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This work establishes the advantages and disadvantages of using a solid state metathesis approach for the synthesis of layered mixed anion compounds, where a salt byproduct provides additional reaction driving force, in comparison to the conventional solid state synthesis approach. We evaluate several reactions across a range of temperatures, and can conclude that the two methods do yield different results, and the metathesis approach has some advantages. It provides greater selectivity and formation of target phases at lower temperatures, which may be beneficial for some applications. However the conventional approach can replicate this success at higher temperatures, and does not produce the salt byproduct thus does not require an additional purification step. The work establishes the differences between the two approaches, and confirms that the conventional approach should remain as the principal method for the synthesis of this class of compound.

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COMMUNICATION

Metathesis and the building block approach to novel layered copper oxyselenides – useful tool or synthetic dead-end?

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The use of metathesis, or ionic double displacement reactions, for the synthesis of layered copper oxyselenides is explored, and compared to the conventional solid state reaction approach across a range of temperatures. We have determined that metathesis does offer some advantages in product selectivity at low temperature but due to more complex synthetic requirements does not warrant more widespread adoption.

Metathesis, or salt forming, reactions are ionic double displacement reactions long established in both organic and inorganic chemistry to utilize the formation of a stable salt as a thermodynamic sink to drive forward a desired reaction.[1-5] In this paper we will discuss the use of metathesis reactions in the context of a class of mixed anion layered materials that our research group has been focussed on for a number of years. These are of the type $A_xB_yO_zCu_2Ch_2$, where typically: *A* = Sr, Ba; *B* = Ga, Sc, In or Zn; and *Ch* = S or Se.[6-10] These are a well-established class of material, adopting tetragonal space groups with distinct layers of ternary metal oxide separated by copper chalcogenide layers.[11] Many related compounds are also known where the oxide layers are separated by iron pnictide layers,[12, 13] or more rarely, other 'heavy-anion' layers such as chromium arsenide,[14] or zinc arsenide.[15] These mixed anion materials have been investigated for their potential as LED emitters,[16] p-type transparent conductors,[17] and superconductors.[18]

In the majority of cases, these are synthesized by solid-state reaction (SSR) or what we will call the ***conventional*** approach, whereby elements and binary oxides, chalcogenides or pnictides are ground together in appropriate stoichiometric ratios, and then reacted at elevated temperatures in vacuum sealed silica ampoules to produce the target material. However, Cario *et al* have reported that these layered materials can also be synthesized by an alternative ***metathesis*** route from pairs of precursors in which the respective oxide and chalcogenide or pnictide layers are 'pre-assembled'.[19, 20] For example,

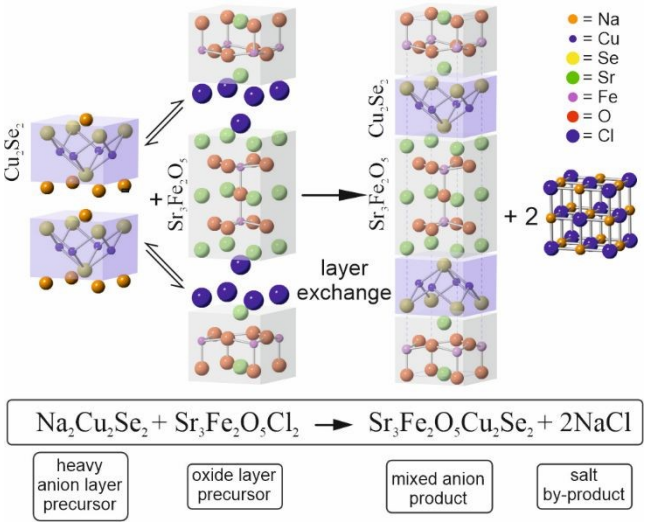

Figure 1 Example layered metathesis reaction, showing unit cells of precursors and products, to emphasize the structural fragments that are 'preassembled' in the precursors.

$Sr_3Fe_2O_5Cl_2$ and $Na_2Cu_2Se_2$ contain the oxide and chalcogenide layers found in $Sr_3Fe_2O_5Cu_2Se_2$, and these can react to form this target, with NaCl as the stable salt by-product. This is shown graphically in figure 1.

In the original work by Cario *et al* the focus was to identify 2D secondary building units from known compounds which could be combined to form novel layered structures, in a building block approach to materials design and discovery.[21] The oxyhalide structures such as $Sr_3Fe_2O_5Cl_2$ and the ternary selenide $Na_2Cu_2Se_2$ (which adopts the *PbFCl* structure type) were identified, amongst others, as containing compatible secondary building units based on charge and size considerations. However, it was realised that as well as being inspiration for possible layers, the composition of these materials meant that they could also be used as precursors for a direct metathesis reaction. This was successful, but for all cases considered the conventional approach was also able to synthesize the target materials, although a higher reaction temperature was used (800 °C) compared to the metathesis approach (600 °C).[22] There was no suggestion by the authors

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that the 'pre-assembled' layers in either $Sr_3Fe_2O_5Cl_2$ or $Na_2Cu_2Se_2$ would remain intact during the reaction, and this is unlikely given the standard model of solid state reactions with ion diffusion at particle boundaries to form grains of the product phase. Instead, they are simply a convenient pair of precursors with the correct stoichiometry, as a consequence of containing the desired secondary building units.

Given our interest in this class of layered copper oxyselenide, we decided to explore if this type of metathesis reaction should be used more widely. We wanted to determine what advantages the metathesis approach could have. Does the formation of the salt by-product act as a driving force for reliable use of lower synthetic temperatures? Do metathesis reactions allow access to metastable phases not synthesizable by conventional routes? Do the preassembled layers remain intact in any meaningful way during the reaction? These possible advantages are worth considering, but must be balanced against the associated challenges of the route. The metathesis approach initially seems more simple, with only two precursors required, but these are themselves relatively complex products which must be prepared in advance (see ESI for the details), compared to the simple binary precursors required for the conventional approach, which can either be purchased or have relatively trivial preparation methods. Finally, if the metathesis reaction is successful, the salt by-product must still be removed to produce a pure product – a step not required in the conventional route.

Given this context, we initially attempted the synthesis of two layered copper selenides, scandium-containing $Sr_3Sc_2O_5Cu_2Se_2$ and iron-containing $Sr_3Fe_2O_5Cu_2Se_2$ using both a conventional and metathesis approach, as shown in equation 1 and 2 below, where *M* = Sc or Fe. Identical reaction conditions were used for both the conventional and metathesis approaches, at temperatures of 500 °C, 600 °C, 700 °C, 800 °C, and 900 °C. A single heat cycle of 12 hours, without pelletisation, was used due to the high air sensitivity of the $Na_2Cu_2Se_2$ precursor.[23]

Metathesis: $Sr_3M_2O_5Cl_2 + Na_2Cu_2Se_2 \rightarrow Sr_3M_2O_5Cu_2Se_2 + 2\ NaCl$ Equation 1

Conventional: $2\ SrO + M_2O_3 + SrSe + Cu_2Se \rightarrow Sr_3M_2O_5Cu_2Se_2$ Equation 2

The results of the attempt to synthesize these layered oxyselenides are summarised in figure 2. The Rietveld fits can be found in the ESI in figures S1-S10, and are quantified in table S1. At the lowest attempted reaction temperature of 500 °C, the metathesis reaction produced a product which was 40.5 wt.% $Sr_3Fe_2O_5Cu_2Se_2$, which represents approximately 47% reaction completion (as NaCl must be formed as well, at 100% reaction completion the sample would contain 86 wt.% of the layered product). The remaining phases in the sample were the unreacted layered precursors and NaCl, as expected, a trace amount of SrSe, but also with significant conversion of unreacted $Na_2Cu_2Se_2$ to the more stable $NaCu_3Se_2$, which may also be a reaction intermediate, and evidence that the pre-assembled layers do not remain intact and unaltered during reaction. At 600 °C the reaction is 88% complete, and at higher temperatures 100% complete, based on analysis of the powder x-ray diffraction data, with no by-products apart from NaCl (with the exception of a small amount of SrSe observed in the highest temperature reaction at 900 °C). As these samples contain the salt by-product, they are not phase pure as made, but we were able to wash a sample of $Sr_3Fe_2O_5Cu_2Se_2$, prepared at 700 °C using the metathesis reaction, with water followed by vacuum drying. This removed the NaCl and produced a phase pure material, with no detectable impurity after a 16 hour X-ray diffraction measurement (ESI figure S11).

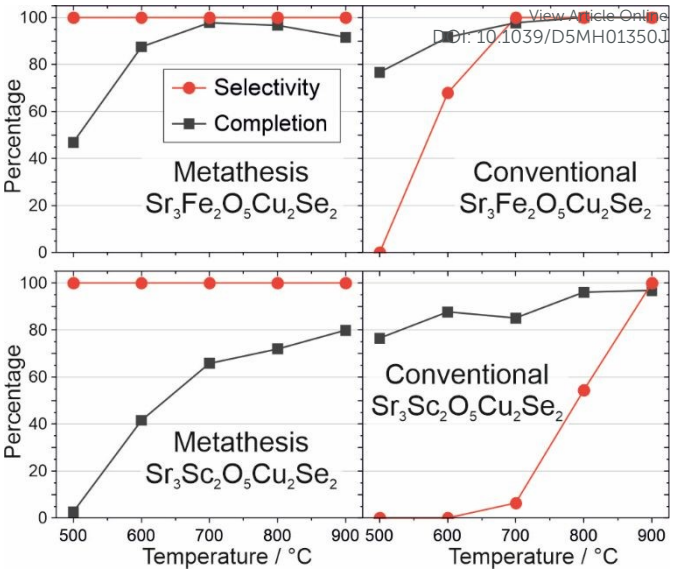

Figure 2. Results of analysis of powder diffraction using Rietveld refinement, to determine the reaction completion and reaction selectivity, based on wt.% using conventional and metathesis approaches from 600 °C to 900 °C. Selectivity here is the wt. fraction of target *325* compared to the total mass of *325* and *426* phase, while % completion compares the fraction of precursors converted to *any* layered product (*325* or *426*).

Surprisingly, the conventional route also had relatively high reaction completion at the lower temperatures, but not to form the target product of $Sr_3Fe_2O_5Cu_2Se_2$, but instead a competing phase with a larger ternary oxide layer, $Sr_4Fe_2O_6Cu_2Se_2$. These two structure types can be designated based on the ratio of the ions in the oxide layer, i.e *325* and *426*. The *426* ($Sr_4Fe_2O_6Cu_2Se$) differs from the *325* ($Sr_3Fe_2O_5Cu_2Se_2$) by the addition of an extra SrO layer which shears and displaces the polyhedra in the *perovskite*-like oxide layer. It has been previously identified that there is a delicate balance between the stability of the *426* and *325* structure for a given combination of ions, often with only one or the other being stable.[8, 24] Prior work has shown that for the Sr-Fe-O-Cu-Se system both can be made using conventional synthesis at high temperature, if appropriate precursor ratios are used.[19, 25] Therefore it is surprising that our attempts at the conventional reactions at 500 °C and 600 °C lead to preferential formation of the *426* over the *325*, with the *426* being the only layered product observed at 500 °C, and still preferred over the *325* in an approximate 2:1 ratio at 500 °C, despite the precursor ratio being correct for formation of the *325*. At 700 °C the situation corrects itself, with the *325* product, $Sr_3Fe_2O_5Cu_2Se_2$, being the only layered product, alongside trace SrSe, and at 800 °C and 900 °C the samples are 100% pure, with $Sr_3Fe_2O_5Cu_2Se_2$ as the only phase that can be identified in the PXRD patterns.

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These results align well with prior work which showed that $Sr_3Fe_2O_5Cu_2Se_2$ could be made by both conventional and metathesis approach. Our results additionally show that the conventional approach has poor selectivity at low temperature, with the *426* being preferentially formed below 700 °C, but this is avoided in the metathesis approach, with 100% selectivity and only the expected layered *325* product is observed at all temperatures. From this we can conclude that both methods are viable for the synthesis of iron-containing $Sr_3Fe_2O_5Cu_2Se_2$, although the metathesis route has the advantage of better selectively at lower reaction temperatures, with the caveat of more complex precursors and the need to wash the salt by-product.

For the reactions conducted to synthesise the scandium containing analogue, $Sr_3Sc_2O_5Cu_2Se_2$, the metathesis reaction was less effective (results summarised in figure 2, and in detail ESI in table S3 Figures S13-22). The layered precursors remain almost completely unreacted at 500 °C (2.7% completion), with the reaction completion increasing to 40% at 600 °C, 63% at 700 °C, 69% at 800 °C and finally 76.8% at 900 °C, although these may be improved with multiple cycles. SrSe is observed as a side product at all these temperatures, and again the unreacted $Na_2Cu_2Se_2$ has converted to $NaCu_3Se_2$.The selectivity for the metathesis reaction is 100% at all temperatures. In contrast, the conventional route shows good reaction completion at all temperatures (77% to 97%), albeit with trace amounts of Cu and SrSe, but with almost exclusive formation of the unexpected and competing *426* phase between 500 °C and 700 °C. It is only at the highest temperatures of 800 °C and 900 °C, that the expected *325* product is formed with 55% and 100% selectivity respectively. Therefore, we can conclude again that both methods can be used, with the metathesis showing better selectivity at lower temperatures, but lower reaction completion. Overall, the reduced complexity of the conventional method, and ability to form effectively phase pure product without the need to wash out the NaCl, and with only the minor penalty of a higher synthesis temperature, would strongly favour the use of the conventional approach for synthesis of $Sr_3Sc_2O_5Cu_2Se_2$.

$Sr_3Co_2O_5Cl_2 + Na_2Cu_2Se_2 \rightarrow Sr_3Co_2O_5Cu_2Se_2 + 2\ NaCl$ Equation 3

$Sr_4Co_2O_6Cl_2 + Na_2Cu_2Se_2 \rightarrow Sr_4Co_2O_6Cu_2Se_2 + 2\ NaCl$ Equation 4

Two further metathesis reactions were attempted, using cobalt containing oxide layers, in an attempt to synthesise $Sr_3Co_2O_5Cu_2Se_2$ and $Sr_4Co_2O_6Cu_2Se_2$ as highlighted in equations 3 and 4. To our knowledge neither of these phases have been reported by any synthetic route in the literature. Both metathesis reactions were attempted at 600 °C, as this is highest temperature where a consistent difference between the conventional and metathesis reactions was observed, but neither yielded the targeted product. Details of the PXRD results can be found in ESI table S4 and figures S23-S24. In both cases a mixed anion layered compound was identified, but instead of the *325* or *426* target, it was the previously reported *212* phase $Sr_2CoO_2Cu_2Se_2$,[26] alongside NaCl, CoO and SrSe as by-products. $Sr_2CoO_2Cu_2Se_2$ was found as the majority phase in both reactions (71.9 wt.% in the attempt at the *325* structure, and 64.9 wt.% in the attempt at the *426*), with no evidence of the layered precursors remaining, indicating high reaction completion, with the SrSe and CoO by-products appearing due to the incorrect stoichiometry of the precursors for the observed product. These reactions show that, for this particular case, the metathesis reaction is not successful at synthesising the plausible but unknown metastable phases of $Sr_3Co_2O_5Cu_2Se_2$ and $Sr_4Co_2O_6Cu_2Se_2$, although this cannot be extended to the general case to state that the metathesis approach could never be used to synthesize a metastable phase. What is confirmed however, is that although a metathesis reaction is occurring, as NaCl is formed, the mechanism is entirely conventional even at this low temperature, with the 'preassembled' oxide layer completely rearranging into the layer found in the *212* phase, and by-products CoO and SrSe.

From the experiments reported here, we can now make some conclusions about the effectiveness of the metathesis approach compared to the conventional approach for the synthesis of these layered copper oxyselenides. For this particular class of oxyselenides, taking advantage of the $Na_2Cu_2Se_2$ precursor with various oxide layer precursors, it is clear that the method is of limited advantage compared to the conventional approach. It does allow for slightly reduced synthesis temperatures and greater selectivity where there is a balance between the *325* and *426* phases. However, all of the mixed anion layered products prepared from metathesis reactions in this work can also be made phase pure using the conventional routes at higher temperatures. It is also clear that the concept of any advantage of a 'pre-assembled' layer is not valid, as in numerous cases layered products are formed which do not match the composition of the oxide layer in the metathesis precursor. Instead, the ion diffusion mechanism is occurring, with the metathesis formation of NaCl driving greater reaction completion at lower temperature. Overall, however, the disadvantages of the metathesis approach are numerous. The more complex precursors require additional synthetic steps, and may not be accessible for all targets of interest. The reactions will always form the salt by-product, which must be washed out if a pure sample is required. There are perhaps some niche cases where a lower reaction temperature is essential, where it may be worth making use of the approach. However, we must conclude that for these layered mixed anion materials, the metathesis approach may be, if not a dead-end, then certainly a synthetic cul-de-sac.

Conflicts of interest

There are no conflicts to declare.

Data availability

Data supporting this study are openly available from the University of Southampton repository at DOI:10.5258/SOTON/D3596.

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