

## General Synthetic Strategies

The evolution of many scientific ideas transforms *discovery* into *design*. Solid-state chemists continue to discover new compounds and structures, many of which exhibit important emerging properties related to energy storage and transport, catalysis, and quantum phenomena. The philosophy of designing materials requires deeper interpretations of what is meant by “*design*”. In particular, synthetic chemists can design structures and compositions, compound function and properties, and synthetic procedures, which can expand the toolbox available to other synthetic chemists. As the field of solid-state chemistry continues to mature, the community is increasingly successful at these three aspects of “*design*” by striving toward *proactive* synthetic strategies, which rely on sound predictions and reaction control. Nevertheless, much can be gained from *reactive* strategies by carefully observing outcomes and thoroughly analyzing results.

READING: A.K. Cheetham and P. Day, Eds., *Solid-State Chemistry: Techniques*, pp. 1-38.  
A.R. West, *Solid State Chemistry and Its Applications*, 1984, Chapter 1.

(7) What are the goals of synthesis? There are many different motivations for carrying out careful synthesis. Here is my own perspective of what chemists expect to accomplish:

- (a) To prepare *new compounds* – “We cannot predict what we cannot imagine.”<sup>10</sup> Numerous attempts to prepare unprecedented compounds generally involve trial and error, founded on some theoretical or computational motivation, and are called *exploratory*.<sup>11</sup> Initial procedures are often traditional (sometimes called “brute force”, “shake and bake”, or “heat and beat”), and typically result in thermodynamic control. As our synthetic toolbox expands, solid-state chemists gain increasing access to kinetically stable products. What guides the search for new compounds or what determines the targets? The answer really depends on the research goals of the group, team, or company involved. Some motivations include:
- Establishing unusual or extreme oxidation states of metal atoms.<sup>12</sup> Two notable cases are negatively charged alkali metals (*alkalides*),<sup>13</sup> which are kinetically stabilized by being coordinated (encapsulated) by organic crown- and cryptand-type ligands, and high oxidation state noble metals, such as Au<sub>2</sub>F<sub>10</sub>.<sup>14</sup> In addition to their fundamental interest, such compounds offer tremendous potential as strong reducing or oxidizing agents, respectively.
  - Examining unexplored or under-explored phase spaces. These investigations can identify unprecedented element-element bonds. Two examples that I find especially interesting are:
    - (i) Li<sub>12</sub>Si<sub>7</sub><sup>15</sup> was discovered by examining the Li-rich region of the Li-Si system for possible electrode materials in Li-ion batteries. The compound can be formulated as Li<sub>24</sub>(Si<sub>4</sub><sup>8-</sup>)(Si<sub>5</sub><sup>8-</sup>)<sub>2</sub> because its crystal structure contains trigonal planar Si<sub>4</sub> stars (isoelectronic to CO<sub>3</sub><sup>2-</sup>) and planar Si<sub>5</sub> rings.

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<sup>10</sup> R.E. McCarley<sup>†</sup>, Iowa State University Chemistry Professor, personal communication.

<sup>11</sup> I. Amato, “Exploring the New Material World”, *Science*, **1991**, 252, 644-646 (Research News article).

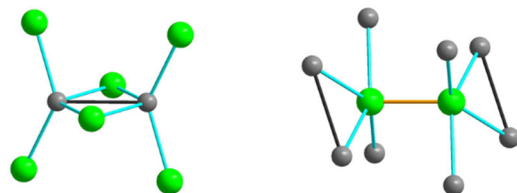
<sup>12</sup> W.T.K. Chan, W.-T. Wong, *Polyhedron*, **2013**, 52, 43-61.

<sup>13</sup> J.L. Dye, *J. Chem. Educ.* **1977**, 54, 332-339.

<sup>14</sup> I.-C. Hwang, K. Seppelt, *Angew. Chem. Intl. Ed.* **2001**, 40, 3690-3693.

<sup>15</sup> H.G. von Schnering, R. Nesper, J. Curda, K.F. Tebbe, *Angew. Chem. Intl. Ed.* **1980**, 19, 1033-1034.

- (ii)  $\text{ZnAs}$ <sup>16</sup> arose from a systematic examination of the Zn-As system under high pressure. The compound is semiconducting with multi-center bonded rhomboid  $\text{Zn}_2\text{As}_2$  rings connected by As-As bonds.<sup>17</sup>  $\text{ZnAs}$  is metastable at ambient pressure with respect to  $\text{Zn}_3\text{As}_2$  and  $\text{ZnAs}_2$ .



**ZnAs:** (Left) Zn-Zn contact (2.72 Å) as part of the planar  $[\text{Zn}_2\text{As}_2]$  rhombus. Each Zn atom is in a distorted tetrahedral environment. (Right) As-As contact (2.43 Å) with their Zn neighbors.

- Targeting analogue compounds by making isovalent/isoelectronic substitutions. One example with technological implications is replacing oxide with other chalcogenides in perovskite-type structures, e.g.,  $\text{SrTiS}_3$  and  $\text{LaYS}_3$ . These semiconducting compounds offer potential applications for energy harvesting, solid-state lighting, and infra-red detection.<sup>18</sup> The examination of the Zn-As system mentioned above was also partially motivated to search for analogues to the Zn-Sb system.<sup>17</sup>
- Confirming or refuting theoretical predictions. As the computations of solid-state electronic structures have evolved, predictions of stable solid-state compounds multiplied but seldom with experimental verification. One example from my own research is hexagonal  $\text{ZrMoP}$ ,<sup>19</sup> which we predicted by calculating total electronic energies for model di-metal phosphides in different structure types for various valence electron counts and then successfully prepared. Early efforts for compound prediction used *phenomenological structure maps*<sup>20</sup> and *quantum structural diagrams*,<sup>21</sup> both of which relied on atomic parameters derived from density functional or pseudopotential theory. A recent strategy is the *inverse design approach*,<sup>22</sup> which combines theoretical calculations with combinatorial and traditional experimental characterization and has been successful for uncovering new semiconducting half-Heusler  $\text{ATX}$  compounds  $\text{TaTsn}$  ( $T = \text{Co, Rh, Ir}$ ). The same approach suggests that the isovalent analogues  $\text{VTsn}$  ( $T = \text{Co, Rh, Ir}$ ) are unstable. Nevertheless, as Zunger emphasizes,<sup>23</sup> “real materials rarely behave as models suggest,” and “theories must shift, from describing possible properties in hypothetical structures to revealing real structures that can host exotic properties with impunity.”

New materials, in general, will advance the “cutting edge” of what is possible and can lead to new structures and unusual or unprecedented properties. Often, elucidation of a structure inspires further systematic experimentation on the material.

Predicting the outcome of any solid-state reaction is especially challenging, if not virtually impossible. Therefore, exploratory synthesis remains an important research strategy. Efforts increasingly emphasize using computations and machine learning to provide viable synthetic

<sup>16</sup> J. Clark, K.J. Runge, *Z. Naturforsch. B*, **1976**, *31*, 158-162;

<sup>17</sup> A. Fischer, D. Eklöf, D.E. Benson, et al., *Inorg. Chem.* **2014**, *53*, 8691-8699.

<sup>18</sup> Y.-Y. Sun, M.L. Agiorgousis, P. Zhang, S. Zhang, *Nano Lett.*, **2015**, *15*, 581-585.

<sup>19</sup> G.J. Miller, J. Cheng, *Inorg. Chem.* **1995**, *34*, 2962-2968.

<sup>20</sup> D.G. Pettifor, *J. Phys. C: Solid State Phys.* **1986**, *19*, 285-313.

<sup>21</sup> K.M. Rabe, *J. Alloys Cmpd.* **1993**, *197*, 131-135.

<sup>22</sup> A. Zakutayev, X. Zhang, A. Nagaraja, et al., *J. Am. Chem. Soc.* **2013**, *135*, 10048-10054.

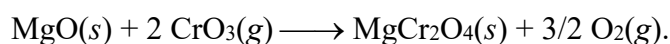
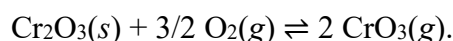
<sup>23</sup> A. Zunger, *Nature* **2019**, *566*, 447-449.

targets (see the *Materials Genome Initiative*<sup>24,25</sup> at <https://www.mgi.gov>), but never underestimate the creativity that can arise from chemical intuition. Nevertheless, whatever the initial objective of any synthetic strategy, be prepared to accept surprises!

- (b) To prepare *known compounds with controlled (high) purity* – These developments typically follow discovery to increase synthetic yields, minimize waste, and improve the characteristics of the desired products by eliminating contaminants or separating side products from the target compounds.<sup>26</sup> New compounds are seldom prepared “neat”. Perhaps they are formed from solution-based methods or require another product to act as a thermodynamic driving force. As a result, the synthetic chemist must pay careful attention to the purities and chemical behavior of all starting reagents, container materials, and gaseous atmospheres. After reaction, separation or purification steps may be needed. For example, passing Cl<sub>2</sub>(g) over heated Nb(s) foil produces the lemon-yellow solid NbCl<sub>5</sub>(s) that is initially impure. Sublimation of the yellow solid product separates NbCl<sub>5</sub>(s) from NbOCl<sub>3</sub>(s), a fine, white powder. *Adventitious* oxygen comes from the Nb metal surface as well as with the chlorine gas. During the reaction, the gas stream beyond the reaction tube should be bubbled through NaOH(aq), which limits exposure to chlorine gas according to



Another important strategy to produce pure solids is to use a reagent that reversibly converts a non-volatile reactant or product to gaseous species. This approach is called *chemical* or *vapor phase transport*. Traditional sintering of two solid reactants to form a solid product can be driven effectively by introducing a gaseous *transport agent* that will preferentially react with one solid reactant to form a new gaseous species that reacts with the other solid reactant. For example, preparing the spinel-type oxide MgCr<sub>2</sub>O<sub>4</sub>(s) by fusing MgO(s) and Cr<sub>2</sub>O<sub>3</sub>(s) via reactive sintering struggles to form the spinel that can be readily separated from any remaining reactant species. O<sub>2</sub>(g) can be added as a transport agent because it oxidizes Cr<sub>2</sub>O<sub>3</sub>(s) to the volatile CrO<sub>3</sub>(g), which then reacts with MgO(s):



Crystals of the MgCr<sub>2</sub>O<sub>4</sub>(s) spinel form away from the reactants via vapor transport and, as a result, are readily isolated. The first equilibrium can be used to purify Cr<sub>2</sub>O<sub>3</sub>(s).

- (c) To prepare *known compounds as single crystals* – Controlling the morphology of any solid product can have profound influence on its characteristics and applications. Single crystals are important for measurements of physical properties that have tensor characteristics such as magnetization and electrical resistivity. Single crystals also significantly reduce or eliminate any effects on these measurements caused by grain boundaries in polycrystalline samples. Such crystals are often grown from solution (fluxes) or via some kind of epitaxial growth procedure on a well-ordered substrate. As the arsenal of crystal growing techniques expands, the ability to control solid-state and crystal morphologies increases.<sup>27</sup>

<sup>24</sup> Y. Zhang, D.A. Kitchaev, J. Yang, et al. *npj Comput. Mater.* **2018**, 4, <https://doi.org/10.1038/s41524-018-0065-z>; *Modern Methods of Crystal Structure Prediction*, Ed. A.R. Oganov, Wiley-VCH, Weinheim, Germany, 2011.

<sup>25</sup> P. Raccuglia, K. Elbert, P. Adler, et al. *Nature*, **2016**, 533, 73-76.

<sup>26</sup> J. S. Abell, *Handbook on the Physics and Chemistry of Rare Earths*, Vol. 12, K.A. Gschneidner, Jr. and L. Eyring, Eds., Elsevier, 1989, Ch. 80, pp. 1-51.

<sup>27</sup> J. Hulliger, *Angew. Chem. Int. Ed. Engl.* **1994**, 33, 143-162.

**Crystal Growth Techniques:** Growing crystals is a non-equilibrium process. If no seed crystal is present in the parent phase, then crystals must first nucleate, which requires supercooling and supersaturation so that the system is away from equilibrium. In such cases, when a crystal forms, it grows rapidly at first and with a high concentration of defects that can propagate into later stages of near-equilibrium crystal growth. Therefore, many crystal growth procedures use seed crystals to avoid the nucleation problem. On the other hand, if a crystal is in dynamic equilibrium with the growth system, then the free energy is at a minimum and no growth occurs. Therefore, equilibrium must be disturbed by a change in temperature, pressure (including strain), or chemical potential. However, to control crystal growth, the process must be near equilibrium.

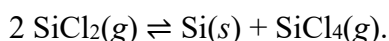
Many procedures have been developed for effective crystal growing. Any crystal growth procedure requires control over a phase change, which leads to four primary categories of methods: (1) from the solid-state; (2) from the melt; (3) from the vapor; and (4) from solution.

READING: B. R. Pamplin, Ed. *Crystal Growth*, 2<sup>nd</sup> Ed., Pergamon Press, Oxford, 1980.

**(8) Solid-State Growth:** Because most solid-state growth processes require atomic diffusion, which is very slow at normal temperatures, other strategies are generally preferred. Nevertheless, crystal growth from solids includes well-established metallurgical processes, such as annealing and sintering, which have been utilized for various metals, oxide ceramics, and semiconductors. *Annealing* is a general heat treatment of a solid over a specified time. *Sintering* is annealing of a pre-compressed powder sample, typically at a temperature ca. two-thirds of the absolute melting point.<sup>28</sup> During sintering some particles join and grow at the expense of surrounding grains, and much of the void volume that resulted from the initial misfit of particles is eliminated. These changes lower the free energy of the sample. Furthermore, the sample does not melt during these procedures, and the outcome is usually incomplete and unreliable.

**(9) Vapor-State Growth:** Crystal growth from the vapor can offer exceptional purity and morphological control of the sample. These methods include sublimation, epitaxial growth, and vapor transport. *Sublimation* is a purification method rather than a crystal growth strategy. Nevertheless, it is effective for growing crystals of volatile elements and certain binary compounds with volatile components, like elemental sulfur and cadmium sulfide. *Vapor transport* utilizes a transport agent to create a gaseous mixture that leads to crystal formation by controlling temperature gradients in a closed tube. *Epitaxial growth* mechanisms involve forming crystals one monolayer at a time and allow exceptional control over the dimensions of the growth direction. Epitaxial growth is useful for device fabrication, especially in the optoelectronics industry, and encompasses three different approaches:<sup>29</sup>

(i) *Vapor Phase Epitaxy* (VPE) is used primarily for homoepitaxy, i.e., growing the same substance as the substrate, such as growing Si. Any one of the reactants SiH<sub>4</sub>, SiH<sub>2</sub>Cl<sub>2</sub>, SiHCl<sub>3</sub>, or SiCl<sub>4</sub> is diluted in H<sub>2</sub> and placed in proximity to a heated Si substrate. Silane pyrolysis yields Si and H<sub>2</sub>, whereas the chloride molecules give SiCl<sub>2</sub> and HCl. The subsequent equilibrium yields Si:



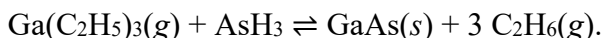
(ii) *Molecular Beam Epitaxy* (MBE) is useful for growing all types of semiconductors and is especially able to control sub-monolayer coverage of a substrate, but ultra-high vacuum is

<sup>28</sup> J.E. Burke, J.H. Rosolowski, General Electric Co. Technical Information Series, Report #73CRD268, Sept. 1973.

<sup>29</sup> J. Singh, *Electronic and Optoelectronic Properties of Semiconductor Structures*, Cambridge University Press, Cambridge, 2003.

required. MBE can readily grow heterostructures, which are mixtures of well-controlled layers of different compounds. The ultra-low pressures allow monitoring during crystal growth as well as chemical analyses.

- (iii) *Chemical Vapor Deposition* (CVD; MOCVD = metal-organic CVD) is typically used for heteroepitaxy, and often employs complex molecules. For example, GaAs films can be deposited by the reaction between organogallium compounds and arsine, such as:



Crystal growth can occur far from equilibrium conditions, and significant safety precautions are often necessary.

During solid-state growth from the gas phase, the flux of gas molecules hitting a substrate surface is directly proportional to the partial pressure of the gas, and inversely proportional to the square root of the molecular weight and temperature:

$$\text{Flux} \left( \frac{\text{molecules}}{\text{cm}^2 \cdot \text{sec}} \right) = \frac{p}{\sqrt{2\pi M k T}} \sim \frac{(3.51 \times 10^{22}) \cdot p \text{ (torr)}}{\sqrt{M(\text{g/mol}) \cdot T(\text{K})}}.$$

**(10) Melt Growth:** Crystal growth from the melt is the accepted method for growing large, high-quality single crystals of metals, semiconductors, salts, and some organic solids relatively rapidly. Important techniques were developed in the electronics, optics, and synthetic gemstone industries. However, effective growth from the liquid state normally requires congruently melting substances and manageable vapor pressures at the melting points. A solid substance melts *congruently* if it transforms to the liquid state without changing composition. A solid melts *incongruently* if it gives a mixture of a solid and liquid, both with compositions different from the starting solid. Two important melt-growth techniques for laboratory samples include *crystal pulling* (*Czochralski*) and *directional freezing* (*Bridgman-Stockbarger*):

- (i) The *Czochralski* technique involves lowering a seed crystal into a melt of the desired crystal, with the top surface of the melt just above the melting temperature. As the seed crystal is slowly withdrawn from the melt, it is slowly rotated to inhibit the natural tendency to grow along certain orientations that produce faceting. This method is commonly used to grow semiconductors like Si, GaAs and InP.
- (ii) In the *Bridgman-Stockbarger* technique, a crystal nucleates and grows from the melt on a seed by translating the melt from a hot zone to a cold zone (in the Stockbarger modification, there is a hot zone, an adiabatic loss zone, and a cold zone). The seed crystal need not be the best specimen because part of it will be remelted, which provides a fresh interface for crystal growth. Also, translation occurs by moving either the crucible or the furnace. This technique can be implemented in either a vertical or horizontal configuration; horizontally grown crystals exhibit high crystalline quality.

Bridgman growth can be accomplished on a diffractometer for substances that have relatively low melting points and are difficult to handle. One example is the structural study of  $\text{Mn}_2\text{O}_7$ , which is liquid at room temperature and prepared by the reaction between potassium permanganate and sulfuric acid:



$\text{Mn}_2\text{O}_7$  forms as a ring above the solution and is then sublimed into a glass capillary. The capillary is inserted in a goniometer head with a Bridgman heating plate surrounding the capillary, and the entire ensemble is placed on the X-ray diffractometer. By controlling a

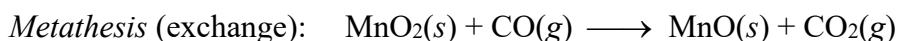
cooling gas (nitrogen) with a heating plate surrounding the capillary, a single crystal suitable for structural analysis could be grown in a controlled manner.<sup>30</sup>

**(11) Solution Growth:** In melt growth, the crystal establishes equilibrium with the pure liquid state. In solution growth, the crystal establishes equilibrium with a homogeneous liquid mixture. From a different but related viewpoint, the solvent freezes during melt growth, whereas the solute crystallizes (precipitates) below its melting point during solution growth. Crystal growth from solution generally involves achieving supersaturation, either by supercooling or solvent extraction via slow evaporation. Solution growth procedures are slower than melt growth and can lead to less pure crystals because it is possible for solvent to be included in the precipitated crystals. Nevertheless, metal-rich crystalline samples for physical property measurements can be grown using various fluxes, which serve as solvents. In addition, *liquid phase epitaxy* is an important technique for growing layers a few microns thick of III-V semiconductors and alloys used for light-emitting diodes.<sup>31</sup>

**Examples of Solid-State Reactions:** How can one increase the chances of finding a new solid-state compound or controlling the nature of a solid product? Although single-phase products are most desirable, they are not always possible. High-temperature reactions have been the most common preparative strategies, but various lower-temperature approaches have been and continue to be developed to access compounds that decompose at high temperatures. Elucidating reaction pathways, i.e., establishing mechanistic understanding, can broaden the scope of accessible solids. For some further reading, see

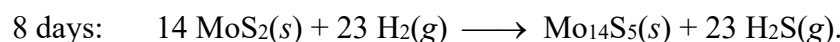
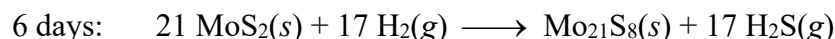
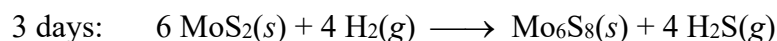
- Stein, S.W. Keller, T.E. Mallouk, "Turning Down the Heat: Design and Mechanism in Solid-State Synthesis", *Science*, **1993**, 259, 1558;
- A.J. Martinolich, J.R. Neilson, "Toward Reaction-by-Design: Achieving Kinetic Control of Solid State Chemistry with Metathesis", *Chem. Mater.* **2017**, 29, 479-489.;

**(12) Gaseous Component(s):** Utilization of gas-phase reactants or relying on generating gaseous products can create useful thermodynamic driving forces and enhance reaction kinetics to form solids. There are three broad types of reactions:



Exchange reactions are frequently entropy-driven with  $\Delta S > 0$ , like this example. In addition, CO serves as a reducing agent of the metal oxide.

$\text{H}_2(\text{g})$  is an effective reducing agent to produce interesting solids. Hydrogen reduction of  $\text{MoS}_2$  with a Pt catalyst at  $1000^\circ\text{C}$  affords various reduced molybdenum sulfides:<sup>32</sup>



The products were identified by X-ray powder diffraction, and these chemical equations simply account for the observed products. Note that as reaction time increases, the  $\text{H}_2/\text{MoS}_2$  molar ratio also increases. Identification of the two Mo-rich sulfides were based

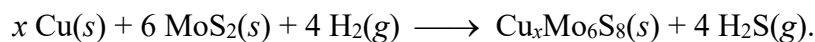
<sup>30</sup> A. Simon, R. Dronskowski, B. Krebs, B. Hettich, *Angew. Chem. Int. Ed. Engl.*, **1987**, 26, 139-140; R.

Dronskowski, B. Krebs, A. Simon, G. Miller, B. Hettich, *Z. Anorg. Allg. Chem.* **1988**, 558, 7-20.

<sup>31</sup> D. E. Bugaris, H.-C. zur Loye, *Angew. Chem. Int. Ed.* **2012**, 51, 3780-3811.

<sup>32</sup> K.S. Nanjundaswamy, J. Gopalakrishnan, *J. Solid State Chem.* **1987**, 68, 188-191.

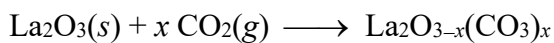
on the diffraction patterns for Nb<sub>21</sub>S<sub>8</sub> and Nb<sub>14</sub>S<sub>5</sub>, the structures of which are derived from condensation of [Nb<sub>6</sub>S<sub>8</sub>] face-capped metal octahedral clusters. The presence of Mo<sub>6</sub>S<sub>8</sub>(s) as an intermediate phase during H<sub>2</sub> reduction motivated successful syntheses of Chevrel-type phases using the same strategy by including an additional metal:



Chevrel phases are ternary compounds containing [Mo<sub>6</sub>X<sub>8</sub>] (X = S, Se, Te) face-capped Mo<sub>6</sub> octahedral clusters. This diverse class of chalcogenides includes superconductors with high critical fields (PbMo<sub>6</sub>S<sub>8</sub>) and effective catalysts for hydrodesulfurization (HoMo<sub>6</sub>S<sub>8</sub>). These ternary compounds can be prepared by heating the elements, whereas the binaries “Mo<sub>6</sub>X<sub>8</sub>” cannot be obtained by this traditional route.



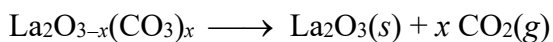
These reactions are generally enthalpy-driven because  $\Delta S < 0$ . This example allows metal embrittlement. The reaction starts with large chunks of Gd. After reaction with hydrogen, the resulting hydride can be crushed using a mortar and pestle to create a hydride powder.



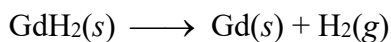
This is an example of an acid-base reaction. The surface of La<sub>2</sub>O<sub>3</sub> is susceptible to this reaction in air, even at room temperature, and can affect the kinetics of using La<sub>2</sub>O<sub>3</sub> as a solid-state reagent.



These reactions are generally entropy-driven because  $\Delta S > 0$ . However, there will often be diffusion limitations because the solid product forms on the solid reactant. This example allows subsequent fusion of BaO into other possible components. BaCO<sub>3</sub> melts at 811°C whereas BaO melts at 1923°C. At just below 811°C, the equilibrium pressure of CO<sub>2</sub> is  $\sim 10^{-4}$  atm. Therefore, if BaCO<sub>3</sub> is heated in air, which has a partial pressure of CO<sub>2</sub> as  $\sim 4 \times 10^{-4}$  atm, this decomposition requires heating above the melting point of BaCO<sub>3</sub> to have a favorable Gibbs free energy.

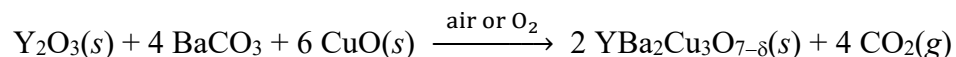


This reaction reverses the combination of La<sub>2</sub>O<sub>3</sub> and CO<sub>2</sub> mentioned above, and is favored at high temperatures. Therefore, La<sub>2</sub>O<sub>3</sub>, as received from a manufacturer, should be heated to  $\sim 1000^\circ\text{C}$  under vacuum for several hours to remove unwanted surface CO<sub>2</sub>.



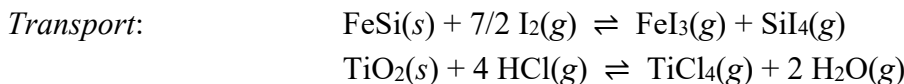
Dehydrogenation of the metal hydride proceeds at elevated temperatures under vacuum. If the metal hydride is a powder, the reaction produces small metal particulates. An optimal temperature for this reaction is  $\sim 2/3$  the melting point of Gd, but the metal likely retains some interstitial H. If the metal has a significant vapor pressure, such as Sm or Eu, then this reaction is not effective to produce small metal particles.

Decomposition reactions have been used to prepare cuprate superconductors, e.g.,



Additional O<sub>2</sub>(g), which is provided either as a purified gas stream or via heating in air, is necessary to achieve the superconducting phase YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$</sub> (s). In the absence of oxygen, then the typical product is YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6.5</sub>(s), which is not superconducting. As noted above, the decomposition of BaCO<sub>3</sub> can be problematic so that final traces of CO<sub>2</sub> are difficult to remove. Some ways to address these challenges include using Ba(NO<sub>3</sub>)<sub>2</sub> as

a another source of BaO and to carry out the reaction with air/O<sub>2</sub> at lower temperatures after initial formation of the quaternary oxide.



These reactions are controlled equilibria carried out in two-zone or multi-zone furnaces. The gaseous reactants, called transport agents, convert the solid into gas-phase species that diffuse throughout the container. Common examples of transport agents include I<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>O, and HCl. Formation of the pure solid is driven by the equilibrium constant; the pure solid will grow in the zone where  $K(T)$  is lower. Transport reactions are very effective for growing very pure crystalline solids.

**(13) High Pressure:** Pressure is applied force per unit area. Important units of pressure are atmosphere (atm), bar, torr, and pascal (Pa), which is the SI unit. One atmosphere (1 atm) is the average sea-level atmospheric pressure of earth and is frequently used as standard pressure. One pascal (1 Pa) is one Newton per square meter (1 N/m<sup>2</sup>). Some useful relationships are:

$$1 \text{ atm} = 1.01325 \text{ bar} = 760 \text{ torr} = 101,325 \text{ Pa} = 0.101325 \text{ MPa}.$$

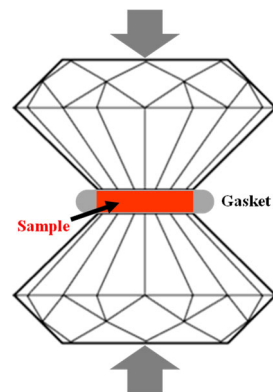
Some important natural pressures are (i) atmospheric pressure  $\sim 0.0001$  GPa; (ii) pressure at the deepest part of the ocean  $\sim 0.1$  GPa; and (iii) pressure at the earth's center  $\sim 350$  GPa.

Application of high pressure can expand the number of compounds existing in a phase space. The development of the diamond-anvil cell has allowed pressures that approach values well beneath the earth's surface. When pressure is applied to solid particles during reaction, then contact areas and reactive interfaces increase, with internal stresses leading to faster atomic diffusion. Furthermore, compression of solids provides  $p\Delta V$  work that can lead to *new* phases that are not stable at ambient pressure. Different high-pressure approaches include:

*Applying high hydrostatic pressure on a sample:* This can be accomplished by compressing the sample between hard surfaces. An effective device uses opposing anvils (shown here); force is applied to the larger faces and the sample, which is enclosed in a gasket, is compressed between the smaller faces. Pressures  $\sim 3$  GPa (30,000 atm) could be achieved since the early 1900's. Multi-anvil devices, when fitted with a resistance heater, allowed studies up to  $\sim 30$  GPa and 2000°C.

The invention in 1958 of the diamond-anvil cell revolutionized high pressure chemistry and physics.<sup>33</sup> Pressures of the order 10<sup>2</sup> GPa are routinely accessible and have revealed unusual chemistry. Some significant examples include

- (i) NaCl<sub>3</sub>:<sup>34</sup> Unexpected compositions in the sodium-chlorine system arise at pressures exceeding  $\sim 60$  GPa. This compound is cubic (*cP8*), space group  $Pm\bar{3}n$ . Na atoms are surrounded by distorted icosahedra of Cl; Cl atoms have 2 Cl neighbors at 2.295 Å and 8 additional neighbors at 2.81 Å. These distances are longer than the Cl–Cl distance in Cl<sub>2</sub> (1.98 Å) but much smaller than a van der Waals contact ( $\sim 3.50$  Å).



<sup>33</sup> P.C. Burnley, "The Diamond Anvil Cell (DAC)" at

[https://serc.carleton.edu/NAGTWorkshops/mineralogy/mineral\\_physics/diamond\\_anvil.html](https://serc.carleton.edu/NAGTWorkshops/mineralogy/mineral_physics/diamond_anvil.html)

<sup>34</sup> W. Zhang, A.R. Oganov, et al., *Science*, **2013**, 342, 1502-1505.

- (ii)  $\text{H}_3\text{S}$ :<sup>35</sup> High pressure studies of the H–S system have revealed superconductivity with critical temperatures exceeding 200 K. Like the sodium-chlorine system, unusual compositions occur, such as this phase, which exists at pressures above 155 GPa. Its structure is cubic (*cI8*), space group  $Im\bar{3}m$ . H atoms fill all (distorted) octahedral voids of BCC-packed S atoms.
- (iii)  $\text{Na}_2\text{He}$ :<sup>36</sup> This remarkable discovery benefitted from using a structure-predicting, first-principles algorithm to search systematically for stable helium compounds. This compound, obtained at pressures exceeding 300 GPa, is the cubic anti-fluorite type (*cF12*). According to electronic structure calculations, it can be described as an *electride*, so that cationic Na atoms and electron pairs form a rocksalt-type arrangement with He atoms filling all tetrahedral holes of the FCC Na array.

*Using high pressure of a reactive gas:* Common gas-phase reactants for high pressure syntheses are  $\text{O}_2$  and  $\text{F}_2$ . In addition to commercial sources (gas cylinders),  $\text{O}_2$  can be generated by the decomposition of chlorates or perchlorates.  $\text{F}_2$  requires use of Teflon or Monel (Ni-rich alloys containing mostly Cu plus some other metals) autoclaves. According to Hoppe,<sup>37</sup> HF or  $\text{O}_2$  impurities in commercial grade  $\text{F}_2$  can activate fluorination and need not be extensively removed. Using these gases at high pressures can lead to some interesting compounds with metals in exceptionally high oxidation states:

- (i)  $\text{Ag}_2\text{NiO}_2$ :<sup>38</sup> Exploring  $d^{10}$ - $d^{10}$  interactions led to reactions between  $\text{Ag}_2\text{O}$  and  $\text{NiO}$  at  $550^\circ\text{C}$  and 65 MPa  $\text{O}_2$  pressure (to avoid decomposition of  $\text{Ag}_2\text{O}$ ). This compound shows a surprising charge distribution  $[\text{Ag}_2]^+[\text{NiO}_2]^-$  with subvalent Ag and high oxidation state Ni(III). The compound is metallic and orders antiferromagnetically.
- (ii)  $\text{LaCuO}_3$ :<sup>39</sup> This rhombohedral perovskite is stabilized under high  $\text{O}_2$  pressure. It is prepared at  $1400^\circ\text{C}$  and 5 GPa  $\text{O}_2$  by reacting  $\text{La}_2\text{O}_3$  with  $\text{CuO}$  and  $\text{KClO}_4$ , which decomposes to  $\text{KCl}$  and  $\text{O}_2$ . Under ambient pressure, the compound becomes oxygen-deficient,  $\text{LaCuO}_{3-x}$ . When heated at ambient pressure, it decomposes to  $\text{La}_2\text{CuO}_4$  and either  $\text{CuO}$  or  $\text{Cu}_2\text{O}$ .
- (iii)  $\text{BaPrF}_6$ :<sup>37</sup> Tetravalent rare-earth cations, except Ce(IV), are unusual, although not unprecedented.  $\text{BaPrF}_6$  can be obtained as a white powder by first perfluorinating  $\text{BaPrCl}_5$  at  $400^\circ\text{C}$  and following up with 300 atm  $\text{F}_2$  at  $500^\circ\text{C}$ .
- (iv)  $\text{O}_2\text{AuF}_6$ :<sup>37</sup> Pentavalent Au is especially unusual given the high electronegativity of Au. Lemon-yellow crystals form by reacting  $\text{AuF}_3$  with 3:1 mixture of  $\text{F}_2:\text{O}_2$  at  $\sim 3000$  atm and  $\sim 330^\circ\text{C}$  over 2 weeks.

*Using high solvent pressures under solvothermal conditions:* These are heterogeneous chemical reactions carried out in a solvent at high temperature and pressure relative to ambient conditions. Typically, the solvent achieves near-critical or supercritical behavior. Hydrothermal conditions effectively form oxides, hydroxides, and minerals. Ammonothermal conditions produce amides, imides, and nitrides.

<sup>35</sup> V.S. Minkov, V.B. Prakapenka, E. Greenberg, M.I. Eremets, *Angew. Chem. Intl. Ed.* **2020**, *59*, 18970-18974.

<sup>36</sup> X. Dong, A.R. Oganov, et al., *Nature Chem.* **2017**, *9*, 440-445.

<sup>37</sup> R. Hoppe, *Isr. J. Chem.* **1978**, *17*, 48-52.

<sup>38</sup> M. Schreyer, M. Jansen, *Angew. Chem. Intl. Ed.* **2002**, *41*, 643-646.

<sup>39</sup> M. Karppinen, H. Yamauchi, T. Ho, H. Suematsu, O. Fukunaga, *Mater. Sci. Eng.: B* **1996**, *41*, 59-62.

Solvothermal conditions can be created by (a) polar protic solvents like H<sub>2</sub>O, NH<sub>3</sub>, HCl, and ethanol; (b) polar aprotic solvents like ethylene diamine and THF; and (c) nonpolar solvents like benzene and CO<sub>2</sub>. This strategy continues to grow in significance as it is used to produce functional materials such as semiconductors, piezoelectrics, and catalysts. The following table summarizes a few solvents, their significant physical properties, and examples of compounds obtained under solvothermal conditions:

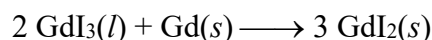
Solvent	Normal Boiling Point (°C)	Critical Temperature (°C)	Critical Pressure (atm)	Example Products
H <sub>2</sub> O	100	374	218	α-SiO <sub>2</sub> , ZnO, α-MnS
NH <sub>3</sub>	-33.3	132	111	GaN, Cu <sub>3</sub> N, α-MnS
HCl	-85	51.6	81.6	SbSeI, BiSbI
Ethanol	78.4	242	62.2	Li <sub>1-x</sub> Mn <sub>2</sub> O <sub>4-y</sub>
Ethylene Diamine	116	305	161	CuInSe <sub>2</sub> , Cu <sub>7</sub> Te <sub>4</sub>
THF	66	267	51.2	β-MnS
C <sub>6</sub> H <sub>6</sub>	80.1	289	48.3	Se, BN, γ-MnS
CO <sub>2</sub>	-78.5	31.2	72.8	PVC

An interesting outcome of this approach is that changing solvents can lead to different structural outcomes, as evidenced for MnS. The thermodynamically favored rocksalt-type α-MnS is obtained from several solvents, whereas metastable β-MnS (sphalerite-type) and γ-MnS (wurtzite-type) form, respectively, in tetrahydrofuran and benzene.<sup>40</sup>

Further reading:

- *Preparative Methods in Solid State Chemistry*, Ed. P. Hagenmuller, Academic Press, **1972**.
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- G. Demazeau, "Solvothermal reactions: An original route for the synthesis of novel materials," *J. Mater. Sci.* **2007**, *43*, 2104-2114.
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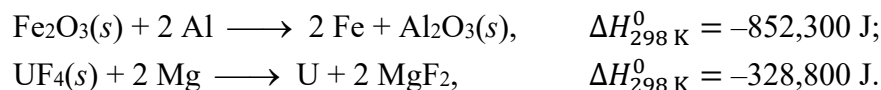
**(14) Liquid-Phase Components:** By introducing a liquid-phase component, generally by fusion induced at higher temperature, then contact areas between reactants, atom mobilities, and reaction rates increase. The liquid phase may also dissolve products, a process that can assist separation and purification. In particular, a condensed phase may be prepared *neat* if one or more of the reactants become liquid, such as this synproportionation reaction:



This approach is particularly useful if the solid product melts *congruently*. However, as the liquid is depleted, then diffusion problems inherent for solid-state reactions may occur in the product.

Metathesis reactions that are sufficiently exothermic can use the heat released to accelerate the reaction or enhance product separation by producing liquids (or even gases). These are *thermite-type* reactions such as

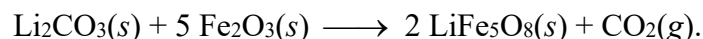
<sup>40</sup> J. Lu, P. Qi, et al. *Chem. Mater.* **2001**, *13*, 2169-2172.



The corresponding standard enthalpies at 298 K are both highly exothermic. For the first reaction, after taking into account the heat capacities of Fe and Al<sub>2</sub>O<sub>3</sub> and the molar enthalpies of any phase transitions, the reaction between 1 mole of Fe<sub>2</sub>O<sub>3</sub>(s) and 2 moles of Al(s) in an adiabatic container yields the final state of 1 mole of Al<sub>2</sub>O<sub>3</sub>(l), 1.95 moles of Fe(l), and 0.05 mole of Fe(g) at 3343 K. Notice that the enthalpy released by the chemical reaction is sufficient to melt alumina (melting point 2345 K) and to partially vaporize Fe (melting point 1810 K; boiling point 3135 K). To lower the final temperature of this system, adding Fe(s) to the reactant mixture will absorb some of the heat released by the reaction. This thermite reaction is applied to weld steel where conventional welding equipment cannot go. Using a similar analysis for the second reaction, then the reaction of 1 mole of UF<sub>4</sub>(s) and 2 moles of Mg(s) in an adiabatic container produces 1 mole of U(l), 1.23 moles MgF<sub>2</sub>(l), and 0.77 mole MgF<sub>2</sub>(s) at 1536 K, which is the melting point of MgF<sub>2</sub> and above the melting point of U (1408 K). Achieving a temperature above 1536 K can be accomplished by heating the reactants before reaction.<sup>41</sup> A modification of this reaction was used by scientists at Iowa State College in the 1930's to produce large quantities of pure uranium metal for use as part of the Manhattan Project.

**(15) Solutions:** Both solid-phase and liquid-phase solutions are effective media to enhance reaction rates and lower reaction temperatures as compared to traditional solid-state strategies. Reactants dissolved in solvents, such as molten salts, fluxes, or ionic liquids, are homogeneously mixed and have larger atom mobilities than in the solid state, so reaction rates increase. However, if the rate becomes too fast, then finely divided or amorphous materials may result. Nevertheless, this approach can effectively yield large single crystals for physical property measurements, but such crystals are often poor for single crystal diffraction studies because their mosaic character is not optimal. Solid solutions containing reactant elements, on the other hand, do not affect atom mobilities significantly but provide an intimate mixture of these elements. As a result, compounds containing these element combinations become accessible at temperatures lower than what is required for different compounds of these elements to react.

Among possible liquid-phase solvents, eutectic mixtures of two related substances, i.e., salts or metals, are especially effective reaction media because the melting (freezing) point is lower than the melting points of either pure component. For example, a slight molar excess of LiCl with RbCl freezes at 308°C, whereas LiCl freezes at 605°C and RbCl freezes at 718°C. This eutectic mixture of halide salts has successfully produced numerous complex sulfides and sulfosalts. Another useful eutectic solvent is a mixture of sulfate salts, which is effective for the following reaction:



Multiple grinding and firing cycles of the reactant solids never achieve high yields or complete conversion to the ternary oxide. However, a liquid mixture of Li<sub>2</sub>SO<sub>4</sub> and Na<sub>2</sub>SO<sub>4</sub> at 800°C<sup>42</sup> dissolves Li<sub>2</sub>CO<sub>3</sub> while LiFe<sub>5</sub>O<sub>8</sub> precipitates, and the solution can be removed by washing with water.<sup>43</sup>

<sup>41</sup> D.R. Gaskell, *Introduction to the Thermodynamics of Materials*, 4<sup>th</sup> Ed., Taylor & Francis, London, 2009, Ch. 6.

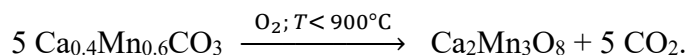
<sup>42</sup> A mixture of two-thirds Li<sub>2</sub>SO<sub>4</sub> (*T<sub>f</sub>* = 860°C) and one-third Na<sub>2</sub>SO<sub>4</sub> (*T<sub>f</sub>* = 885°C) freezes at 590°C.

<sup>43</sup> C.J. Chen, M. Greenblatt, J.V. Waszczak, *J. Solid State Chem.* **1986**, *64*, 240-248.

An example of how solid solution reactants can lead to unprecedented solids comes from a study of the Ca-Mn-O system.<sup>44</sup> Decomposition in air or O<sub>2</sub> of binary mixtures of CaCO<sub>3</sub> and MnCO<sub>3</sub> produce CaO and MnO<sub>2-x</sub> along with various ternary phases which are difficult to separate. On the other hand, decomposition of a solid solution of the carbonates Ca<sub>x</sub>Mn<sub>1-x</sub>CO<sub>3</sub>, which is obtained as an aqueous precipitate, gives high yields of ternary oxides that are stable at lower temperatures. For example, sintering of a mixture of two carbonates yields

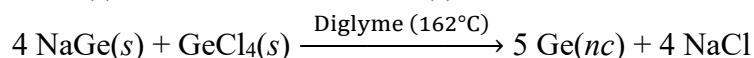
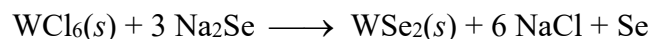


The occurrence and ratio of any ternary oxides depend on reaction time and temperature, but CaMnO<sub>3</sub> and CaMn<sub>2</sub>O<sub>4</sub> are the thermodynamically favored compounds in this temperature range. On the other hand, heating the corresponding solid solution of the carbonates gives

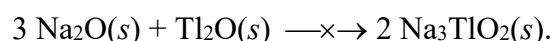
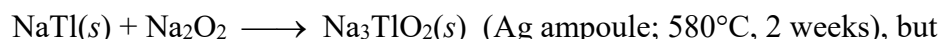


According to the CaO-MnO<sub>2-x</sub> phase diagram at 1.0 atm O<sub>2</sub>, Ca<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> is unstable relative to CaMnO<sub>3</sub> and CaMn<sub>2</sub>O<sub>4</sub> for temperatures above ~890°C.

**(16) Other Methods:** Synthetic strategies generally seek to control reaction rates and outcomes. For example, solid-state and solution-phase metathesis reactions can take advantage of thermodynamic factors to facilitate reactions, as observed for preparing metal dichalcogenides<sup>45</sup> and nanocrystalline germanium:<sup>46</sup>



The formation of WSe<sub>2</sub> requires ignition of the reactant mixture using a hot filament in a stainless-steel container, but the formation of NaCl provides a large thermodynamic driving force. The reaction to form nanocrystalline germanium is also driven by forming NaCl, but it also involves oxidation of the Zintl phase NaGe. In fact, oxidation of Zintl phases represents a constructive approach to make compounds that are challenging to obtain by more conventional strategies. Another example is the synthesis of Na<sub>3</sub>TlO<sub>2</sub>:<sup>47</sup>



Development of alternative synthetic strategies is an ongoing effort in the field of solid-state chemistry. In particular, there is ever growing attention to develop energy efficient processes that minimize waste. Here are three strategies:

*Chimie douce* (“soft chemistry”) is a philosophy of solid-state or materials synthesis to avoid high temperature processing and to take advantage of strategies adopted by Nature to prepare complex solids. Biomineralization<sup>48</sup> is deposition of a solid either within or outside the cells of living organisms, such as Fe or Au in bacteria, silicates in algae, or carbonates in vertebrates. Soft chemistry routes utilize various strategies, two of which include (i) intercalation or de-intercalation of open-network or low-dimensional solids and (ii) sol-gel processes.

<sup>44</sup> H.S. Horowitz, J.M. Longo, *Mater. Res. Bull.* **1978**, *13*, 1359-1369.

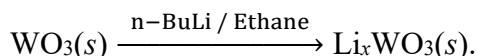
<sup>45</sup> P.R. Bonneau, R.F. Jarvis, Jr., R.B. Kaner, *Inorg. Chem.* **1992**, *31*, 2127-2132.

<sup>46</sup> B.R. Taylor, S.M. Kauzlarich, G.R. Delgado, H.W.H. Lee, *Chem. Mater.* **1999**, *11*, 2493-2500.

<sup>47</sup> G. Wagner, R. Hoppe, *J. Less-Common Met.* **1986**, *120*, 225-237.

<sup>48</sup> L.A. Estroff (guest editor), *Chem. Rev.* **2008**, *108*, No. 11.

Intercalation or de-intercalation involves exposing the solid to a liquid solution.<sup>49</sup> Intercalation is generally an oxidative process because cations transport more easily than anions. For example, n-butyl-lithium is an effective lithiating reagent and can produce metallic lithium tungsten bronzes from insulating tungsten trioxide:



On the other hand, de-intercalation is typically a reducing process, but can be effective to obtain metastable structures and compounds, such as  $\text{Mo}_6\text{S}_8$ , which cannot be obtained by reaction of the elements. By exposing a copper Chevrel phase  $\text{Cu}_x\text{Mo}_6\text{S}_8$  to hydrochloric acid, binary  $\text{Mo}_6\text{S}_8(s)$  forms.<sup>50</sup> These structures are 3-d network structures with pores that allow for effective intercalation or de-intercalation of cations. These processes are especially facilitated by 2-d materials, such as  $\text{TiS}_2$  or  $\text{MoS}_2$ , which swell when placed into a liquid solution. This swelling accelerates potential redox or acid-base chemical reactions between solute species and the solid. Intercalation and de-intercalation reactions are usually topotactic and can give rise to materials and structures that cannot be obtained by traditional routes.

The sol-gel process involves solution-phase mixing of molecular precursors followed by polymerization reactions to obtain a network solid. These approaches are successful for preparing silicates, borosilicates, and organic-inorganic hybrid solids. Further reading:

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- C. Sanchez, L. Rozes, F. Ribot, C. Laberty-Robert, D. Grosso, C. Sassoie, C. Boissiere, L. Nicole, "Chimie Douce: A Land of Opportunities for the Designed Construction of Functional Inorganic and Hybrid Organic-Inorganic Nanomaterials," *C.R. Chimie*, **2010**, *13*, 3-39.

<sup>49</sup> S.M. Whittingham, *Intercalation Chemistry*, Academic Press, London, **1982**.

<sup>50</sup> R. Chevrel, M. Sergent, J. Prigent, *Mater. Res. Bull.* **1974**, *9*, 1487-1498.

Microwave-aided synthesis allows temperatures exceeding 1000°C to be achieved within a few seconds. Distinct advantages include rapid, cost-effective processing with enhanced energy efficiency and access to potentially metastable materials. Microwaves are electromagnetic radiation with wavelengths ~0.01–1.00 m (frequencies ~0.3–30 GHz). To avoid interference with telecommunications, use of microwave radiation is regulated; the most common frequency for laboratory-scale systems is 2.45 GHz.

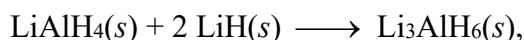
Microwave heating has been applied to make a wide variety of solids, including oxides, chalcogenides, borides, carbides, nitrides, silicides, and pnictides. It is fundamentally different than conventional heating because microwave heating is

- Direct: microwave radiation interacts directly with reaction components, so minimal energy is expended to heat the container and the environment. As a result, the temperature profile of a microwave-heated sample decreases from the interior outward, whereas the temperature profile decreases from the exterior inward for conventional heating.
- Selective: specific reactants that interact more strongly with microwaves will generate higher temperatures in their regions of the sample. For example, this feature enables successful preparation of metal chalcogenides because the metal is heated preferentially while the chalcogenide does not volatilize.
- Volumetric: heating is uniform throughout the sample, as long as the reactants are uniformly distributed in the heterogeneous mixture of solid-state reactants.
- Rapid: microwave energy is quickly transferred into heat, which leads to fast temperature rises. Likewise, when microwave power is turned off, the reaction is essentially quenched, which can lead to metastable products inaccessible by conventional heating and cooling.

Further reading:

- R. Kniep, “Fast Solid-State Chemistry: Reactions under the Influence of Microwaves,” *Angew. Chem. Int. Ed. Engl.* **1993**, 32, 1411.
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Mechanochemistry is the use of mechanical energy to affect chemical reactivity. Other forms of energy applied to induce and sustain chemical reactions include heat (thermochemistry), radiation (photochemistry), and electric potential (electrochemistry). Mechanical energy involves shear and compression forces, which are commonly applied using a ball mill. Reactants, ball bearings, and sometimes milling additives, are placed inside a sealed chamber in which the balls collide with the reactants at high velocities while the chamber is rotated or vibrated. For making soft organic materials, reaction vessels and balls made of steel, agate, or polymethylmethacrylate (PMMA) are useful, whereas zirconia and tungsten carbide are better suited for hard inorganic materials. Ball-milling is considered to be a rapid, clean, and environmentally friendly procedure that has been effective for preparing coordination compounds, polymers, and novel metal hydrides, such as



which converts  $[\text{AlH}_4]^-$  tetrahedra into  $[\text{AlH}_6]^{3-}$  octahedra. Further reading:

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**(17) Quality Criteria:** Setting proper and appropriate *quality criteria* is essential to achieve the desired outcomes of any synthetic effort. The standard goal of any preparation is to achieve the product in as high a yield and purity as possible. Achieving this result requires careful planning and effort at the outset to ensure the purity of all reactants and containers, and to address how the desired compound will be separated from the complete reaction product. Regarding the reactants, in general, always test a manufacturer’s claim of reagent purity. For example, inert gases, which are suffocation hazards in enclosed spaces, may contain a small amount of an odorant that may react at high temperatures. Numerous active metals have surface oxide and may contain interstitial hydride. For example, commercial sources of Ba can have as much as ~20 atomic percent hydrogen. Therefore, purification steps of reactants may be necessary before undertaking any synthetic endeavor. Many gases contain small quantities of oxygen or water, which can be easily removed by passing the mixture over heated Ti sponge or other catalysts. The halogens, iodine and bromine, the chalcogens, sulfur, selenium, and tellurium, as well as some alkaline earth and alkali metals can be purified by sublimation or distillation. Heating late transition metals under a stream of hydrogen gas can remove surface oxide. Regarding reaction products, filtration or centrifugation are useful separation techniques for crystals grown from liquids. However, even these straightforward procedures must be carefully observed. During exploration of the Ta-Au-S system for new compounds, crystals of Ta<sub>2</sub>Cu<sub>0.80</sub>S<sub>6</sub><sup>51</sup> unexpectedly emerged. A reactant mixture containing Ta, Au, and S was heated in an evacuated fused silica tube containing a few microliters of bromine. The resulting product was passed through a 60-mesh brass screen and re-annealed. Microprobe analysis and single crystal X-ray diffraction led to identification of Ta<sub>2</sub>Cu<sub>0.80</sub>S<sub>6</sub>. The authors state, “We believe that the source of the Cu was the brass screen rather than a possible Cu impurity in the Au powder,…”.

What tools are needed to evaluate the quality of reaction products? General analytical methods on bulk solid-state samples include diffraction, microscopy, elemental analysis, and spectroscopy. X-ray diffraction on polycrystalline (powder) samples is a common technique for every solid-state chemistry laboratory. A scanning electron microscope (SEM) equipped with an energy dispersive X-ray spectrometer (EDS) can identify elements on sample surfaces. “Standardless” analyses give accuracies within a few percent; better accuracy is afforded by spectral comparison to known standards. Powerful elemental analysis techniques include electron microprobe (EPMA) and inductively coupled plasma mass spectroscopy (ICP-MS). EPMA works similarly to SEM-EDS and allows non-destructive determination of concentrations of lithium to plutonium to as low as 100 ppm. ICP-MS can detect most of the elements in the periodic table with high accuracy, but the small sample is consumed by transforming all constituents into ions. Spectroscopic techniques include X-ray fluorescence and X-ray photoelectron spectroscopy (XPS or ESCA = electron spectroscopy for chemical analysis). Two other techniques include nuclear magnetic resonance and Mössbauer spectroscopy (especially for Fe, Sn, Gd). Two common issues that create characterization problems are (1) the inclusion of small, adventitious impurities such as H or O

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<sup>51</sup> P.J. Squattrito, P.N. Swepston, J.A. Ibers, *Inorg. Chem.* **1987**, 26, 1187-1188.

atoms that are difficult to detect by many methods; and (2) samples containing two neighboring elements in the periodic table, elements that can be difficult to differentiate.

**(18)** There are numerous examples of compounds reported in the literature that either are revealed to be something else or remain controversial with respect to their chemical composition:

- $\beta$ -tungsten, a possible metastable form of tungsten that is not BCC, was first reported as part of a dendritic deposit formed on a cathode after electrolysis of phosphate melts and subsequently in vapor deposited films or hydrogen reduction of  $\text{WO}_3$ . Much effort concluded that it is really a suboxide, with composition close to  $\text{W}_3\text{O}$  with W atoms occupying all tetrahedral holes of a bcc packing of oxygen atoms. Further research efforts, by reacting  $\text{WO}_3$  with  $\text{H}_2$ , suggests that this metastable phase, indeed, exists.<sup>52</sup>
- Several metal-rich sulfides and halides have small atoms, e.g., H, C, N, or O, occupying interstitial sites within the metal substructure, “impurities” that can be overlooked by diffraction or spectroscopic analysis. One example includes “hexagonal  $\text{Ti}_2\text{S}$ ,” which was prepared in a graphite crucible and turned out to be, in reality,  $\text{Ti}_2\text{SC}$ . Binary  $\text{Ti}_2\text{S}$  can be prepared by inductive heating of  $\text{TiS}$  and  $\text{Ti}$  in a tungsten crucible and is orthorhombic.<sup>53</sup>
- Another example is the intermetallic “ $\text{Sr}_3\text{Sn}$ ,” which turned out to be semiconducting, in contradiction with the prediction of metallic behavior. The structure is described as CCP ordered mixture of Sr and Sn, like  $\text{Cu}_3\text{Au}$ . Ultimately, this compound showed adventitious oxide and was characterized to be  $\text{Sr}_3\text{SnO}$ , with O atoms occupying octahedra formed by six Sr atoms. The structure of  $\text{Sr}_3\text{SnO}$  adopts an anti-perovskite structure. With 16 valence electrons, the suboxide is electron-precise in agreement with its semiconducting properties.
- $\text{In}_5\text{S}_4$  was first reported to be a red, transparent solid, but was obtained in small yield and its preparation was extremely difficult to reproduce using just the two elements.<sup>54</sup> The compound was originally prepared in a Sn-flux but note that In and Sn are adjacent elements in the periodic table. The structure of  $\text{In}_5\text{S}_4$  contains a tetrahedral “ $\text{In}_5^{8+}$ ” cluster with a central In atom surrounded by a tetrahedron of four other In atoms. An “ $\text{In}_5^{8+}$ ” cluster would be an odd-electron cluster with 7 valence electrons, which does not completely account for the four In-In bonds. Further study revealed the compound to be  $\text{In}_4\text{SnS}_4$ , and the 8-electron  $[\text{SnIn}_4]^{8+}$  cluster has saturated, two-center, two-electron In-Sn bonds.<sup>55</sup>

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<sup>52</sup> W.R. Morcom, W.L. Worrell, H.G. See, H.I. Kaplan, *Metall. Trans.* **1974**, 5, 155-161.

<sup>53</sup> J.P. Owens, B.R. Conard, H.F. Franzen, *Acta Crystallogr.* **1967**, 23, 77-82

<sup>54</sup> T. Wadsten, L. Arnberg, J.E. Berg, *Acta Crystallogr. Sect. B* **1980**, B36, 2220-2223.

<sup>55</sup> H.J. Deiseroth, H. Pfeifer, *Z. Kristallogr.* **1991**, 196, 197-205.