

Rapid solid-state synthesis of binary group 15 chalcogenides using microwave irradiation

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Abstract

Solid-state microwave synthesis was found to provide a simple, rapid and economical route to prepare Sb_2Se_3 , Sb_2Te_3 , Bi_2Se_3 and Bi_2Te_3 . These technologically important materials were prepared via solid-state microwave synthesis in as little as 4 min. Through the process of finding the ideal synthetic conditions with which to produce each of these compounds, the effects that several synthetic variables have on the reaction outcomes were explored. Scanning electron microscopy, energy dispersive spectroscopy, powder X-ray diffraction, differential thermal analysis and diffuse reflectance measurements, when appropriate, were used to characterize the materials.

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1. Introduction

Binary group 15 chalcogenides are an important class of materials due to their great potential in several eminent technologies. For example, group 15 chalcogenide solid-solutions, such as $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_{3-y}\text{Se}_y$, are among the most studied materials for use in thermoelectric refrigeration and thermoelectric power generation [1–5]. Furthermore, $A_2\text{Te}_3$ compounds (where $A = \text{Sb}$ or Bi) doped with transition metals such as V, Cr and Fe show promise for use in spin-based devices [6–8]. Additionally, binary group 15 chalcogenides have potential uses in various optoelectronic devices [9,10]. As with all materials that have the prospect of widespread usage, improved preparation methods for binary group 15 chalcogenides are desired. For example, new synthetic routes to prepare these compounds may lower production costs, shorten reaction times or enhance physical properties of these materials. In this work, the solid-state microwave synthetic method was pursued as a new avenue to prepare these materials.

Microwave reactions to prepare organic compounds are relatively common and are most often performed in solution [11,12]. On the other hand, the utilization of microwaves in inorganic synthesis has been less explored [13–20]. Furthermore, reports of microwave reactions in dry, solventless media aimed at preparing inorganic materials are relatively rare [13–18]. However, several important binary chalcogenides have been previously prepared using solid-state microwave synthesis, for example PbSe , PbTe , ZnS , ZnSe , Ag_2S [21], and ZnTe [22]. To the best of our knowledge, there are no reports of bulk, binary group 15 chalcogenides prepared via solid-state microwave synthesis, although several groups have recently prepared binary group 15 chalcogenide nanoparticles via microwave-assisted solution reactions [23–27].

To date, few investigations regarding the mechanism of solid-state microwave reactions have been completed. For this reason, the exact nature of the interactions between microwaves and reactants during synthesis is somewhat unclear and speculative [15]. Only recently, experiments have been designed to probe the interactions of solid matter and microwaves using *in situ* diffraction [28,29]. However, the method is still not straightforward, as there is little to no comprehension regarding some of the reaction

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variables involved in this procedure. This lack of understanding and control is what we believe to be the main obstacle preventing widespread adoption of this method, despite its potential advantages.

Materials that have been prepared by solid-state microwave synthesis can exhibit different morphologies and microstructures than those obtained via other methods [30]. It has also been shown that samples prepared using microwaves may possess enhanced physical properties compared to materials synthesized by other techniques [31]. Perhaps the most important advantage of solid-state microwave synthesis of inorganic compounds, compared to more traditional methods such as high-temperature solid-state synthesis, is the dramatically reduced reaction times. Additionally, unlike some other alternatives to traditional high-temperature synthesis, solid-state microwave synthesis, by its nature, involves no solvent waste. For these reasons, solid-state microwave synthesis offers an easy, energy efficient and relatively green method [32] to prepare technologically useful solid-state inorganic materials.

In this paper, we present the first solid-state microwave preparations of bulk Sb_2Se_3 , Sb_2Te_3 , Bi_2Se_3 and Bi_2Te_3 . These materials were synthesized with as little as four minutes of irradiation time. The products were characterized and compared to materials produced via high-temperature solid-state synthesis. Furthermore, the effects that sample quantity, irradiation time, sample geometry and starting composition have on the phase purity of the products are discussed.

2. Experimental

2.1. Reagents

Chemicals in this work were used as obtained: (i) antimony powder, –200 mesh, 99.995%, Cerac; (ii) bismuth powder, –200 mesh, 99.999%, Cerac; (iii) selenium powder, –200 mesh, 99.99%, Strem; (iv) tellurium powder, –325 mesh, 99.9%, Strem.

2.2. General synthetic procedure

The elements were weighed, combined and ground for 20 min, using a mortar and pestle, in an argon-filled glove box. The materials to be reacted were sealed in a 9 mm o.d. fused-silica tube under a vacuum of $\sim 10^{-3}$ mbar using a natural gas/ O_2 torch. The lengths of the sealed tubes were usually 10–11 cm. The sealed tubes were inserted into either a vertical or horizontal fused-silica holder that was placed onto a quartz brick, which was centered in the microwave cavity floor. Each sample was irradiated in a CEM MDS 2100, 1000 W research-grade microwave for several minutes, with periodic shaking. After irradiation, the tube was opened and the sample examined under a Fisher stereomaster microscope to observe and record its morphology. Selected portions of the sample were imaged using a scanning electron microscope. The semi-quantitative ele-

mental composition was determined on these pieces using energy dispersive spectroscopic analysis. The entire product was ground before powder X-ray diffraction, differential thermal analysis and diffuse reflectance spectroscopy in the UV/Vis/NIR region, when appropriate, were used to characterize the products.

2.2.1. Synthesis of Sb_2Se_3

Antimony selenide was prepared according to the general procedure outlined above. Specifically, 0.2461 g (2 mmol) of antimony and 0.2372 g (3 mmol) of selenium (enough to make ~ 1 mmol Sb_2Se_3) were weighed, combined and ground. The sample was sealed in a tube, placed in the microwave vertically and irradiated at 100% power for 4, one-minute intervals. Between intervals the sample was removed and shaken.

2.2.2. Synthesis of Sb_2Te_3

Antimony telluride was prepared according to the general procedure outlined above. Specifically, 0.2429 g (2 mmol) of antimony and 0.3183 g (2.5 mmol) of tellurium (enough to make ~ 1 mmol “ $\text{Sb}_2\text{Te}_{2.5}$ ”) were weighed, combined and ground. An explanation for the ratio of reactants used in this preparation will be provided in Section 3.1.6. The sample was sealed in a tube, placed in the microwave horizontally and irradiated at 100% power for 10, one-minute intervals with shaking between each minute.

2.2.3. Synthesis of Bi_2Se_3

Bismuth selenide was prepared according to the general procedure outlined above. Specifically, 0.4184 g (2 mmol) of bismuth and 0.3833 g (4.8 mmol) of selenium (enough to make ~ 1 mmol “ $\text{Bi}_2\text{Se}_{4.8}$ ”) were weighed, combined and ground. An explanation for the ratio of reactants used in this preparation will be discussed in Section 3.1.6. The sample was sealed in a tube, placed horizontally in the microwave and irradiated at 100% power for 4, one-minute intervals with shaking between each minute.

2.2.4. Synthesis of Bi_2Te_3

Bismuth telluride was prepared according to the general procedure outline above. Specifically, 0.4179 g (2 mmol) of bismuth and 0.3825 g (3 mmol) of tellurium (enough to make ~ 1 mmol of Bi_2Te_3) were weighed, combined and ground. A phase-pure material could be obtained in the vertical or horizontal position when the sealed tube was irradiated at 100% power for 4, one-minute intervals. Between intervals the reaction tube was removed and shaken.

2.3. Physical measurements

2.3.1. Scanning electron microscopy (SEM)/energy dispersive spectroscopy (EDS)

A CamScan Series 4 scanning electron microscope was used to image samples and a Princeton Gamma Tech

detector was used for EDS. The working distance was 35 mm and the accelerating voltage was set to 22.5 kV. Samples were mounted onto double-sided carbon tape, which was adhered to an aluminum specimen holder. EDS data were collected for 60 s.

2.3.2. Powder X-ray diffraction (PXRD)

Powder patterns were collected using a Rigaku Geigerflex Model D2013 diffractometer operating in Bragg–Brentano geometry. Data were collected from 10° to 80° 2θ with a sampling interval of 0.024° or 0.012° . The scan rate used was between 0.1° and $1.0^\circ/\text{min}$, depending on the sample. The instrument operated at 35 kV and 22.5 mA. Graphite monochromated copper $K\alpha$ radiation with a wavelength of 1.540598 \AA was used for measurements. Samples were prepared for analysis by spreading the powdered sample onto a piece of double-sided tape adhered to a glass slide mounted to an aluminum sample holder.

2.3.3. Optical spectroscopy

Optical diffuse reflectance spectra were obtained using a Cary 5000 UV/Vis/NIR spectrometer. Samples were ground and loaded into a Harrick Praying Mantis diffuse reflectance accessory that uses elliptical mirrors. BaSO_4 was used as a 100% reflectance standard. Scans were performed from 2500 to 200 nm. Wavelength data were converted to electron volts and the percent reflectance data were converted to absorbance units using the Kubelka–Munk equation [33].

2.3.4. Differential thermal analysis (DTA)

DTA was performed using a Shimadzu DTA-50 thermal analyzer. DTA data were recorded using the TA60-WS collection program. The instrument was calibrated with a three-point calibration curve using the melting points of indium, zinc and gold. The temperature was programmed to increase at a rate of $10^\circ\text{C}/\text{min}$ from 25 to 650°C or 750°C , depending on the sample. The temperature was then decreased to 100°C at $10^\circ\text{C}/\text{min}$. To determine reproducibility, a second cycle was performed in the same manner. The reference, Al_2O_3 , and sample were contained in fused-silica ampoules and sealed under a vacuum of $\sim 10^{-3}$ mbar. Approximately 20 mg of sample and 20 mg of reference material were used for measurement. Melting points were determined from the peak (minimum) of the endothermic event. PXRD was performed on all products before and after DTA to ensure that the material had not decomposed or changed phase during thermal analysis.

3. Results and discussion

3.1. Synthesis

3.1.1. Observations during and following synthesis

Within seconds of applying microwave radiation to the sample, a brilliant plasma forms above the reaction mixture. The exact color of this plasma depends upon the

elements that are being irradiated and their amounts, but it is usually blue. In the past, it has been speculated that the plasmas are due to the chalcogen present in the mixture [34]; however, our previous work [16] as well as this work suggest that this is not necessarily true. Irradiation of individual elements identified bismuth, tellurium and antimony as microwave absorbing materials; however, selenium alone has never been observed to form a plasma or heat when exposed to microwaves in our lab.

After microwave irradiation, the reaction tubes were opened and the products removed and examined. In some cases, a thin film of material adhered to the tube wall. The amount and thickness of this film depends on the reaction. The silvery-gray products typically take on the shape of their fused-silica reaction tubes. The ingots appeared highly crystalline and have some void spaces. Samples of Sb_2Se_3 , Bi_2Se_3 and Sb_2Te_3 appear as sintered ingots with no particular crystal shape (Fig. 1, top). This

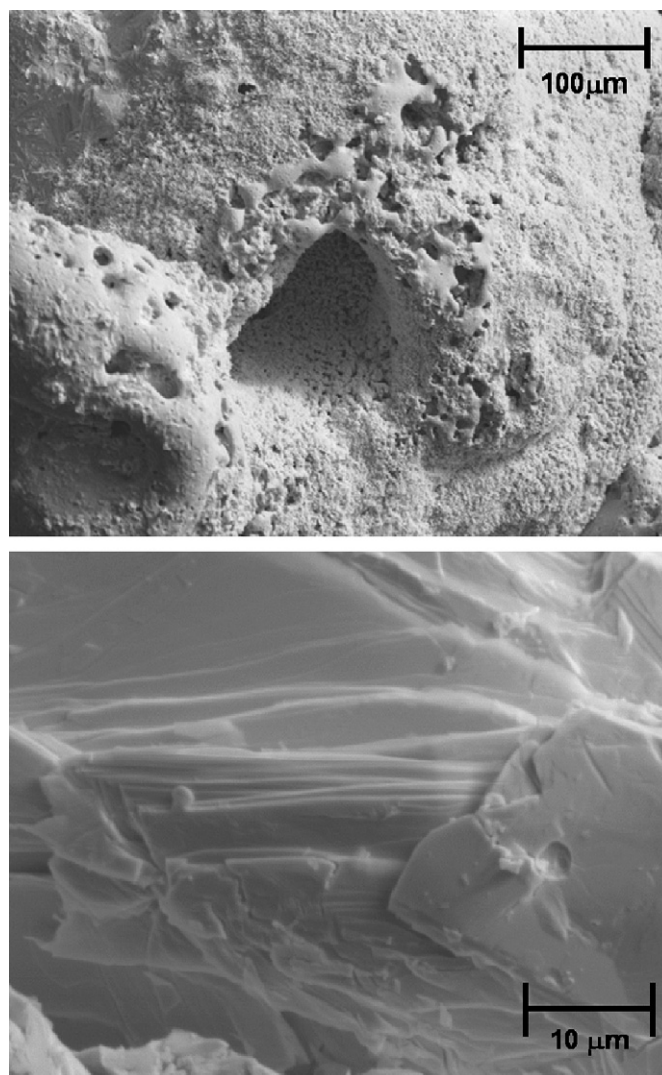


Fig. 1. Scanning electron micrographs of Sb_2Se_3 (top) and Bi_2Te_3 (bottom) prepared via solid-state microwave synthesis in four minutes.

is in stark contrast to samples prepared by traditional, high-temperature solid-state methods where samples of Sb_2Se_3 typically appear needle-like and samples of the other three group 15 chalcogenides display a definite layered morphology. These features are in agreement with their one- and two-dimensional crystal structures. Bi_2Te_3 was the only sample prepared via solid-state microwave synthesis that took on a layered morphology, although this was only apparent after cracking open the ingots and magnifying them with the SEM (Fig. 1, bottom).

3.1.2. Ideal synthetic conditions

We have successfully prepared each of the four title compounds in pure form, as described in the experimental section. It was observed that each of the binary chalcogenides required unique conditions in order to be prepared phase-pure (Figs. 2–5). Recently, we have begun to demonstrate that there are several crucial synthetic variables involved in solid-state microwave synthesis [16,17]. In our study of the synthesis of AgInSe_2 , we showed that sample quantity, irradiation time, irradiation procedure and reactant grinding time can be important variables [16]. More recently, we have synthesized several intermetallic phases where sample quantity and irradiation time also proved to be crucial parameters [17]. While each of these variables seems to be important for all systems studied thus far, the dependence of the reaction outcome on these variables appears to be system dependent. In the current study, we have further investigated some of the above variables, as well as offered some speculation as to why they are important and, additionally, identified two important variables for the first time, sample geometry and starting composition. Most of the discussion below will focus on how one can determine the ideal conditions for solid-state microwave reactions by discussing the synthetic variables explored in this work and their effects on the outcomes of reactions to prepare binary group 15 chalcogenides.

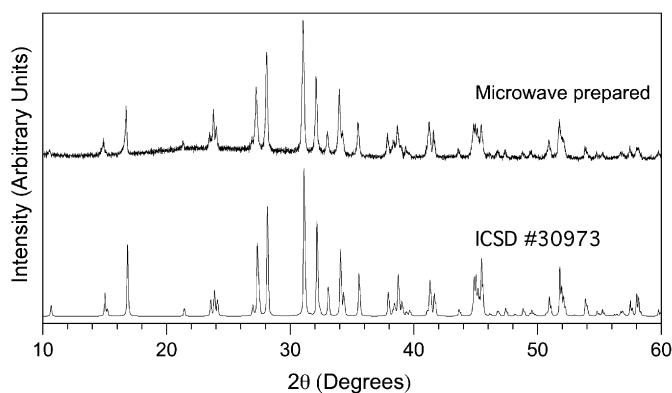


Fig. 2. Powder X-ray diffraction pattern of Sb_2Se_3 prepared via solid-state microwave synthesis compared to a reference pattern. This phase-pure material was prepared in a vertical orientation using 4 min of irradiation time, as described in Section 2.2.1.

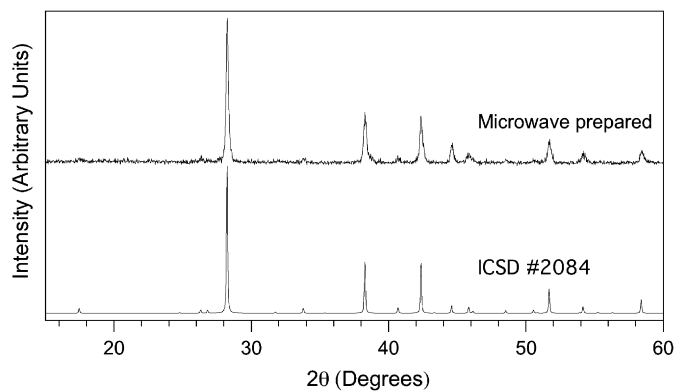


Fig. 3. Powder X-ray diffraction pattern of Sb_2Te_3 prepared via solid-state microwave synthesis compared to a reference pattern. This phase-pure material was synthesized in a horizontal orientation using 10 min of irradiation time as described in Section 2.2.2.

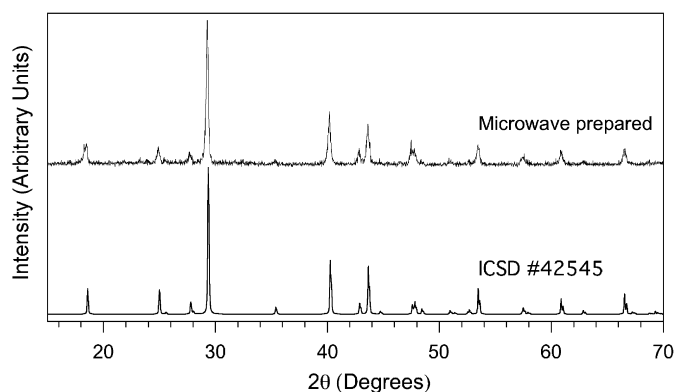


Fig. 4. Powder X-ray diffraction pattern of Bi_2Se_3 prepared via solid-state microwave synthesis compared to a reference pattern. This phase-pure material was prepared in a horizontal orientation using 4 min of irradiation time as described in Section 2.2.3.

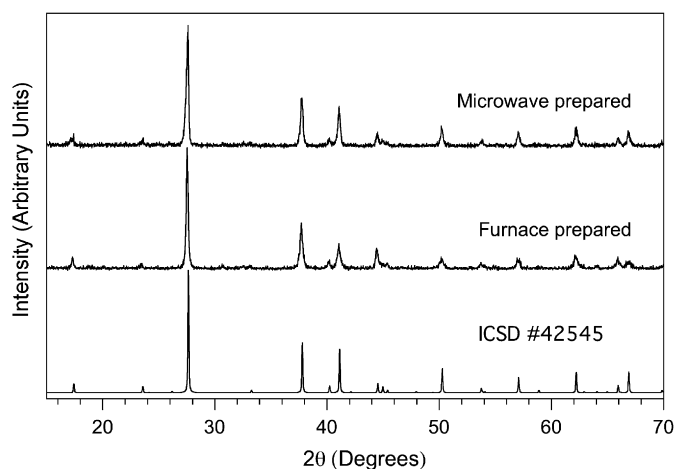


Fig. 5. Powder X-ray diffraction pattern for Bi_2Te_3 prepared in a microwave compared to a sample prepared in a furnace and a reference pattern. This phase-pure, microwave-prepared material was synthesized in a vertical orientation using 4 min of irradiation time as described in Section 2.2.4.

Table 1

Comparison of solid-state microwave reactions performed in an attempt to prepare Sb_2Te_3 using different sample quantities and different irradiation times^a

Sb:Te starting ratio	Quantity (mmol)	Time (min)	Orientation ^b	Ratio ^c
2:3	0.5	4 × 1	Vertical	.40
2:3	0.75	4 × 1	Vertical	.38
2:3	1.0	4 × 1	Vertical	.13
2:3	1.25	4 × 1	Vertical	.20
2:3	1.5	4 × 1	Vertical	.27
2:3	2.25	4 × 1	Vertical	.41
2:3	4.5	4 × 1	Vertical	.55
2:3	1.0	4 × 1	Vertical	.13
2:3	1.0	6 × 1	Vertical	.12
2:3	1.0	8 × 1	Vertical	.12
2:3	1.0	10 × 1	Vertical	.10
2:3	1.0	20 × 1	Vertical	.09

^aAll samples were ground for 20 min and irradiated using 100% microwave power.

^bOrientation refers to the positioning of the reaction tube in the microwave, which, in turn, affects the sample's geometry.

^cThis is a ratio of the relative intensity of the most intense diffraction peak for Te to that of Sb_2Te_3 .

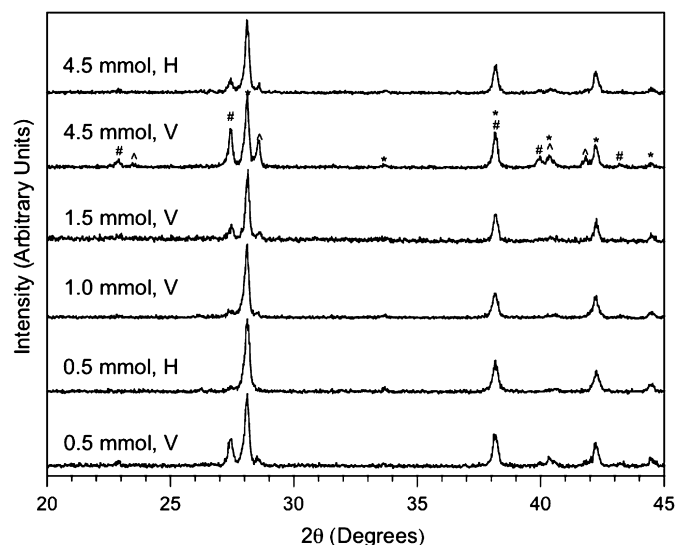


Fig. 6. Powder X-ray diffraction patterns obtained for select microwave reactions intended to make different quantities of Sb_2Te_3 in the horizontal or vertical position. All samples were ground for 20 min and irradiated for 4, one-minute intervals. Asterisks (*) mark diffraction peaks due to the presence of Sb_2Te_3 , while ^ and # represent diffraction peaks for unreacted antimony and tellurium, respectively.

3.1.3. Effect of sample quantity on phase purity

In the case when all other factors were kept constant and only sample quantity was varied, dramatic effects in phase purity were observed. For example, reactions designed to produce various amounts of Sb_2Te_3 were irradiated for 4, one-minute intervals (Table 1) and each reaction that did not produce phase-pure Sb_2Te_3 , contained some unreacted antimony and tellurium. By comparing the relative intensities of the most intense diffraction peaks for Sb_2Te_3

and tellurium, a qualitative ratio of unreacted Te relative to Sb_2Te_3 was determined and used to monitor the progress of these reactions (Fig. 6). The ideal sample quantity was determined to be 1 mmol, because this reaction gave the least amount of unreacted starting materials under these conditions. The ratio of unreacted starting material to product increased as the sample quantity diverges from 1 mmol with a similar trend observed in the corresponding selenium system.

Reactions designed to produce different quantities of Sb_2Se_3 (2:3 ratio of reactants) were irradiated for 4, one-minute intervals in the horizontal position. To qualitatively determine the phase-purity of the reactions, the ratio of unreacted selenium to Sb_2Se_3 was monitored using PXRD, by the method described above. In contrast to the corresponding tellurium system, there is a minimum amount of material required for the reaction to occur, as samples of only 0.5 mmol did not react under these conditions. Interestingly, the same quantity of material did react when irradiated in the vertical position (this will be discussed later in Section 3.1.5). In the cases of Bi_2Se_3 and Bi_2Te_3 , systematic studies of sample quantity were not conducted, because phase-pure products were synthesized early in the investigations.

It is important to note that variations in sample quantity of the amounts studied in this work would not normally have any effect on the outcome of a traditional high-temperature solid-state reaction. Why then does this become so important for solid-state microwave reactions? One possible answer may be the microwave penetration depth. As the microwaves travel through a sample, the material absorbs the energy until it drops to zero. This means that some of the interior of the sample may never experience any microwaves when the sample quantity becomes too large. This is assuming that the same shape and size reaction container and the same orientation is used, so that one of the sample's dimensions is increasing with sample quantity. Therefore, samples designed to yield larger quantities will be more likely to exceed the microwave penetration depth, resulting in incomplete reaction. Another factor may be heat dissipation. This is not a problem in conventional heating where the heat flows from the furnace to the sample. In the case of microwave reactions, only the sample becomes hot, heat flows from the sample to its surroundings while the microwave chamber remains relatively cool. Furthermore, the sample cools quickly when the microwave field is shut off. Sample quantity increases will result in a smaller ratio of interior to exterior particles. Therefore, larger samples will cool slower.

3.1.4. Effect of irradiation time on phase purity

Reactions calculated to yield 1 mmol of Sb_2Te_3 were irradiated for varying times (Table 1) and though a phase-pure sample was never obtained under these conditions, these experiments demonstrate that irradiation time is an important variable in this synthetic method. For Sb_2Te_3 ,

increases in irradiation time resulted in samples with increased phase purity. It seems quite likely that further increases in irradiation time, beyond 20 min, should eventually lead to a phase-pure material; however, these experiments were not carried out, since a phase-pure product could be obtained in only 10 min of irradiation time using a different set of reaction conditions, as described in Section 2.2.2.

Unlike Sb_2Te_3 , increased irradiation time did not always result in increased phase purity for Sb_2Se_3 . For example, phase-pure Sb_2Se_3 (2:3 ratio of reactants) was obtained by the reaction of 1 mmol of sample in the vertical orientation for 4, one-minute intervals; but, samples that were irradiated for 2 min more or less did not yield phase-pure material; instead, increased amounts of unreacted starting materials relative to product were obtained. Although irradiation time is clearly an important factor, there is no general trend to describe the effect of reaction time in all systems studied.

The effects of irradiation time on phase purity were not investigated for the bismuth compounds. In contrast to the antimony systems, all reactions were carried out for 4, one-minute intervals.

3.1.5. Effect of sample geometry on phase purity

Sample geometry, as defined in this work, pertains to the physical dimensions that result from the orientation of a sample. We believe that orienting a sample of fixed dimensions, such as a pressed pellet, horizontally or vertically, will result in identical products when utilizing a multimode microwave, due to the relatively uniform nature of the microwave field in a research-grade microwave. However, orientation becomes important and sometimes problematic when samples have unconstrained dimensions, such as a free-flowing powder that will settle into the shape and size of its container (Fig. 7). In our reactions, we have tried to maintain as consistent a tube length as possible.

Simple changes in sample geometry often result in strikingly different results. For example, it was found that phase-pure Sb_2Se_3 can be prepared when irradiated vertically. Additionally, all Sb_2Se_3 reactions performed vertically, produced more phase-pure products than the corresponding samples prepared horizontally. Despite this, vertical orientation is not best for all samples, for example Sb_2Te_3 (Fig. 6 and Table 2).

Furthermore, not only can sample geometry make the difference between a phase-pure reaction and one that contains unreacted starting materials, but it can also determine whether the reaction takes place at all. In the case of Sb_2Se_3 , reactions to produce only 0.25–0.5 mmol of product did not react or even heat when irradiated for 4 min in the horizontal orientation, although they did so vertically.

Why are the results so different for samples of different geometry? One reason is that although the research-grade microwave may be advertised as having a uniform field, once a sample is placed in the microwave chamber, the field

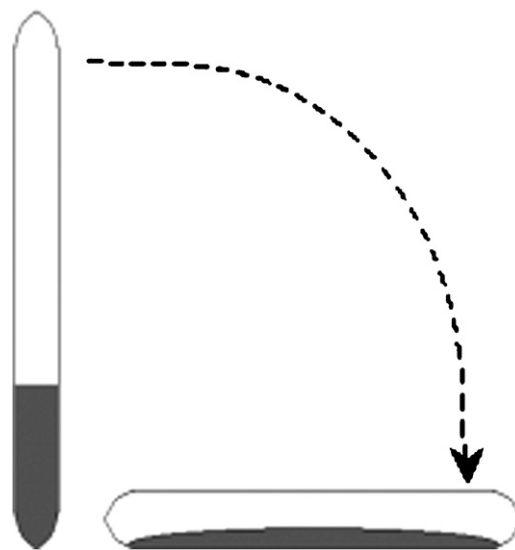


Fig. 7. Schematic illustrating how the geometry of a freely moving powder sample changes when the reaction tube position/orientation is changed.

Table 2

Comparison of solid-state microwave reactions performed in an attempt to prepare Sb_2Te_3 using different sample geometries/orientations^a

Sb:Te starting ratio	Quantity (mmol)	Time (min)	Orientation ^b	Ratio ^c
2:3	0.5	4 × 1	Vertical	.40
2:3	0.5	4 × 1	Horizontal	.10
2:3	2.25	4 × 1	Vertical	.41
2:3	2.25	4 × 1	Horizontal	.13
2:3	4.5	4 × 1	Vertical	.55
2:3	4.5	4 × 1	Horizontal	.22

^aAll samples were ground for 20 minutes and irradiated using 100% microwave power.

^bOrientation refers to the positioning of the reaction tube in the microwave, which, in turn, affects the sample's geometry.

^cThis is the ratio of the relative intensity of the most intense diffraction peak for Te to that of Sb_2Te_3 .

becomes distorted and samples of different geometry distort this field differently. Another reason could be the relationship between surface area and heat dissipation. As discussed above, this is not a problem in conventional heating. However, in a solid-state microwave reaction changes in geometry can result in a change of the exterior to interior particle ratio. In our case, using a 9 mm o.d. tube, samples in the horizontal orientation have a greater number of particles on the surface (Fig. 7). Therefore, the samples in the horizontal orientation cool much faster than those in the vertical position. Another possible reason could be the microwave penetration depth, as discussed above. For example, samples that are irradiated vertically will have a larger smallest dimension and some of the sample's interior may not experience any of the microwave energy, resulting more frequently in an incomplete reaction. One should also consider that there could be more than one factor contributing to this phenomenon.

3.1.6. Effect of starting composition on phase purity

While Sb_2Se_3 and Bi_2Te_3 can be made phase pure from a stoichiometric elemental combination, Sb_2Te_3 and Bi_2Se_3 can only be prepared in pure form by reacting nonstoichiometric ratios of elements. When reactions do not produce a phase-pure product, unreacted starting materials are observed in the powder X-ray diffraction pattern. Although there are phases in the group 15 chalcogenide systems other than 2:3, they have never been observed in the powder X-ray diffraction patterns, even when the reactions are conducted “off-stoichiometry”. Reactions using several different starting compositions were conducted for Sb_2Te_3 (Table 3). When the reaction was stoichiometric, Sb_2Te_3 formed; however, there was also unreacted tellurium present. As the amount of antimony in the reaction mixture is increased, the product becomes more phase pure. This can be explained by the SEM/EDS analysis of the thin film that is formed on the inside of the reaction tube, which shows that the film primarily consists of antimony. It was calculated that the excess antimony used in the best reaction could form a $2.6\ \mu\text{m}$ film on the tube wall.

Bi_2Se_3 experiments began with the expectation that increased bismuth content may be necessary to produce a phase-pure product, similar to Sb_2Te_3 ; however, these reactions resulted in products containing significant amounts of unreacted starting materials. Consequently, reactions with increasing amounts of excess selenium were carried out. When the amount of selenium was increased to “ $\text{Bi}_2\text{Se}_{4.8}$ ” phase-pure material was finally obtained. In this case, SEM/EDS indicated that the film on the reaction tube consisted almost entirely of selenium. It was calculated that if all the excess selenium in the “ $\text{Bi}_2\text{Se}_{4.8}$ ” reaction deposits on the tube wall, a $14.2\ \mu\text{m}$ film would be produced. The thicknesses of the films calculated for these reactions are in a reasonable range for typical thin-film materials. However, even though it seems quite reasonable to believe that the excess reactant is entirely incorporated in the film on the reaction tube, it is still indeed possible that the resulting products could be slightly off-stoichiometry. Even the smallest change in composition in these materials could

have a profound effect on the physical properties. Therefore, future work involves determining the thermoelectric properties of these materials [35].

In any synthetic method involving rapid heating, loss of volatile materials is always a potential problem and therefore, not unique to microwave reactions. Reactions that we have performed to prepare other compounds, work well with stoichiometric mixtures and there is little to no formation of thin films on the reaction tubes [16,17].

3.2. Physical characterization of materials

3.2.1. Powder X-ray diffraction

All group 15 binary chalcogenides were prepared phase pure in the microwave as indicated by PXRD analysis (Figs. 2–5). Samples of phase-pure chalcogenides were also synthesized in a furnace for comparison. Analysis of the diffraction patterns shows that a sample of Sb_2Se_3 , prepared in the microwave in only 4 min, has comparable crystallinity to a sample prepared in the furnace at $650\ ^\circ\text{C}$ in 44 h. The full-width at half-maximum (FWHM) for the diffraction peaks in the two patterns was nearly identical, $\sim 0.21^\circ$. In the case of Bi_2Te_3 , only a small difference was observed; the $\text{FWHM} = 0.244^\circ$ for the microwave prepared sample and the $\text{FWHM} = 0.209^\circ$ for the furnace-prepared sample (Fig. 5).

3.2.2. Optical spectroscopy

Optical diffuse reflectance measurements in the UV/Vis/NIR region were performed on powdered samples of Sb_2Se_3 . The other group 15 chalcogenides have bandgaps further into the IR region and cannot be measured on this instrument. Analysis of several Sb_2Se_3 products obtained from different reaction conditions all showed an optical absorption edge of approximately 1.08 eV, indicating that Sb_2Se_3 is a relatively narrow gap semiconductor, consistent with the black color of the material and the band gap of 1.2 eV found in the literature [36] (Fig. 8).

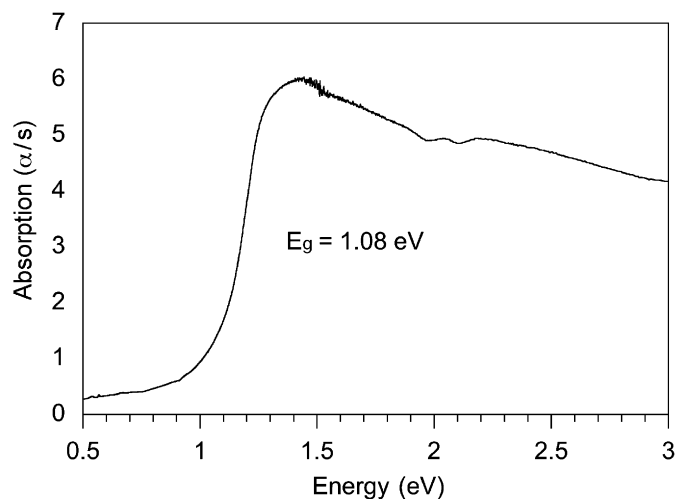


Fig. 8. Diffuse reflectance spectrum converted to absorption for Sb_2Se_3 prepared via solid-state microwave synthesis.

Table 3

Comparison of solid-state microwave reactions performed in an attempt to prepare Sb_2Te_3 using different ratios of starting materials^a

Sb:Te starting ratio	Quantity (mmol)	Time (min)	Orientation ^b	Ratio ^c
2:3	1.0	10 × 1	Horizontal	.08
2:2.67	1.0	10 × 1	Horizontal	.07
2:2.5	1.0	10 × 1	Horizontal	phase pure

^aAll samples were ground for 20 min and irradiated using 100% microwave power.

^bOrientation refers to the positioning of the reaction tube in the microwave, which, in turn, affects the sample's geometry.

^cThis is the ratio of the relative intensity of the most intense diffraction peak for Te to that of Sb_2Te_3 .

Table 4
Comparison of melting points obtained from samples prepared via solid-state microwave synthesis to those found in the literature

Compound	Melting point (this work) (°C)	Melting point (Literature) (°C)
Sb ₂ Se ₃	606	612 [36]
Bi ₂ Se ₃	695	706 [37]
Sb ₂ Te ₃	615	620 [37]
Bi ₂ Te ₃	588	585 [37]

3.2.3. Thermal analysis

Differential thermal analysis was performed for phase-pure samples of all 4 group 15 chalcogenides studied in this paper. The melting points, as determined from the differential thermal analysis results, for all 4 compounds were comparable to those found in the literature [37,38] (Table 4).

4. Conclusion

Solid-state microwave synthesis offers a fast, economical and green route for the preparation of binary group 15 chalcogenides. Through the process of preparing these materials phase pure, the effects that several reaction variables have on the outcome of the reactions were documented. Sample quantity, irradiation time, sample geometry and starting composition all have a profound influence on the reaction outcome. While it is not possible to know the exact reasons why sample quantity and geometry are important from these experiments alone, it is still very important to report these findings, because these variables are not usually encountered in conventional heating, and are factors that can hinder others from effectively utilizing the solid-state microwave synthesis technique. Future work will involve the use of an IR temperature sensor, since connecting temperature to the above variables may shed some light on their importance. The information garnered from studying the solid-state microwave synthetic method using simple binary compounds, such as those reported here, will help to design the syntheses of more complex materials via this method in the future. Additionally, one should keep in mind that using a different preparation method, such as the one reported here, could result in materials whose physical properties differ from those prepared via other methods. Therefore, future studies are aimed at determining the thermoelectric properties of these microwave-prepared, binary group 15 chalcogenides [35].

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