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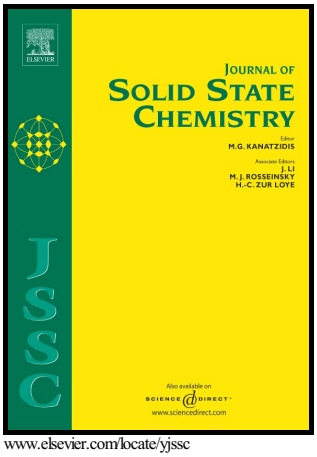

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Accessing magnetic chalcogenides with solvothermal synthesis: $KFeS_2$ and KFe_2S_3

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Abstract

Semiconducting binary sulfides are often produced with controlled size and shape by solvothermal synthesis using amine solvents. The versatility of this method, however, has not been extended to dense ternary sulfides that include alkali and transition metal ions, which are renowned for their complex magnetic and electronic properties. We report the solvothermal synthesis of the alkali–transition metal sulfides $KFeS_2$ and KFe_2S_3. The latter compound is not accessible by direct solid-state synthesis. Magnetic susceptibility measurements indicate antiferromagnetic ordering of $KFeS_2$ and KFe_2S_3, which contain single and double chains of FeS_4 tetrahedra, respectively. Given the ability to access KFe_2S_3 here, further development of this method may lead to isolation of new functional compounds.

Keywords:
Solvothermal synthesis, Antiferromagnets, Chalcogenides, Magnetic materials, Neutron scattering

1. Introduction

The solvothermal synthesis of binary sulfides has been extensively utilized to create functional materials with controlled form, often with nanometer-scale dimensions. These methods have occasionally been extended to synthesize ternary semiconductors with monovalent Cu or Ag: sulfides of type I-III-VI with Fe, Ga or In,[1, 2, 3, 4, 5, 6] I-V-VI type sulfides with Bi[7, 8, 9] or Sb,[10] and I-IV-VI type sulfides with Sn.[11, 12] Nanoparticles of Cu_2MoS_4,[13] and Cu(Ag)-Pd-S[14] systems have also been reported. The proposed mechanism involves the formation of soluble complexes of both metals in a compound (Cu and Bi for example), simultaneously. To achieve this condition, the metals in the complexes should have similar electronegativities. For this reason, all the ternary compounds above contain Cu^+ or Ag^+ to avoid the formation of phase-separated binary sulfides. In those cases, the goal is to produce known compounds with facile mixing and mild conditions.

In isolated cases, as in $NaInS_2$ and $KInS_2$,[15] the ability to incorporate alkali ions in amine synthesis has been demonstrated. We instead seek to understand whether these solvothermal methods provide advantages in exploratory synthesis. The formation of $NaInS_2$ led us to consider that similar electronegativities or solubilities of the two cations may not be required, and diverse ternaries may form in these reactions, rather than binaries.

Our recent work on exploratory synthesis of alkali-transition metal ternary sulfides has shown that there are many computationally-predicted compounds that are near stability, but do not form by traditional solid-state methods.[16] We set out to determine if solution-based methods afford tunable ternary sulfide formation in the K–Fe–S system, which is known to contain at least eight crystalline ternary phases.[17, 18, 19, 20, 21, 22, 23] This exploratory effort is inspired by the ability of solvothermal reactions to access a unique chemical landscape and create hybrid structures.[24, 25] Surprisingly, despite a strong motivation to synthesize chalcogenides with magnetic correlations, to date, no syntheses of such ternary compounds with 3*d* magnetic cations have been reported.

Here, we investigate the solvothermal synthetic routes to the ternary magnetic sulfides $KFeS_2$ and KFe_2S_3, despite the difference in Pauling electronega-