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Rapid microwave-assisted preparation of binary and ternary transition metal sulfide compounds

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Abstract

Transition metal chalcogenides are of interest for energy applications, including energy generation in photoelectrochemical cells and as electrodes for next-generation electrochemical energy storage. Synthetic routes for such chalcogenides typically involve extended heating at elevated temperatures for multiple weeks. We demonstrate here the feasibility of rapidly preparing select sulfide compounds in a matter of minutes, rather than weeks, using microwave-assisted heating in domestic microwaves. We report the preparations of phase pure FeS_2, CoS_2, and solid solutions thereof from the elements with only 40 minutes of heating. Conventional furnace and rapid microwave preparations of $CuTi_2S_4$ both result in a majority of the targeted phase, even with the significantly shorter heating time of 40 minutes for microwave methods relative to 12 days using a conventional furnace. The preparations we describe for these compounds can be extended to related structures and chemistries and thus enable rapid screening of the properties and performance of various compositions of interest for electronic, optical, and electrochemical applications.

Keywords: Transition metal sulfides, Rapid preparation, Microwave-assisted heating

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1. Introduction

Simple and complex transition metal chalcogenides are of interest for a number of energy applications, including solar and photoelectrochemical energy generation [1, 2, 3] and as high capacity electrode materials for electrochemical energy storage [4, 5, 6, 7]. Pyrites, such as FeS_2, CoS_2, and their solid solutions, have shown promising performance for photoelectrochemical applications [2, 8], as well as for so-called "beyond intercalation" electrochemical energy storage [9]. Another promising alternative to commercial Li-ion batteries are those based on multivalent ions, including Mg^{2+}, for which $Cu_{0.1}Ti_2S_4$ prepared from $CuTi_2S_4$ is a promising cathode candidate [10].

The photoelectrochemical activity of FeS_2 with small concentrations of Co substituted for Fe is reported to have better performance than pure FeS_2 films [2]. The substitution of Co for Fe alters the band structure [11], which impacts optical absorption and electronic properties [2] and can lead to enhanced photoelectrochemical activity. In this way, these and other properties can be tuned over the solid solution $Fe_{1-x}Co_xS_2$. This concept can also be extended to compounds in the pyrite structure with other transition metals (TM) and their solid solutions.

In addition to energy generation, compounds with the pyrite structure, including FeS_2 and CoS_2 [Figure 1(a) and (b)], have also been studied as conversion electrode materials [12, 13, 14, 15, 16], in which electrochemical charge storage involves extensive chemical and structural evolution relative to commercial electrode materials that store charge by intercalation. This gives rise to the much higher theoretical capacities of conversion materials [9, 17, 18]. Despite promising theoretical performance, electrode materials that operate by conversion typically have poor room temperature reversibility. However, FeS_2 has been shown to have compelling, near theoretical performance in secondary cells at slightly elevated temperatures (333 K), particularly when paired with solid [19] or ionic liquid electrolytes [20]. CoS_2 has also been recently revisited for secondary energy storage, but is more promising for supercapacitor applications [21, 22, 23]. Other sulfides have also shown promise for next-generation energy storage, most recently, Cu-deficient thiospinel of the form $Cu_\delta Ti_2S_4$, such that $\delta \approx 0.1$, with Cu removed by chemically oxidizing $CuTi_2S_4$ [Figure 1(c)] [10]. Sun *et al.* observed high capacity, good capacity retention, and high rate capability for $Cu_\delta Ti_2S_4$ relative to other Mg-ion cathode candidates [4, 10].

Conventional preparations of pyrites and their solid solutions reported in the literature typically involve three or more heat treatments at 973 K, with each heating step lasting one week or longer, resulting in syntheses that require three or more weeks at elevated temperatures [11, 27].
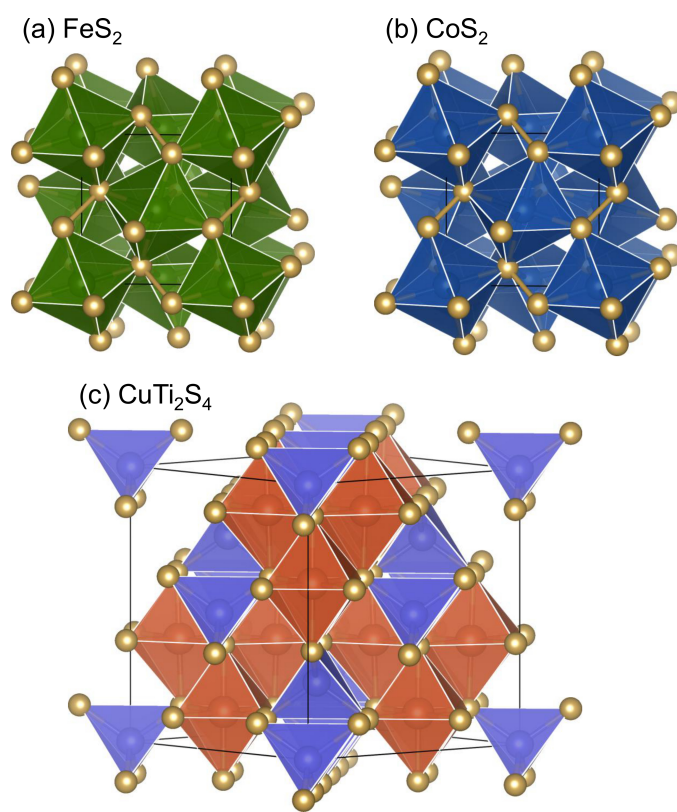
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Figure 1: Structures of pyrites, (a) FeS$_2$ ($Pa\bar{3}$, ICSD collection code 656511) [24] and (b) CoS$_2$ ($Pa\bar{3}$, ICSD collection code 164456) [25], and (c) thiospinel CuTi$_2$S$_4$ ($Fd\bar{3}m$, ICSD collection code 53336) [26]

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Martinolich *et al.* have demonstrated the preparation of FeS_2 and other pyrites through solid state metathesis reactions, which circumvent kinetic barriers and allow for the low temperature (500 K to 650 K) synthesis of these compounds in several days [28, 29]. Soheilnia *et al.* reported the preparation of phase pure $CuTi_2S_4$ (a precursor for $Cu_\delta Ti_2 S_4$) from the elements after heating at 973 K for one week [30], but reports typically require heat treatments of multiple weeks [31, 32].

Given the promise of the described and related chalcogenide materials and their solid solutions for various applications, developing methods to decrease preparation time would expedite the discovery and evaluation of compounds not yet tested for these applications. Microwave (MW) irradiation and MW-assisted heating have been shown to greatly reduce the time and energy required to prepare inorganic materials [33]. MW preparation has been reported for ceramics, including phosphors for solid-state lighting [34, 35], materials for catalysis [36] and batteries [23, 37], and has even been successfully demonstrated for intermetallics [38, 39]. Landry *et al.* prepared chalcopyrite semiconductors $CuInS_2$, $CuInSe_2$, and their solid solutions ($CuInS_{2-x}Se_x$) from the elements using MW irradiation (without the use of a secondary susceptor) and reduced the heating time to just 5% of the conventional furnace preparation time. [40, 41].

We report here the rapid preparation of several binary, solid solution, and ternary transition metal sulfides from the elements in 40 min by MW-assisted heating, in which activated charcoal serves as a susceptor to transfer heat to reactants [34]. FeS_2 and CoS_2 were prepared phase pure, while for their solid solution, $Fe_{0.5}Co_{0.5}S_2$, we found a distribution of compositions present when following the same MW procedure. For $CuTi_2S_4$, we compare the products of two procedures, both with two heating steps: one using a conventional furnace and the other via rapid MW-assisted heating. For both, we find Cu-deficient spinel as the majority phase, with some binary and ternary impurities. Phase purity of the solid solution and $CuTi_2S_4$ could be achieved by additional grinding and heating steps or through the optimization of MW conditions.

2. Experimental Methods

Powders of the elements were ground using an agate mortar and pestle. Two 100 mg bar pellets of each mixed powder were pressed to 2 metric tons. Pellets were sealed in 3/8 in (9.53 mm) silica tubes (Technical Glass Products Inc.) under 25 inHg (85 kPa) of Ar. Sealed tubes were immersed in activated charcoal (1220 mesh, ®DARCO, Sigma-Aldrich), which acted as a susceptor to transfer

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heat to the reactants [34], in an alumina crucible. The crucible was put into the annulus of high-temperature alumina, insulating foam, which sat on the outer edge of the plate of a Panasonic Inverter (NN-SN651B, 1200 W, 2.45 GHz) microwave during heating.

For FeS_2, CoS_2, and their solid solutions, samples were heated at 30% power (360 W) for 20 minutes and slowly cooled to room temperature for a minimum of 2.5 h. Following, tubes were flipped over and the same heat treatment was repeated. A similar procedure was employed for the MW preparation of $CuTi_2S_4$ at 50% power (600 W) and with regrinding and pelletizing of powders in an Ar glovebox between the two heatings. An excess of S was used for all samples to account for its volatilization at the pressures and temperatures employed. The metal to sulfur ratios of the powders ground for each compound were as follows: CoS_2, 1:2.3; FeS_2, 1:2.25; $Fe_{0.5}Co_{0.5}S_2$, 1:1:4.6; and $CuTi_2S_4$, 1:2:4.25. The following starting materials were used: S (Aldrich, 100-mesh), Ti (Alrich, 99.5%), Fe (Aldrich, 99.99+%), Co (Sigma-Aldrich, 99.8%), and Cu (Alfa Aesar, 99.9%).

$CuTi_2S_4$ prepared in a conventional furnace was compared to the product of MW-assisted heating. For this, pellets were also sealed in silica tubes under 25 inHg (85 kPa) of Ar and heated in two steps: 1123 K for 7 days and 1273 K for 5 days. Between heatings, pellets were ground and repressed into pellets in an Ar glovebox.

Room temperature powder synchrotron X-ray diffraction (XRD) was collected through the rapid-access mail-in program at beamline 11-BM-B ($\lambda = 0.414568\,\text{Å}$) of the Advanced Photon Source at Argonne National Laboratory. Rietveld refinement was performed using the program Topas [42] and crystal structures were visualized using VESTA [43]. Micrographs were collected using a FEI Nova Nano 650 FEG Scanning Electron Microscope in secondary electron mode with a beam voltage of 4 kV and a working distance of 4 mm. Powders of FeS_2, CoS_2, and $Fe_{0.5}Co_{0.5}S_2$ were prepared for scanning electron microscopy (SEM) on conductive carbon tape.

3. Results and Discussion

Synchrotron powder XRD and Rietveld refinement confirm the phase purity of FeS_2 and CoS_2 prepared by MW-assisted heating (Figure 2). These isostructural materials are composed of an *fcc* sublattice of the metal, M, octahedrally-coordinated by S, with each S part of a disulfide unit, $[S_2]^{2-}$ [Figure 1(a) and (b)].

Figure 3 shows the synchrotron XRD data and Rietveld refinement of the prepared solid solution with a nominal composition of $Fe_{0.5}Co_{0.5}S_2$. While the peak positions and relative intensities are
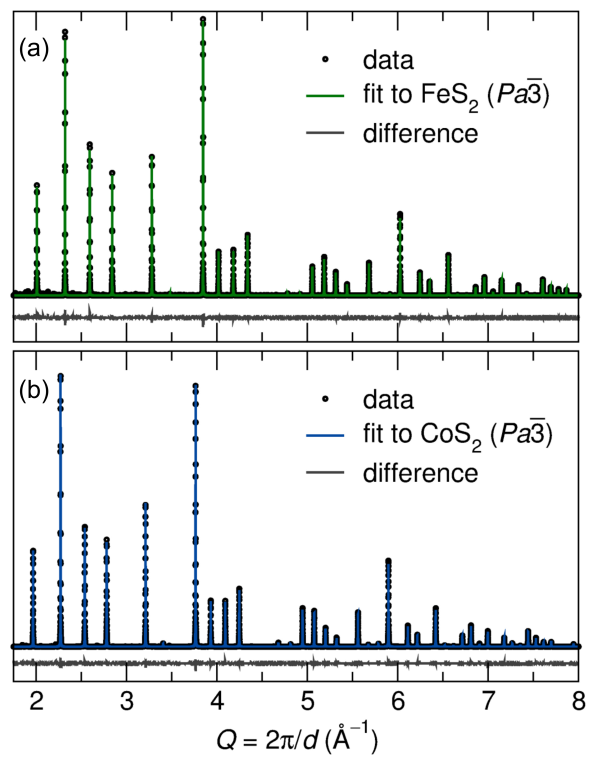
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Figure 2: Synchrotron XRD and Rietveld refinement confirm the preparation of phase pure (a) FeS_2 and (b) CoS_2 by MW-assisted heating.
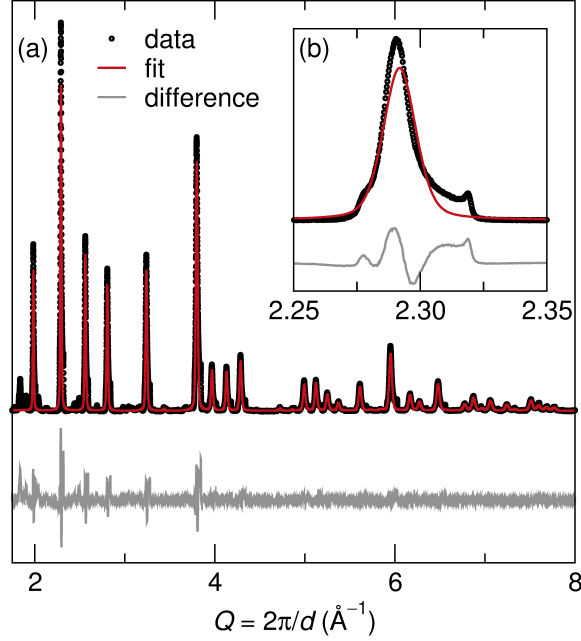
Figure 3: (a) Data and Rietveld fit of solid solution with the nominal composition $Fe_{0.5}Co_{0.5}S_2$. The inset (b) shows deviation of the data peak shape from the fit; this is likely due to the presence of various solid solutions at a distribution of compositions.

captured by the phase of this composition described by Bouchard [27], the refined lattice parameter, 5.486(1) Å, is slightly larger than the published value, 5.4780(5) Å, suggesting the prepared phase is slightly Co-rich. Closer inspection of the data reveals irregular peak shapes [Figure 3(b)], likely arising from the presence of several solid solutions with a range of compositions and, thus, lattice parameters. There are several low Q impurity peaks that could not be identified through comparison to either the elements or known binary and ternary phases. Solid solutions typically require additional heating steps to achieve phase purity [11], so additional regrinding and heating steps might result in a more homogeneous product with more symmetric peak shapes.

Micrographs of FeS_2, CoS_2, and $Fe_{0.5}Co_{0.5}S_2$ (Figure 4) show representative particle size distributions and shapes. FeS_2 has $\approx 5\,\mu m$ aggregates of smaller particles with no well-defined shape [Figure 4(a)]. CoS_2 has similarly sized clusters composed of smaller spherical particles, which range in size from 50 nm to 2 μm [Figure 4(b)]. The solid solution shows more faceted, plate-like particles that range in size from about 500 nm to 5 μm [Figure 4(c)].
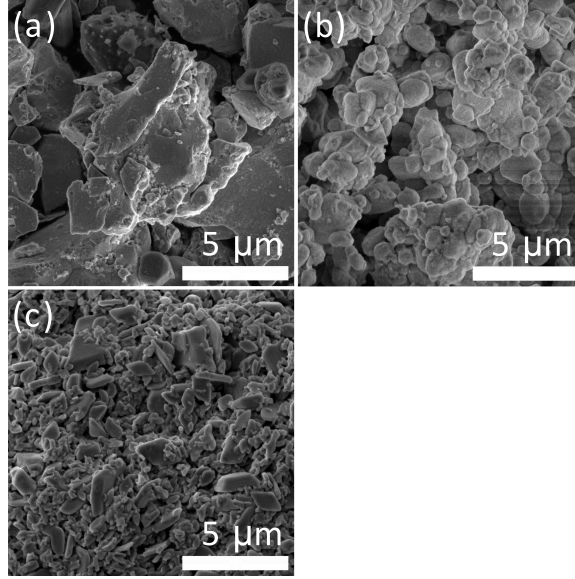
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Figure 4: SEM shows particle shape and size distribution of (a) FeS_2, (b) CoS_2, and (c) $Fe_{0.5}Co_{0.5}S_2$.

$CuTi_2S_4$ has a spinel structure, with Cu^{1+} and Ti^{3+} tetrahedrally- and octahedrally-coordinated by S, respectively [Figure 1(c)]. We compare $CuTi_2S_4$ prepared using a conventional furnace with that prepared by MW-assisted heating, each with two heating steps between which powders were reground and pressed into pellets. The phase fractions and compositions of both products are evaluated by Rietveld refinement of synchrotron XRD data (Figure 5). For both cases, Cu-deficient $Cu_{1-y}Ti_2S_4$ ($Fd\bar{3}m$) was the majority phase (≈ 58 mol%, ≥ 82 wt%) (Table 1). In both samples, unreacted Cu metal precursor ($Fm\bar{3}m$) remained and a layered, Cu-deficient $Cu_{1-z}TiS_2$ ($R\bar{3}m$) was present. The sample prepared by MW-assisted heating also had ≈ 8 wt% $Ti_{0.67}S$ ($P6_3/mmc$). As described for the solid solution, additional heating and grinding steps will improve the yield of the goal phase.

4. Conclusions

We report the preparation of phase pure FeS_2 and CoS_2 from the elements in 40 min of heating, rather than the multiple weeks required using a conventional furnace, using MW-assisted heating with charcoal as a susceptor. The solid solution prepared by the same methods results in a slightly Co-rich solid solution near the nominal composition, $Fe_{0.5}Co_{0.5}S_2$. Irregular peak shape suggests

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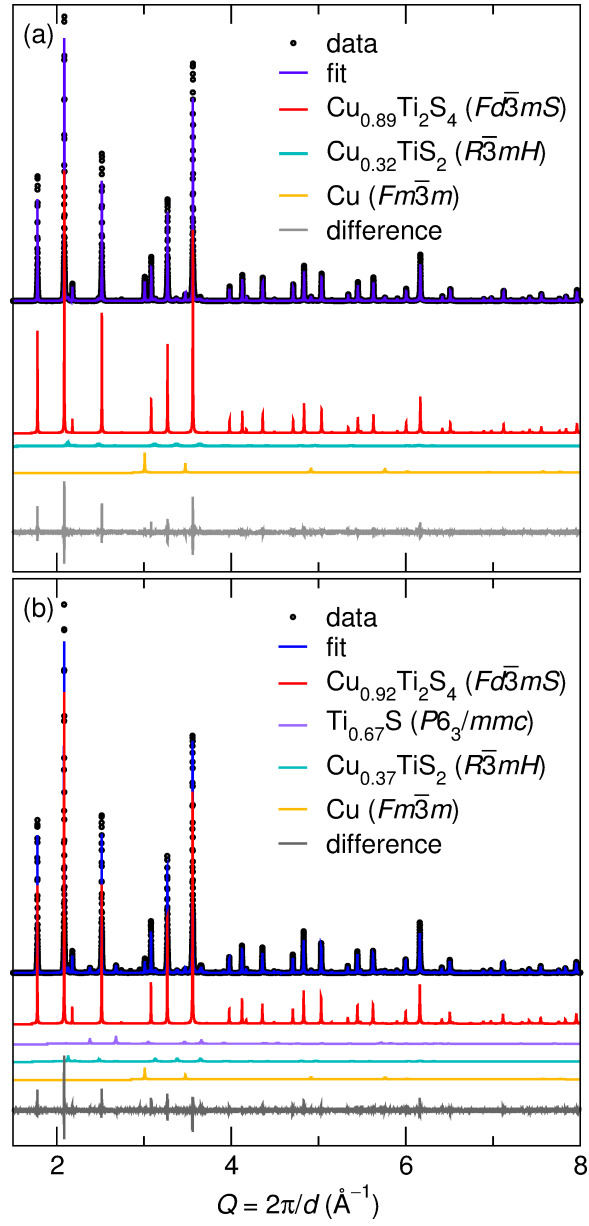
Figure 5: Synchrotron XRD and Rietveld refinement show a majority of the goal phase, $Cu_{1-y}Ti_2S_4$, results from (a) conventional furnace and (b) rapid microwave preparations. A ternary impurity and precursor Cu are also present. Phase fractions are provided in Table 1.

Table 1: Compositions and phase fractions of products from the Rietveld refinements of thiospinel $CuTi_2S_4$ prepared by conventional furnace and rapid MW-assisted heating methods.

furnace			microwave		
phase	*mol %*	*wt %*	*phase*	*mol %*	*wt %*
$Cu_{0.89}Ti_2S_4$	58.0	85.3	$Cu_{0.92}Ti_2S_4$	57.9	82.2
$Cu_{0.32}TiS_2$	32.4	11.5	$Cu_{0.37}TiS_2$	11.6	7.9
Cu	9.7	3.2	$Ti_{0.67}S$	25.2	8.2
			Cu	5.3	1.7

the presence of solid solutions over a range of compositions and lattice parameters. Inhomogeneity of solid solutions is common, even by conventional methods, and could be reduced through additional grinding and heating steps. The preparation of $CuTi_2S_4$ had a lower yield of the goal phase than the pyrites, but similar phase fractions of Cu-deficient thiospinel resulted from MW and conventional furnace preparation, which involved 40 min and 12 days (17,280 min) of heating, respectively. By optimizing MW conditions (power level and time), the yield of thiospinel is expected to improve while maintaining much shorter heat treatment times than are required using conventional furnaces. As for the solid solution, additional grinding and heating steps as well as thoroughly grinding powders to reduce the particle size of metal precursors will improve homogeneity [41].

Continued interest in energy generation and storage requires the study of structure-composition-property relationships of relevant material systems, including the sulfides discussed here. The described preparation methods can be refined to improve the purity and homogeneity of products and can even be applied to related compounds. An additional benefit to the reported syntheses are that they can be done from the elements; several MW-based preparations of chalcogenide compounds employ salts or more complex precursor materials and can require the use of a solvent or additional purification steps [23, 44, 45]. As such, the methods described here can be employed to rapidly prepare, and screen, related chalcogenides and their solid solutions from the elements, potentially accelerating materials discovery.

5. Acknowledgments

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