{ kJ mol}^{-1}$  for eqn (2).

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