Microwave Metallurgy: Synthesis of Intermetallic Compounds via Microwave Irradiation

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For years, we have been told not to put metals in the microwave. A close examination of the literature, however, reveals that *powdered* metals can be used to synthesize a wide variety of compounds in a microwave. Carbides, borides, halides, nitrides, and chalcogenides have all been prepared via solid-state microwave synthesis from precursors that included powdered metals, metal oxides, or metal halides.[1−6] A logical extension of this work would be to synthesize intermetallic compounds via the solid-state microwave synthetic method. However, the current understanding of the interactions of solids with microwaves has limited the use of this method for the preparation of intermetallics.[1a]

Intermetallic compounds are useful for applications including hydrogen storage,[7] electronics,[8] and catalysis[9] and exhibit intriguing properties such as superconductivity[2,3,10] and ferromagnetism.[11] However, these compounds are normally difficult and time-consuming to synthesize because of the large energy barrier for the diffusion of solids. Traditionally, intermetallic compounds have been prepared by high-temperature solid-state synthesis, using a furnace, and/or arc melting. Solid-state microwave synthesis offers a quicker and greener option, primarily due to the short reaction times.[12] Recently, several intermetallic compounds such as Li_3Bi and Li_3Sb have been prepared in a microwave in only a few minutes.[13] In related work, Bocarsly and co-workers reported the solid-state transformation of a cyanogel to an alloy with the aid of microwave radiation.[14] Here, we report on the general synthesis of a variety of intermetallic compounds using the solid-state microwave synthetic method.

The intermetallic compounds that have been prepared in this work by solid-state microwave synthesis have a variety of uses. Ag_3In is used as a solder in the electronics industry because of its increased corrosion resistance compared to pure silver. It can be prepared electrochemically as a coating in a relatively short time,[8] but bulk preparation of Ag_3In for property measurements requires 48 h using a furnace.[15] Solid-state microwave synthesis reduces this preparation time to only 2 min. Recently, Bi_2Pd has been investigated for catalytic purposes, specifically, the oxidation of glucose to gluconic acid.[16] Bi_2Pd supported on SiO_2 for catalytic research has been prepared in about 12 h,[16] and bulk Bi_2Pd has been synthesized via arc melting.[17] Solid-state microwave synthesis offers a relatively simple alternative to synthesize Bi_2Pd in as little as 4 min (Figure 1).

One important aspect of these reactions is their expeditious nature; products are always prepared in much less time than a traditional, high-temperature solid-state reaction. Within seconds of applying microwave radiation to the sample, a brilliant plasma (Figure 1) is formed above the metal powders and the reactants begin to heat. In as little as a couple of seconds, materials can reach high temperatures in the range of 500−1100 °C, or greater. The products can exhibit a number of different morphologies ranging from sintered powders to solid ingots (Figure 2).

For this series of experiments, metal powders were weighed, but not ground,[18] and then combined in 9 mm fused-silica tubes. The tubes were then irradiated in a 1000 W CEM MDS 2100 microwave set at 100% power. A variety of reaction times were employed on a system-

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(18) Attempts to grind the starting materials for a number of reactions, which contained soft metals (for example, indium), did not lead to homogeneous mixtures; instead, the metal powders agglomerated.

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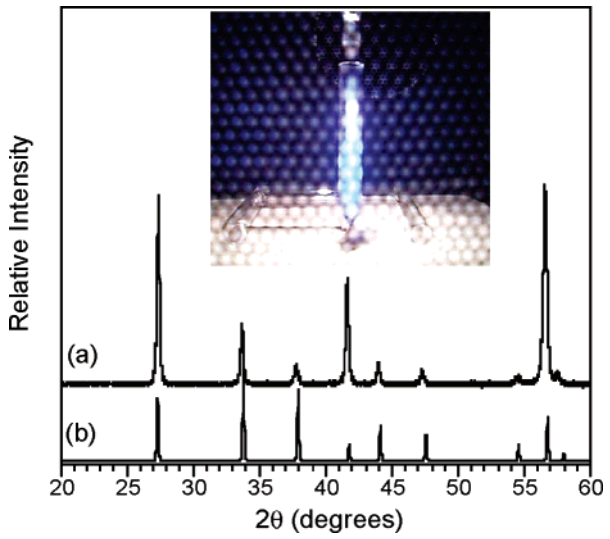

Figure 1. Powder X-ray diffraction pattern of a sample of (a) phase-pure Bi_2Pd prepared by solid-state microwave synthesis compared to (b) Bi_2Pd (JCPDS 00-013-0160). Experimental intensities vary from the reference because of the inability to effectively grind the soft ingot that was obtained after reaction. The inset shows a digital photo of the reaction to make Bi_2Pd taken through the microwave door. The reaction tube is situated in a vertical fused-silica holder, which is barely visible in the photo. The holder is placed on top of a quartz brick, which is positioned in the center of the microwave cavity floor.

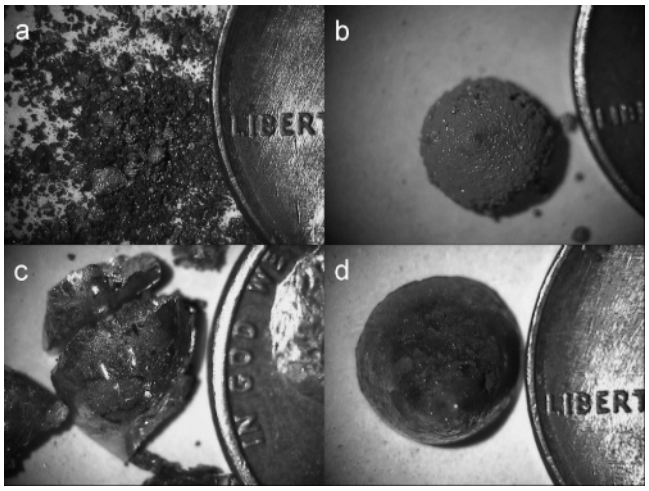

Figure 2. Images obtained with a digital microscope show a variety of morphologies that can result from solid-state microwave synthesis: (a) Bi_3Ni, a sintered powder; (b) $AuIn_2$, a sintered ingot; (c) Bi_3In_5, a cracked ingot; and (d) Bi_2Pd, a solid ingot. A penny was used as a scale in the images.

dependent basis. Following irradiation, the tubes were opened and the samples were collected and analyzed using powder X-ray diffraction.

Our work with the above compounds, in addition to those described in Table 1, demonstrates that solid-state microwave synthesis of alloys and intermetallics is not an isolated phenomenon for a few selected substances. We believe that given any reaction between two or more powdered metals to form an alloy or intermetallic, if at least one metal can be an absorber of the microwave radiation, the reaction should proceed. Using this synthetic method, we have prepared a variety of intermetallic compounds (Table 1). The list includes compounds containing main group and transition metals. It was observed that all group 11 elements formed intermetallic compounds with indium upon microwave irradiation, contrary to previous reports, which state that irradiation of copper and indium resulted in phase segregation.[5]

Table 1. Intermetallic Compounds Prepared by Our Lab Using Solid-State Microwave Synthesis

target compd	elemental ratio	irradiation time (min)	product phase(s)[a]
$Cu_{11}In_9$	1:1	3 × 1	$Cu_{11}In_9$, Cu, In
Ag_3In	3:1	2 × 1	Ag_3In
$AgIn_2$	1:2	2 × 1	$AgIn_2$, Ag_9In_4
Ag_9In_4	9:4	2 × 1	Ag_9In_4, $AgIn_2$
$AuIn_2$	1:2	1 × 10	$AuIn_2$, Au, In
Bi_3In_5	3:5	1 × 2	Bi_3In_5, BiIn
Bi_3Ni	3:1	1 × 10	Bi_3Ni, Bi
Bi_2Pd	2:1	1 × 4	Bi_2Pd

[a] Product phases were identified using powder X-ray diffraction. The first product listed is the major phase of the reaction, followed by minor phases.

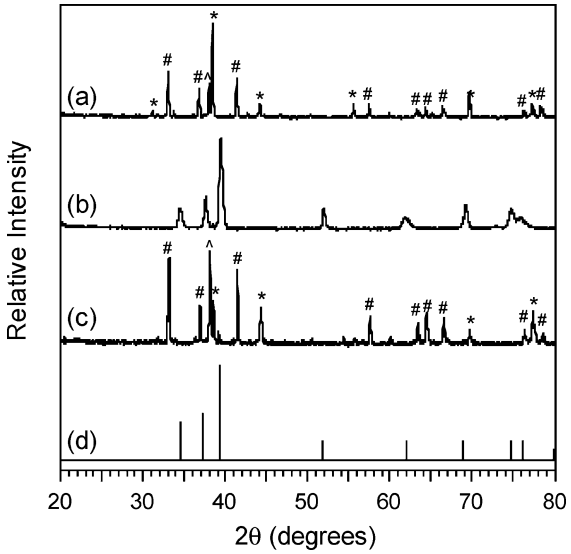

Figure 3. Powder X-ray diffraction patterns obtained for selected microwave reactions intended to produce 1 mmol of Ag_3In, irradiated for different time periods (a) 3, (b) 2, and (c) 1 min, compared to (d) Ag_3In (JCPDS 00-015-0163). Peaks due to $AgIn_2$ (JCPDS 00-025-0386), Ag_9In_4 (JCPDS 00-029-0678), and indium (JCPDS 01-071-0128) are indicated with *, #, and ^, respectively.

One caveat of this method is that there are many important synthetic variables that can have a profound effect on the reaction outcome. Some of our previous work has documented this fact.[19] For some intermetallic compounds, we optimized the syntheses in order to find the proper conditions to prepare phase-pure products; in the process, the effects of irradiation time and sample quantity were studied. For other systems, only a few reactions were performed, until the desired product was the major phase; further synthesis optimization is still necessary (Table 1).[20]

Keeping all other variables constant, irradiation time in the Ag−In system was found to have an important effect on the product, with pure Ag_3In[21] being obtained only when the sample was irradiated for 2 min (Figure 3). When the reaction time was either increased or decreased by 1 min, the resulting samples contained little or no Ag_3In; instead,

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the products were mixtures of Ag_9In_4,[22] $AgIn_2$,[23] and indium. Using a constant irradiation time of 10 min, we studied the effect of sample quantity in the Au−In system. The phase purity of samples intended to synthesize 1 to 3 mmols of $AuIn_2$ increased as the sample quantity was increased, with the only impurities being a small amount of unreacted starting material.

For some unsuccessful reactions to prepare intermetallics via solid-state microwave synthesis, the product contained no competing phases. Instead, the unwanted diffraction peaks were attributed to unreacted starting material. In these cases, it was assumed that the reaction had not had enough time to go to completion, but unfortunately, the product mixture could not be re-placed in the microwave and irradiated for additional time. This is the result of an increase in particle size of the materials, which changes the metals' behavior in the microwave from absorbing to reflecting. In an attempt to take the reactions to completion before a change in absorptivity rendered this impossible, a single, long irradiation time was chosen for the systems that exhibited no competing phases.

In some reactions, such as Bi−Pd, one must be careful when increasing irradiation time. These reactions can reach temperatures in excess of 1100 °C in as little as 2 min. In these cases, we have difficulty conducting the experiment in fused-silicia ampoules because the tube implodes as the fused-silica softens at elevated temperatures. To date, there have been no explosions during the synthesis of intermetallic compounds in our microwave. ***Caution:*** *These experiments were all conducted in a reinforced, research-grade microwave; domestic microwaves are not recommended for the heating of metals. Even with a research-grade microwave,*[24] *there are still safety issues that should be addressed.*[25]

In conclusion, solid-state microwave synthesis has proven to be a viable method for the preparation of a wide variety of intermetallic compounds, for example, Bi_2Pd and Ag_3In. This method contributes to a relatively new palette of several other nontraditional techniques, such as metal fluxes,[26] mixed-metal eutectic fluxes,[27] and solution methods,[28,29] which provide convenient avenues toward the synthesis of intermetallics. Reaction times for solid-state microwave synthesis are greatly reduced compared to other synthetic methods. Though this method is not without its caveats, we believe it has real potential in this area because many of these intermetallic compounds are of technological interest and a quicker, greener synthetic method[12] could be advantageous to their development.

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Supporting Information Available: Additional experimental details and powder X-ray diffraction patterns. This material is available free of charge via the Internet at http://pubs.acs.org.

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