Protocols for High-Temperature Assisted-Microwave Preparation of Inorganic Compounds

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Abstract

Assisted microwave heating involves the use of a susceptor to initially heat up reactants in a microwave reaction. Once hot, the reactants themselves become directly susceptible to microwave heating, and interdiffuse to form products. Assisted-microwave methods are appealing for a wide variety of high-temperature solid-state reactions, reaching reaction temperatures of 1500°C and more. Among the many advantages are that the direct volumetric heating associated with microwaves allows for rapid reaction times while employing significantly less energy than conventional furnace-based preparation. Shorter reaction times and selective heating permit volatile reactants to be incorporated stoichiometrically in the product. Undesirable reactions with containers or enclosures are also minimized. The morphology of powders obtained through microwave reactions are also more uniform and comprise smaller particles than obtained conventionally. This Methods/Protocols article is presented as a user manual for carrying out assisted-microwave preparation of bulk complex oxides in air or reducing atmospheres, sol-gel based processing of complex oxides, air sensitive intermetallics, and transition metal chalcogenides.

Introduction

Over the past few decades, microwave-based methods have been extensively employed for solution chemistry including organic synthesis,[1] polymerization reactions,[2] and hydrothermal processing.[3–5] Interest in microwave-based solution processing has led to the widespread development of sophisticated laboratory-scale microwave reactors that can control temperature and pressure during reaction. The enhancement in reaction time provoked questions on whether an athermal 'microwave effect' was causing the extreme increase in reaction rates. The fast reaction rates have since been attributed to the rapid temperature increase, thermal gradients, selective heating, and ability to superheat solvents without boiling in the microwave.[6–8]

In regard to the solid state there is a relatively long history of microwaves being employed for the processing of ceramics,[9,10] where they are understood to display distinct advantages over conventional heating for annealing (homogenization) and sintering (densification) due to the way heat is delivered, as will be discussed below.[11] In a similar vein, Roy *et al.* demonstrated fully dense sintered metallic parts in just 10 to 30 minutes using microwaves.[12]

The use of microwave ovens for the preparation of inorganic solids was given widespread currency by Baghurst and Mingos in 1988, when they discovered certain oxides coupled well to microwaves and could exceed temperatures of 700°C in less than a minute using a 500 W domestic microwave oven.[13] They prepared ternary oxides and the superconductor $YBa_2Cu_3O_{7-x}$ using the higher-absorbing reactant species to heat reactants that did not couple well to microwaves.[13,14] An early report of microwave methods involving metal powders was in 1992, when Whittaker and Mingos prepared metal chalcogenides from elemental starting materials.[15] While continuous metal films and solid metal lead to large electric discharges, small metal powders do not allow for large potential differences between particles, and no sparking occurs.[16]

Increased understanding of the interaction between microwaves and materials, espe-

cially metal powders, as well as the factors in experimental setups that affect reactions, has allowed the use microwave ovens for high temperature reactions.[17–20] Building on this, microwave reactions have been used to prepare inorganic materials including battery materials,[21,22] chalcogenides,[23,24] intermetallics,[25,26] and oxides.[27] An assortment of techniques such as solvothermal synthesis of metal-organic frameworks[28] and sol-gel synthesis of nanoparticles[29,30] have been adapted for microwave preparation.

Assisted-microwave preparation refers to the use of a susceptor — a material that couples strongly to microwaves at room temperature and therefore heats rapidly — to initially heat reactants. Once hot, the reactants couple directly to the microwaves (*ie.* they become susceptors) and heat quickly and evenly as discussed below. Assisted-microwave reactions have the advantages of rapid reaction times, energy savings, and even the potential to form metastable phases by circumventing reversible thermodynamic processes.[31] New chemistries that were difficult to access with conventional methods become possible with assisted microwave heating. The speed at which known and new compounds are prepared on the laboratory scale helps accelerate materials discovery.

Microwaves are electromagnetic waves with frequencies between 300 MHz and 300 GHz, corresponding to wavelengths from 1 m to 1 mm. Domestic microwave ovens use a frequency band centered around 2.45 GHz, with a wavelength of 12.4 cm, designed to efficiently heat water with reasonable penetration depth into foodstuffs, without interfering with wavelengths used for communications.[31] The methods outlined in this contribution are based around the use of 2.45 GHz multi-mode microwave ovens with a maximum output of 1.2 kW (Panasonic model NN-SN651B) but other similar ovens are potentially as effective. Ovens that allow control of power levels, as opposed to control of the duty cycle, are preferred. This allows, for example, the ability to heat at 60% power (720 W) rather than employing a 60% duty cycle corresponding to heating 60% of the time at 100% power.

The manner in which microwaves heat materials is fundamentally different from con-

ventional heating in a furnace, which can potentially result in different reaction pathways, structural differences, or metastable products.[11] In comparison to conventional methods which rely on heat transfer and therefore thermal conduction in the sample, microwave heating relies on a material directly converting microwave energy into thermal energy through interaction with the electromagnetic field. This results in even heating across the sample volume and rapidly rising temperatures, in contrast to conventional heating which is limited by thermal conductivity. The energy input goes only to heating the sample and (ideally) not to the surrounding environment or containment material, reducing energy consumption. In samples where some reactants are susceptors while others are not, selective heating can occur resulting in large thermal gradients, which sometimes can be employed to stabilize metastable phases.

Microwave heating mechanisms

Two major heating mechanisms in microwaves are relevant here: dipolar polarization and conduction loss. These are respectively due to the electric component of the alternating microwave field interacting with charge fluctuations and charge carriers in the material they are interacting with. Heating due to the alternating magnetic field can also result in eddy currents, which resistively heat the sample. Reviews by Rao *et al.*,[31] Bhattacharya and Basak,[32] and Kitchen *et al.*[11] provide detailed discussions on microwave heating mechanisms.

A materials response to an electric field is measured by its permittivity (ϵ') and dielectric loss (ϵ''), which determine its ability to store electric energy and convert electric energy to heat, respectively. Energy is stored in the polarization of dipoles, while conversion of electric energy to heat results from the dipolar relaxation and conduction of free electrons. The reorientation dynamics of electric dipoles is on the same timescale as the alternating microwave electric field, and the phase lag between the materials polarization and applied

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electric field is given by δ. The dielectric loss tangent, $\tan(\delta) = \epsilon''/\epsilon'$, describes the efficiency with which a material converts electromagnetic energy to heat due to this dipolar reorientation. This mechanism dominates in liquids and dielectric insulators, while conduction losses dominate in metals and semiconductors. The interaction of charge carriers with the applied electric field leads to conduction losses from ohmic heating due to the intrinsic resistance of a material. High conductivity materials will also heat by significant eddy current losses due to the alternating magnetic field.

The penetration depth, or distance into the sample at which the microwave radiation becomes attenuated to $1/e$ of its initial intensity, is determined by how strongly the material interacts with the electromagnetic field, *i.e.* $\tan(\delta)$. Materials with a small penetration depth on the order of micrometers, known as skin depth, are reflecting. Bulk metals are microwave reflectors. Metal powders, in contrast, will interact with microwaves. While this is not fully understood, Mondal *et al.* describes mechanisms for this interaction.[33] Smaller particle sizes will heat more strongly as they have more surface to volume ratio. Despite skin depths of less than $5\,\mu$m at room temperature, particles over $100\,\mu$m are able to be heated in the microwave.

Materials with a intermediate penetration depths on the order of centimeters are highly absorbing, and have large $\tan(\delta)$. These microwave absorbers act as good susceptors, and are easily heated.

Longer penetration depths ($> 10\,\mathrm{m}$), corresponding materials with low $\tan(\delta)$ are transparent to microwaves at the length scale of a laboratory experiment. These materials are suitable for insulation and containing reactants since they will not couple to microwaves and heat up. Materials such as SiO_2 and BN have a very small $\tan(\delta)$ over a large range of temperatures. For materials that must be reacted in an inert environment, samples are sealed in fused silica ampoules, which will not interact with the microwaves, under vacuum or $1/4$ atm of Ar. Penetration depth and loss tangents for a variety of common microwave absorbing, transparent, and reflecting materials has been provided in a review
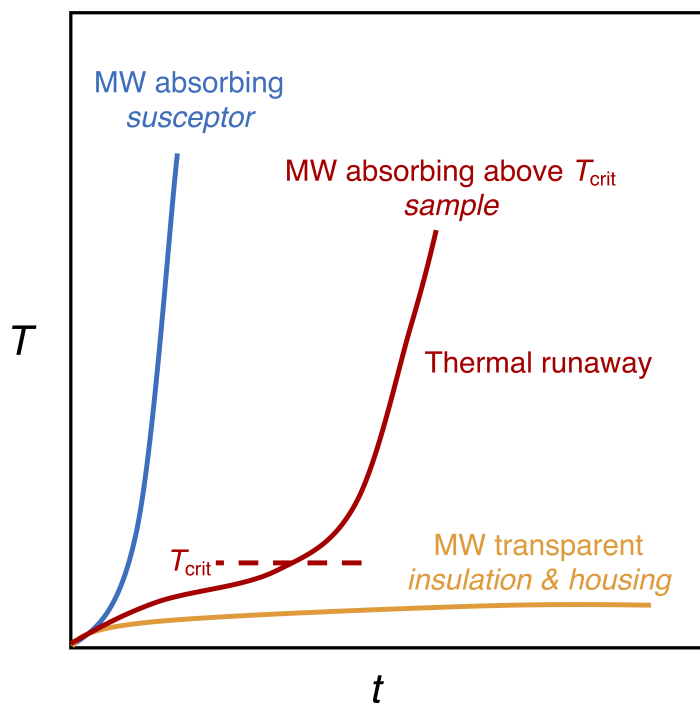
by Bhattacharya and Basak.[32]

Figure 1: Schematic of temperature as a function of microwave time for different types of materials. Susceptor materials are highly absorbing and heat rapidly. Samples are generally low absorbing at room temperature, but heat *via* the susceptor until they reach a critical temperature, above which they absorb microwaves. Insulation and housing is transparent to microwaves at room temperature, although some materials (*i.e.* alumina) couple to microwaves at elevated temperatures.

Microwave $\tan(\delta)$ of most materials can change significantly with temperature. While some materials couple well at room temperature (*eg.* graphitic carbon, SiC, water), many materials will not, and so a susceptor is used to first heat the material until it reaches a temperature where it is directly activated by microwaves (T_{crit}). A good example of such a reactant materials is alumina, which has a small $\tan(\delta)$ at room temperature, but the microwave heating efficiency increases by over 3000% at 1473 K.[34] A schematic of temperature as a function of microwave time for different materials is given in Figure 1, inspired by data presented across a number of different figures in the review of Rao *et al.*[31]

It is important to note that any material in the chamber that absorbs microwaves will

partition power from the reaction. Using a larger amount of susceptor material will take longer to heat up and may not allow the sample to reach as high a temperature because less power is available for the reaction. Once the sample is directly heated, its temperature will rise rapidly, causing coupling to increase, which increases temperature further, a phenomenon known as thermal runaway. Often power cycles are used to combat this, where initial heating is performed at high power, and once an appropriate temperature is reached the power is reduced so the temperature is maintained.

Materials

Assisted-microwave preparations have been demonstrated to produce high quality, crystalline, phase pure products. The ability to heat rapidly, selectively, and evenly across the sample volume provides advantages over conventional heating methods, as illustrated by the following example systems. The types of reactions described below rely on microwaves first heating a highly absorbing carbon susceptor, which heats reactants until they couple to microwaves. While not discussed in detail in this contribution, microwave preparation of carbides involves heating the carbon present in the reactant mixture. Carbides can be prepared more rapidly, at a lower temperature, and using less energy in a microwave than by conventional methods.[35–39]

Complex oxides

The preparation of complex oxide phosphors for solid state lighting is often energy intensive and time consuming. Conventional heating for hours or days at temperatures above $1500°C$ in environments with low O_2 partial pressures is necessary for the preparation of the Ce- substituted garnet $Y_3Al_5O_{12}$:Ce (YAG:Ce), the canonical phosphor material for solid state white lighting. Assisted-microwave preparation of YAG and other phosphors from oxide precursors requires only 20 to 45 minutes, reducing the preparation time and energy

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consumption by more than 90%.[40,41] These reactions may be performed with reducing environment obtained by placing a lid on the crucible to form a reducing CO atmosphere due to the carbon susceptor, or by placing the microwave oven in a nitrogen glovebag. Reaction conditions and relevant information for microwave preparation of select phosphors and complex oxides may be found in Table 1.

In the conventional preparation of phosphors for white lighting applications, the combination of the extremely high temperatures necessary to react refractory starting materials and the flowing H_2/N_2 gas needed to reduce the rare earth limits possible compositions due to reduction of metal oxides such as germanium and sodium oxide, as well as volatilization of starting materials. Assisted-microwave preparation circumvents these issues, allowing for new phosphor materials discovery. Brgoch *et al.* have presented the assisted-microwave preparation of two cerium substituted sodium rare earth silicates, $NaY_9Si_6O_{26}:Ce^{3+}$ and $Na_3YSi_2O_7:Ce^{3+}$, from a stoichiometric ratio of starting materials.[42] Conventional preparation in furnaces would have required excess of the Na precursors to compensate for volatilization.

The assisted-microwave method offers a degree of morphological control of complex oxides when combined with a sol-gel approach. The dried gel (process is described by Birkel *et al.*[43] and Misch *et al.*[44]), may be ground and microwave-heated to obtain a final product in just a few minutes of heating, rather than hours or days by conventional methods. In conventional preparation of orthosilicate phosphors, the high temperatures and long heating steps allow for sintering and growth of particles, limiting morphological control. By exploiting the rapid reaction time afforded by microwave preparation, size and surface area may be tuned through microwave power and time settings. The combined sol-gel assisted-microwave method has been demonstrated in rare-earth doped phosphors Eu^{2+}-doped M_2SiO_4 (M = Ca, Ba)[43] and substituted oxide catalysts Pd-substituted LnFeO$_3$ (Ln = Y, La)[44], where surface area plays an important role. The phase evolution of the gel, for which details of the preparation are provided in the reference, is evaluated using X-

ray diffraction at different intervals. The initial dried gel is mostly amorphous, and phase formation, crystallinity, and particle size have been monitored as functions of time in the microwave oven and estimated reaction temperature.

The rapid reaction time leads to significant time and energy savings in materials systems with sluggish diffusion kinetics, such as complex noble metal oxides. In the preparation of $La_2Ba(Pd,Pt)O_5$, the use of elevated temperature to overcome the slow diffusion kinetics is complicated by an autoreduction of (Pt,Pd)O, even under flowing O_2.[45] Conventional furnace methods take days or weeks to prepare a phase pure product.[46] Misch *et al.* demonstrated preparation of these complex oxides in a microwave oven in just 5 min, with an additional 15 min to 20 min yielding more crystalline and phase pure products.[47]

Intermetallics

While bulk metals are microwave reflectors, intermetallics may be prepared from pure elemental powder starting materials. The metallic powders couple to microwaves at elevated temperature, as skin depth increases. The heating mechanism in metals is dominated by conduction losses and eddy current losses. The studies mentioned below use powders with particle sizes between $3\,\mu$m and $45\,\mu$m. Some powders are hand ground in a mortar and pestle from bulk pieces of starting materials, such as manganese. In these cases, the particle size is not known. Due to oxidation at elevated temperatures, starting materials are sealed in evacuated fused silica ampoules, allowing for rapid, air-free preparation in the microwave oven.

Thermoelectric semiconducting half-Heuslers TiNiSn and TiCoSb have been prepared by assisted-microwave techniques from elemental starting materials.[50] Microwave processing decreased preparation time from over 1 week to less than 1 minute, while maintaining thermoelectric physical properties of TiNiSn. The addition of excess nickel to the half-Heusler TiNiSn results in a secondary $TiNi_2Sn$ full Heusler phase that improves thermo-

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Table 1: Relevant information for microwave preparation of selected phosphors and complex oxides in air. Microwave power is based on power setting and total output power of the microwave used. T_{max} is estimated from IR pyrometer readings aimed at the center of the inner crucible holding the sample. The following starting materials were used as sources for metals in each of these reactions with the exception of sol-gel syntheses (*): Na_2CO_3, $CaCO_3$, $BaCO_3$, $SrCO_3$, MgO, Al_2O_3, Eu_2O_3, SiO_2, Y_2O_3, Lu_2O_3, CeO_2, Pt,Pd(II) acetylacetonate.

Composition	Sample mass (g)	Microwave conditions	T_{max} (^oC)	ref.
$Ca_2MgSi_2O_7$:Eu^{2+}	–	–	1200	40
$Y_3Al_5O_{12}$:Ce^{3+} $Lu_3Al_5O_{12}$:Ce^{3+}	0.5 to 1.0	750 to 850 W for 18 min	–	41
$NaY_9Si_6O_{26}$:Ce^{3+}	–	1000 W for 5 min 375 W for 90 min	–	42
$Na_3YSi_2O_7$:Ce^{3+}	–	675 W for 8 min 325 W for 15 min	–	42
*(Ca,Ba)SiO_4:Eu^{2+}	0.25 to 0.5	1300 W for 10 min + 10 – 12 min	1150	43
*$LaFeO_3$	0.25	1250 W for 150 s	800	44
*$YFeO_3$	0.25	1250 W for 2 min	800	44
$La_2Ba(Pd,Pt)O_5$	0.25 to 0.5	1300 W for 15 – 20 min	1050	47
$(Ba_{1-x}Sr_x)Al_2$ Si_2O_8:Eu^{2+}	–	1000 W for 10 min 375 W for 30 – 90 min	1250	48
$BaMgAl_{10}O_{17}$:Eu^{2+}	0.5	720 W for 25 min	–	49

electric properties. This two-phase material may be achieved in just 4 minutes in the microwave.[51] In contrast, excess nickel added to the half-Heusler MnNiSb sits on the empty tetrahedral site, forming a solid solution with the full Heusler MnNi$_2$Sb. While a miscibility gap is predicted in these compounds at low temperature, the practical microwave preparation temperature results in the solid solution.[52] In addition to MnNiSb, several other magnetic intermetallic compounds including MnCoP, MnB, FeB, MnFe$_2$Si, MnNi$_2$Sn, and (Mn,Fe)$_2$(P,Si) have been prepared using the assisted-microwave method.[53–55] Reaction conditions for selected intermetallics and transition metal chalcogenides are provided in Table 2.

Transition metal chalcogenides

Transition metal chalcogenides, which have diverse applications from electrochemical energy storage to spintronics, require slow heating rates in conventional syntheses to prevent ampoule explosions due to the volatility of chalcogens. Conventional preparations of these materials consist of a series of steps at elevated temperature (973 K), resulting in several days or weeks of heating with grinding and re-pelletization between heat treatments.[56–58] Lower temperature (500 K to 650 K) metathesis reactions have allowed some pyrites to synthesized in just days by circumventing kinetic barriers.[59,60] Butala *et al.* demonstrated microwave preparation of Fe$_{1-x}$Co$_x$S$_2$ and CuTi$_2$S$_4$, accelerating reaction times to less than 40 minutes.[61] The microwave electromagnetic field interacts strongly with the transition metal, selectively heating the metal powder and allowing the reaction to occur rapidly at metal sites before significant sublimation of the chalcogen.[11,15] Since chalcogens are usually weakly absorbing, they do not heat up as quickly, which is advantageous because of issues of pressure build-up in the ampoule. Due to the selective nature of microwave heating and rapid heating of the metal powder, reaction times are reduced from weeks to minutes, resulting in time and energy savings.

Table 2: Relevant information for microwave preparation of intermetallics and transition metal chalcogenides. All samples were prepared from stoichiometric amounts of elemental precursors, with the exception of MnCoP, which used Mn_3P_2 as well as elemental cobalt and red phosphorous. Samples were reacted in evacuated fused silica ampoules to avoid oxidation.

Composition	Sample mass (g)	Microwave conditions	Susceptor mass (g)	ref.
TiCoSb	–	700 W for 1 min	3.6	50
$TiNi_{1+x}Sn$	5.0	700 W for 4 min	3.6	51
$MnNi_{1+x}Sb$	1.0	840 W for 2.5 min	7.0	52
MnCoP	0.3	840 W for 2.5 min	7.0	53
$MnFe_2Si$	1.0	840 W for 2.5 min, 1080 W for 3 min	7.0	53
$MnNi_2Sn$	1.0	1200 W for 3 min	6.5	53
MnB, FeB	0.3	840 W for 3 min	6.5	53, 54
$(Mn,Fe)_2(P,Si)$	5.0	360 W for 20 min	6.0	55
FeS_2, CoS_2	0.2	360 W for 20 min $\times 2$	75 to 80	61
$CuTi_2S_4$	0.2	600 W for 20 min $\times 2$	75 to 80	61

Experimental procedure

This section details the general procedure followed for assisted-microwave materials preparation with insights gained from processing the aforementioned materials. Stoichiometric amounts of reactants are ground and then pressed into a pellet, usually 6 mm in diameter to avoid microwave absorption issues. For assisted-microwave solid state reactions, the use of well ground powder of the starting materials is essential. In bulk metals, there is small penetration depth of the microwaves and large electric field gradients give rise to electric discharges. In powders, there is no electric discharge and rapid heating can occur due to eddy currents.[31] Surface defects, charge, and polarization in powders can enhance the dielectric loss, leading to rapid heating. Powders may be hand-ground with an agate mortar and pestle, or ball-milled to ensure a homogeneous product. As reaction times are short, diffusion is limited and so small particle sizes are desirable. Smaller particle size also increases the surface to volume ratio, and therefore the volume which may interact with microwaves as penetration depth in metals is small. Particle sizes for metal precursors ranged between 3 μm to 45 μm. Pelletization, while not a necessary step in all reactions, increases contact between powder particles, and pellets may be sintered in the microwave oven. The use of pellets also minimizes the potential for contamination due to contact with the container. Volatile reactants may require a slight excess to ensure the final product has the desired composition. Microwave methods are well suited for sample masses 200 mg to 5 g, though reaction conditions must be optimized for the mass used.

For reactions in an inert atmosphere, the pellet is then sealed in a fused silica ampoule under vacuum or partial pressure of argon, shown in Figure 2(a). The ampoule is evacuated and flushed with argon three times before sealing to ensure no oxygen is present. Fused silica is used due to its transparency to microwaves, even at elevated temperatures. However, for long high temperature reactions the sample will conductively heat the ampoule, which could cause softening. In these cases a crucible (for example, of BN) should be used to contain the sample inside the ampoule. Similarly, crucibles should be used
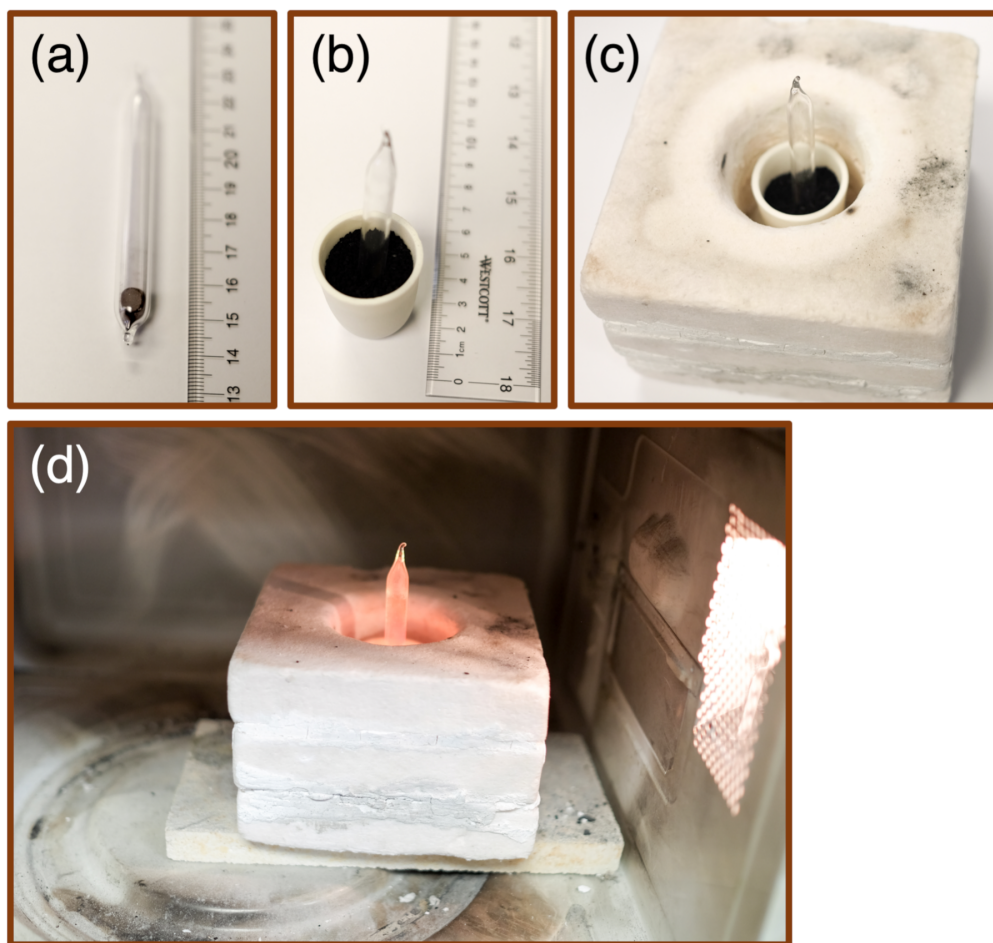
Figure 2: The steps for this experimental procedure are shown here. (a) A pellet is sealed in an evacuated fused silica ampoule and (b) nested in a crucible containing roughly 6 g of activated charcoal. (c) The crucible is placed in an alumina foam housing (d) off center in the microwave cavity and heated using an appropriate power cycle.

when reactants may react with the silica ampoule. The volume of the ampoule should be considered when working with volatile reactants, which could build pressure and explode the ampoule. The microwave ovens are kept in a fume hood and reactions are run with the sash down in case of ampoules breaking. However, for ampoules not fully submersed in the susceptor, the far end of the ampoule will be much cooler, and volatile reactants may condense on this side, preventing pressure build up.[16]

Samples may also be reacted in air by placing the pellet/powder in a crucible.[40,49] If a more reducing atmosphere is needed, the entire microwave oven may be placed inside a glovebag (Atmosbag L, Sigma Aldrich) with flowing nitrogen or argon mixed with 5% hydrogen.[40,41] The flow rate must be adjusted such that the bag does not inflate as the air inside it heats up. A slightly reducing atmosphere can also be achieved with a carbon susceptor by covering the crucible such that a CO atmosphere is trapped.

As the dielectric loss tangent is both material and temperature dependent, many materials do not couple to microwaves in a domestic microwave oven (2.45 GHz) at room temperature. For this reason, a susceptor that is highly absorbing is used to initially heat the material until it reaches a critical temperature and begins to be directly activated by the microwaves. The sealed evacuated ampoule or small crucible is placed in a larger alumina crucible filled with the susceptor (Figure 2(b)), activated charcoal (DARCO© $12-20$ mesh, Sigma-Aldrich). Other susceptors may be used as well, and a temperature versus time plot for the susceptor at different microwave powers is useful in designing power cycles for a reaction. This is discussed in depth in the troubleshooting section below.

The amount of material absorbing microwaves strongly affects the temperature that the reactants will reach, since it determines how much microwave power is available for the reaction. While the susceptor is used to initially heat the reactants, some power goes towards heating the susceptor even once the reactants are absorbing. The use of excess susceptor material therefore decreases the heating rate and the overall temperature that may be reached. For high temperature experiments, typically 3 g to 7 g of activated char-

coal is used as susceptor. Lower temperature experiments involve samples in an evacuated fused silica ampoule fully immersed in 75 g to 80 g activated charcoal. Fully immersing an ampoule in charcoal can help keep volatile reactants in the vapor phase, rather than condensing at the top of the ampoule, by ensuring a more uniform temperature throughout the ampoule.
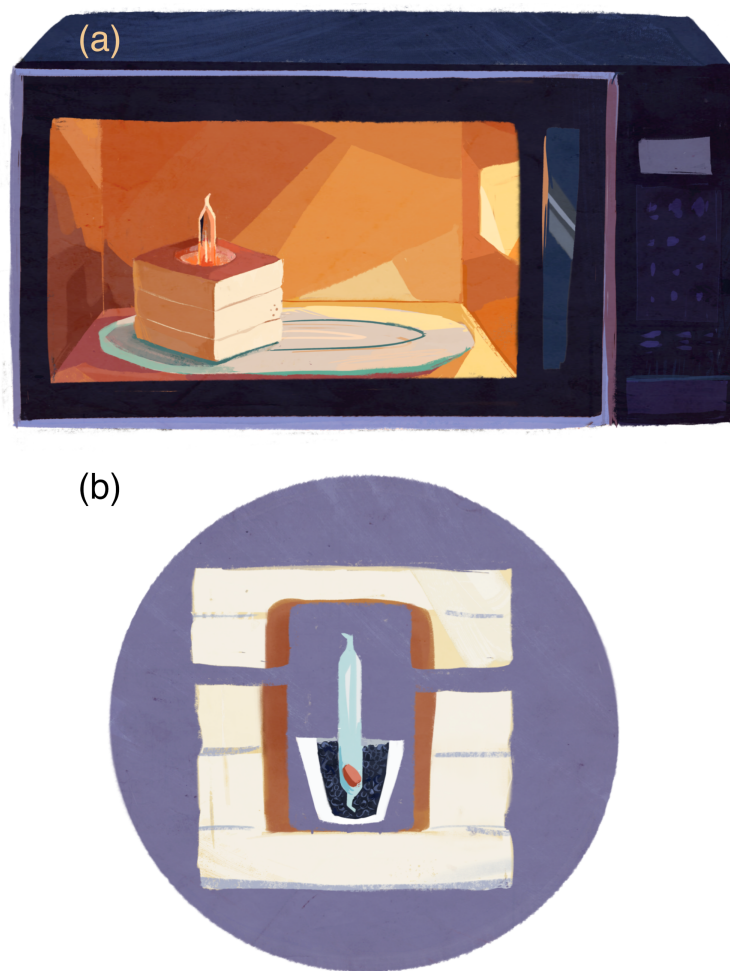

Figure 3: (a) Schematic illustration of the microwave chamber for a typical air-free reaction, showing placement of the insulation in the microwave cavity. (b) The cross sectional view shows the pellet sealed in a fused silica ampoule nested in the charcoal susceptor, and then placed in the insulation. In the case of complex oxides, the fused silica ampoule is replaced by a small crucible containing reactants, which is then nested in the larger crucible containing activated charcoal.

The crucible containing the susceptor and sample ampoule/crucible is placed inside thermal insulation made from alumina fiberboard or low density foam as shown in Fig-

ure 2(c) and illustrated schematically in Figure 3(b).[40] Good insulation material will have a long penetration depth of microwaves even at high temperatures, meaning it will neither reflect nor absorb the microwave energy. The insulating housing is placed off center in the microwave cavity, as shown in Figure 3(a). When a microwave rotation plate is used, this off-centering averages out local maxima and minima as it spins due to the inhomogeneous distribution of the electromagnetic radiation within the cavity. In cases where spinning is not used, for example in Figure 2(d), care is taken to place the sample at the same position each time to minimize inconsistencies. An overview of the experimental setup is illustrated in Figure 3.

Power settings, power cycles, and reaction times are chosen depending on the material (and how it couples to microwaves) and the quantity of absorbing species in the microwave oven. A lower power setting should be used when there is a known decomposition temperature of the desired material at an easily reachable temperature. Melting is not necessary for a successful reaction and can even be contraindicated, as many reactions occur in the solid state. In the case where a reaction is partially complete but a longer dwell time is needed, power cycle control can be used to maintain the temperature without raising it. The power level can be lowered to supply enough energy to continue the reaction without causing runaway heating. Parameters for some different reaction conditions are provided in Table 1 and Table 2. For the chalcogenides, shaking the ampoule between heating segments redistributes the chalcogen that has deposited on the colder end of the ampoule.[16]

An estimate of maximum temperature can be obtained using an infrared pyrometer or by immediately inserting a thermocouple into the charcoal near the sample. Interestingly, samples microwaved for longer may actually be colder. While this could be due to placement, susceptor, or other differences in the procedure, it may be that the product is not a microwave absorber. In this case, once the reaction is complete and starting materials used up, the product does not continue to heat. Depending on the properties of the material and microwave conditions, reactants may melt together which can be determined afterwards

because they take the geometric form of the ampoule.

Ampoules may be air or water quenched out of the microwave oven, or allowed to cool in the charcoal bath. Due to the rapid heating and cooling possible in assisted-microwave preparation, phase formation and evolution may be studied using a series of samples reacted for different lengths of time. This has been successfully applied in previous studies,[44,47] and helps to determine the actual reaction time needed to form the product. Additional annealing time in the microwave oven or in a conventional furnace may increase crystallinity, atomic order, and homogeneity.

Troubleshooting

The goal of this section is to identify factors having a significant impact on reactions, and aid users in setting up reaction conditions for new systems. Parameters such as susceptor choice and mass, sample mass, insulation, and atmosphere are discussed here.

Susceptor. The choice of susceptor plays a large role in microwave reactions. The purpose of a susceptor is to heat quickly and transfer this heat to the sample such that the sample reaches a temperature where it will begin to couple to microwaves. Once this coupling occurs and the material begins to heat itself, it will often reach a much higher temperature than the susceptor. Microwave absorbers such as graphitic carbon or SiC make good susceptors due to their ability to heat rapidly. However, the penetration depth of microwaves into SiC is small, and using this material may shield the sample.

Parameters such as particle size and water adsorbed also play a role in heating. With each use, some charcoal is burned, and so fresh charcoal should be used each time for the most consistent results. It is useful to make calibration curves using a particular carbon source to estimate the temperatures that will be reached for different times at a specific microwave power, and for a given mass of susceptor. One such calibration is shown in Figure 4. It is best to create calibration curves using a thermocouple inserted into the hot

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charcoal immediately after the power is turned off and the housing removed from the microwave, rather than by using an IR pyrometer. However, this will only give a lower estimate of the temperature since cooling will begin immediately when the power is shut off. The thermocouple is more reliable because an IR pyrometer depends on the emissivity of the susceptor, which can vary widely. In addition, the surface temperature measured by the pyrometer is much lower than deep within the susceptor. These calibration curves can be used to target a specific reaction temperature, while recognizing that the actual sample temperature could vary from that of the susceptor. Once an acceptable temperature is reached, power cycle control may be used to maintain the reaction temperature. This is only estimated as we do not measure temperature *in-situ*.
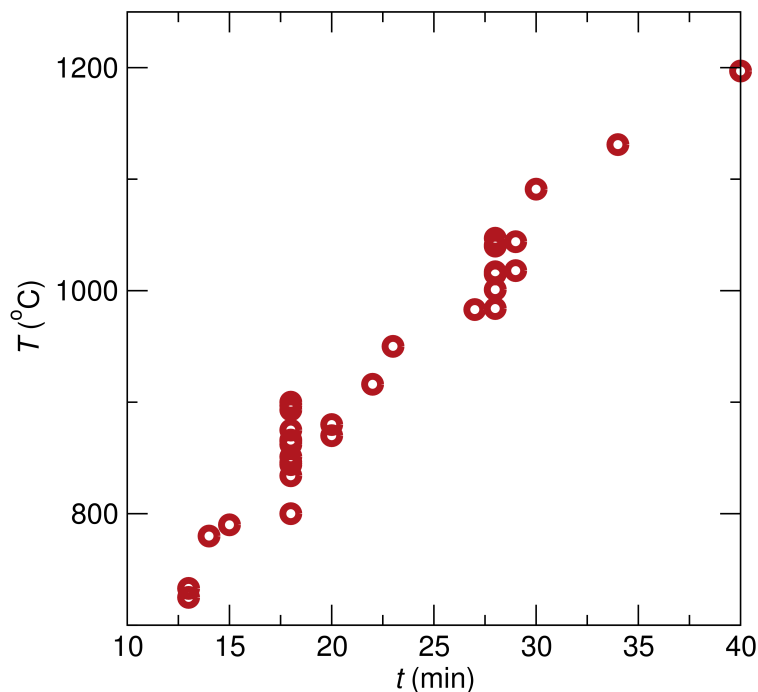

Figure 4: Temperature of $78\,\mathrm{g}$ of activated charcoal as a function of microwave time at power 4 (40% of $1200\,\mathrm{W}$). Values are measured by inserting a thermocouple into the center of the charcoal immediately after microwaving.

For reactions with volatile precursors, fully immersing the ampoule in charcoal keeps these reactants from condensing at cold spots in the ampoules. Even so, a slight excess may be necessary to produce a stoichiometric product. The use of so much susceptor limits

the heating rates and maximum temperature that will be reached because more power is partitioned to heat the susceptor. Since the amount of power available for the reaction depends closely on the susceptor and sample mass, the entire set of reaction conditions must be re-optimized when scaling up a synthetic procedure.

Insulation. The insulating housing containing the crucible with the susceptor and sample protects the microwave oven and helps to keep in the heat produced by the susceptor and sample. The material should be non-absorbing (*i.e.* high penetration depth), so that all of microwave electromagnetic energy goes towards heating the reactants, and the insulation does not shield the inner crucible from microwaves. For this, a low density alumina foam or fiberboard is used. One inch thick high temperature ceramic fiberboard (Skyline Components LLC, Tuscon, AZ) is bonded using a high temperature adhesive cement to form a block three inches tall, and a hole is cut in the center to accommodate the crucible. Another piece of fiberboard may be used as a cover.

Atmosphere. Intermetallics require inert atmosphere to prevent oxidation at elevated temperatures, which is obtained by sealing in an evacuated fused silica ampoule. Fused silica has very low absorption even at elevated temperatures. For this reason, the ampoule will usually not soften even when the sample reaches temperatures well over the softening temperature. However, if a sample maintains this temperature for an extended time it may conductively soften the ampoule, exposing the sample to air and resulting in oxidation. Similarly, if the sample reacts with silica it may cause the ampoule to break. In these cases, the sample should be placed in an alumina or boron nitride crucible before sealing into the ampoule to prevent contact with the silica. A comparison of fused silica ampoules after a reaction in a furnace and in a microwave oven is of interest. In the furnace, the significant time at high temperature frequently results in crystallization (devitrification) of the silica and some reaction between the silica and starting materials. Because silica is such a poor microwave susceptor, it does not attain high temperatures and neither devitrification, nor interactions with reactants occurs in the case of microwave heating.

Oxides, on the other hand, are reacted in air or a reducing atmosphere. To prevent reaction of the oxides with the alumina crucible pellets are placed on a sacrificial layer of powder with the same composition as the sample, between the crucible and sample pellet. The reducing atmosphere can be achieved by placing a lid on the large alumina crucible containing the carbon susceptor and sample crucible. The lid traps some of the reducing carbon monoxide (CO) atmosphere. However, the air inside the microwave cavity is cycled through, and so it is more effective when required, to place the entire microwave in a glovebag with flowing 5% H_2/N_2 gas.

Hazards. To date, we have had no safety issues with microwave ovens in the lab. The microwaves ovens are operated in a fume hood in case of ampoules breaking during reactions, as is standard for conventional syntheses. Heating carbon powder or granular charcoal can lead to inhalation hazards, and the top insulation cover should be removed in the fume hood after heating. Insulated gloves and tongs should be employed when handling the insulating housing and the crucible after heating. Inadequate insulation can lead to damage to the microwave including ignition of combustible components. Ensuring that the outside of the insulation does not reach excessive temperatures, and keeping flammable material away from the microwave during operation and cool down is essential. The microwave oven should not be operated with no absorbing material within.

Characterization

Materials prepared by assisted-microwave methods are subject to standard inorganic materials characterization. Synchrotron powder X-ray diffraction (XRD) is effective for evaluating phase purity, identifying secondary phases, and determining crystallographic parameters. It has been shown that highly crystalline, phase pure materials can be produced using microwave methods provided conditions are optimized. Lab X-ray diffraction allows products to be measured *ex-situ* after reactions are stopped at regular intervals to deter-
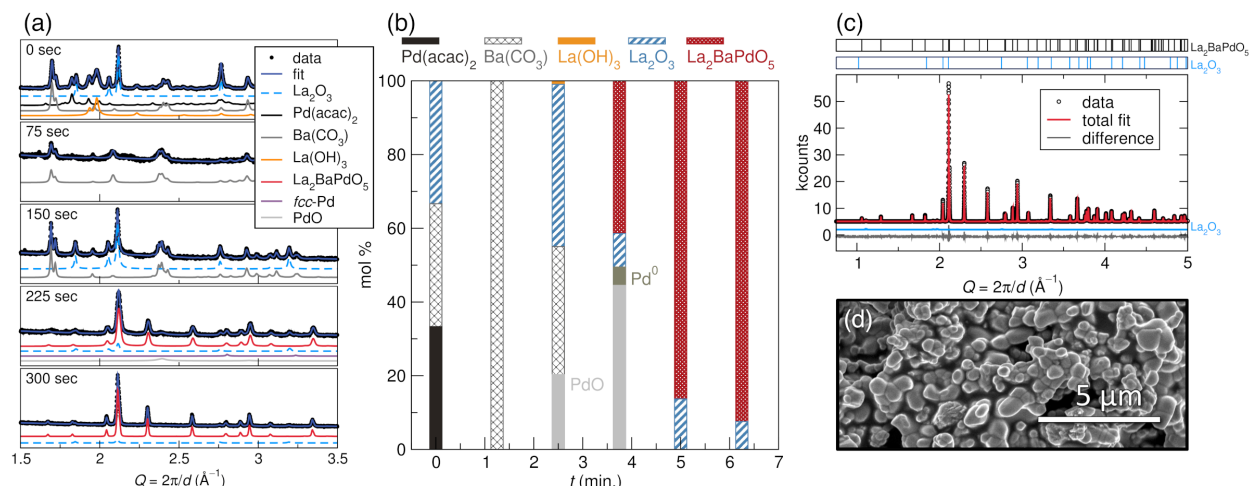
Figure 5: (a) The phase evolution during microwave preparation is observed through *ex-situ* laboratory X-ray diffraction. The formation of La_2BaPdO_5 occurs in less than 225 seconds, with the yield increasing with additional microwave time. (b) Phase fractions at each time interval are determined by Rietveld refinement of the resulting XRD pattern. (c) Final products are scrutinized using synchrotron XRD at Argonne National Lab using the 11-BM beamline, allowing precise analysis due to the higher quality data. (d) Particle size, homogeneity, morphology are observed using scanning electron microscopy equipped with instruments for compositional analysis. Reproduced with modifications, with permission from ref. 47. Copyright 2014 American Chemical Society.

mine intermediate phases. This can be useful in optimizing reaction conditions to ensure a completed reaction, improve crystallinity, or maximize surface area. Figure 5(a) depicts the phase evolution monitored *via* laboratory X-ray diffraction of La_2BaPdO_5 starting from precursors palladium acetyl acetonate, $BaCO_3$, and La_2O_3.[47] Rietveld refinement of the diffraction pattern allows the phases present at different instants of time, and their phase fractions, to be tracked as shown in 5(b). Initially, $BaCO_3$ and an amorphous background are present after 75 secs. This amorphous background was also seen by Misch *et al.* when preparing La_2BaPdO_5 using a combined sol-gel microwave method.[44] La_2BaPdO_5 starts to form in less than 4 minutes, and the secondary phases decrease with additional microwave heating time. Additional heating leads to a more crystalline product with a larger particle size. The final product is analyzed using synchrotron powder X-ray diffraction (SPXRD) at the 11-BM beamline at Argonne National Laboratory, shown in Figure 5(c). The high Q space resolution and intensity of X-rays at the Advanced Photon Source allow precise de-

termination through Rietveld refinement of crystallographic parameters, secondary phases even when present in miniscule amounts, and phase fractions.

Scanning electron microscopy (SEM) equipped with energy dispersive X-ray spectroscopy (EDS) or electron probe microanalysis (EPMA) is a powerful tool to analyze the difference in morphology between microwave and conventionally prepared materials, and to establish the composition. The rapid heating and reaction in the microwave as compared to conventional methods limits the time allowed for particles to sinter. In this way, much finer particle sizes can be produced by the microwave method. Scanning electron microscopy comparing Ba_2SiO_4:Eu^{2+} prepared by conventional heating and by the assisted-microwave sol-gel combined method suggest that the particle size produced by the microwave method is 0.5 μm to 2.0 μm, which is much smaller than the particles produced conventionally (which are of the order of 10.0 μm or larger.[43] The greater morphological control of materials prepared using a combined sol-gel assisted-microwave method due to shorter heating times is advantageous for catalysts, where large surface area is desired, and for phosphors where scattering between particles can occur and control is desirable.

In addition to the suite of detectors in electron microscopes to detect local chemical composition, X-ray fluorescence spectroscopy (XRF) is a useful tool to determine accurate compositions. Variations from nominal composition could occur due to volatilization of precursors, or reaction with the silica ampoule. These can be appropriately remedied by using the feedback to adjust starting compositions.

Conclusions

Assisted-microwave preparation presents many advantages for obtaining solid inorganic compounds, but the technique is not yet being used to its full potential. The procedures detailed in this contribution are rapid, low-cost, and readily carried out, and highly energy-efficient as well. Crystalline products can be obtained with distinct and beneficial mor-

phological control. The direct volumetric heating results in extremely rapid temperature increases, and the varying interaction of microwaves with different materials allows for selective heating, allowing products to be obtained that may otherwise be difficult to prepare. It is hoped that this Methods and Protocols article will reduce the barriers to adopting the necessary best practices to enable more widespread use of assisted microwave preparation.

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