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

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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 [1–3] 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 FeS2, CoS2, and solid solutions thereof from the elements with only 40 min of heating. Conventional furnace and rapid microwave preparations of CuTi2S4 both result in a majority of the targeted phase, even with the significantly shorter heating time of 40 min 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.

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Rapid preparation
Microwave-assisted heating

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 FeS2, CoS2, and solid solutions thereof from the elements with only 40 min of heating. Conventional furnace and rapid microwave preparations of CuTi2S4 both result in a majority of the targeted phase, even with the significantly shorter heating time of 40 min 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.

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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 [21–23]. Other sulfides have also shown promise for next-generation energy storage, most recently, Cu-capacitor applications [21 for secondary energy storage, but is more promising for supercapacitor applications [21–23]. Other sulfides have also shown promise for next-generation energy storage, most recently, Cu-capacitor applications [21 for secondary energy storage, but is more promising for supercapacitor applications [21–23]. Other sulfides have also shown promise for next-generation energy storage, most recently, Cu-capacitor applications [21 for secondary energy storage, but is more promising for supercapacitor applications [21–23].

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]. 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–650 K) synthesis of these compounds in several days [28,29]. Soheilnia et al. reported the preparation of phase pure CuTi$_2$S$_4$ (a precursor for CuTi$_2$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$_2$–xSe$_2$) 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 40min 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$_2$S$_4$, 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$_2$S$_4$ 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. Powders of FeS$_2$, CoS$_2$, and their solid solutions, samples were heated at 30% power (360 W) for 20 min 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$_2$S$_4$ 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$_2$S$_4$: 1:2.4:2.5. The following starting materials were used: S (Aldrich, 100-mesh), Ti (Aldrich, 99.5%), Fe (Aldrich, 99.99+%), Co (Sigma-Aldrich, 99.8%), and Cu (Alfa Aesar, 99.9%).

CuTi$_2$S$_4$ prepared in a conventional furnace was compared to the product of MW-assisted heating. For this, pellets were also sealed in silica tubes under 25inHg (85 kPa) of Ar and heated in two steps: 1:213 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 ($\lambda = 0.414568$ 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 ESEM 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...
These isostructural materials are composed of an fcc sub-lattice of the metal, M, octahedrally-coordinated by S, with each S part of a disulfide unit, \([S_2]^{2-}\) (Fig. 1(a) and (b)).

Fig. 3 shows the synchrotron XRD data and Rietveld refinement of the prepared solid solution with a nominal composition of \(\text{Fe}_{0.5}\text{Co}_{0.5}\text{S}_2\). While the peak positions and relative intensities are 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 (Fig. 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\(_2\) (Fig. 4) show representative particle size distributions and shapes. FeS\(_2\) has \(\approx 5\ \mu\text{m}\) aggregates of smaller particles with no well-defined shape (Fig. 4(a)). CoS\(_2\) has similarly sized clusters composed of smaller spherical particles, which range in size from 50 nm to 2 \(\mu\text{m}\) (Fig. 4(b)). The solid solution shows more faceted, plate-like particles that range in size from about 500 nm to 5 \(\mu\text{m}\) (Fig. 4(c)).

CuTi\(_2\)S\(_4\) has a spinel structure, with \(\text{Cu}^{1+}\) and \(\text{Ti}^{3+}\) tetrahedrally- and octahedrally-coordinated by S, respectively (Fig. 1(c)). We compare CuTi\(_2\)S\(_4\) 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 (Fig. 5). For both cases, Cu-deficient \(\text{Cu}_{1-x}\text{Ti}_2\text{S}_4\) (Fd\(_3\)m) was the majority phase (\(\approx 58\text{mol\%}, \geq 82\ \text{wt\%}\)) (Table 1). In both samples, unreacted Cu metal precursor (Fm\(_3\)m) remained and a layered, Cu-deficient \(\text{Cu}_{1-x}\text{Ti}_2\) (R\(_3\)m) was present. The sample prepared by MW-assisted heating also had \(\approx 8\ \text{wt\% Ti}_0.67\text{S}\) (P\(_63/mmc\)). 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 40min of heating, rather than the multiple weeks...
lattice parameters. Inhomogeneity of solid solutions is common, the presence of solid solutions over a range of compositions and divided in Table 1.

A ternary impurity and precursor Cu are also present. Phase fractions are provided using a conventional furnace, using MW-assisted heating with charcoal as a susceptor. The solid solution prepared by the conventional furnace microwave

Cu$_{0.92}$Ti$_2$S$_4$ (Fd$ar{3}$mS)

Cu$_{0.32}$TiS$_2$ (R$ar{3}$mH)

Cu (Fm$ar{3}$m)

difference

Table 1

<table>
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<th>microwave</th>
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<td>phase</td>
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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.

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**References**


