The Preparation Science of Solids

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The metals below can reduce the metals above.
The Preparation Science of Solids: Diffusion of ions

Diffusion process for ceramic preparation.

(a) The formation of the product phase of, for example, a complex mixed-metal oxide containing two metal ions at the interface between the two parent simple metal oxides is displayed.

\[ \frac{1}{2} \text{La}_2\text{O}_3 + \frac{1}{2} \text{Cr}_2\text{O}_3 \rightarrow \text{LaCrO}_3 \]

(b) The formation of a ceramic product from heat treatment of a precursor that contains both metal ions, (e.g., decomposition of mixed-metal oxalates), is depicted. Since the ions are already mixed at the length scales of Ångstroms, the diffusion lengths are small.

\[ 3(\text{Co}_{0.33}\text{Fe}_{0.66})\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O} \rightarrow \text{CoFe}_2\text{O}_4 \]

The Preparation Science of Solids: *In-situ* studies of compound formation

(a) Contour plot of PXRD data for the in situ reaction of Ba, Ce, and In precursors, in the temperature range 25 °C to 1200 °C at 25 °C increments showing the evolution of $\text{Ce}_{1-x}\text{In}_x\text{O}_{2-\delta}$ under CO$_2$. The various diffraction peaks are assigned in panel (b).

Crystal structures involved in the transformations of low-dimensional zinc phosphate to higher dimensional materials via hydrothermal treatment.

Phase diagram, with accompanying micrograph, of peritectic reactions in the binary \( \text{CoSn} \) system. The black arrow represents cooling of a 1:3 ratio of \( \text{Co:Sn} \) to form \( \text{CoSn} \) crystals, which react at 571 °C with the surrounding melt to form \( \text{CoSn}_2 \). \( \beta\)-\( \text{CoSn}_3 \) may be formed on further cooling, with a matrix of a solid solution of \( \text{Co} \) in \( \beta\)-Sn with heterogeneous inclusions of \( \alpha\)-\( \text{CoSn}_3 \) obtained upon cooling to 229 °C.

Series of images detailing the progression of the solid-state metathetic reaction between NbCl$_5$ and Li$_3$N, a reaction which occurs during 0.2 s.

Phase diagram for a hypothetical A–B system containing a peritectic compound β and (right) representation of the steady-state growth conditions and composition variations during growth of β.

Crystal structure of the extended transition metal oxide hydride, $\text{LaSrCoO}_3\text{H}_{0.7}$. The pink spheres represent the positions of the hydride ions.

The ability to make such a compound is very much linked to how much more readily the anions move compared with the cations.

The Preparation Science of Solids: Soft-chemical transformations (chimie douce)

Graphical representation of the proton-exchange mechanism followed by the topochemical dehydration of parent Ruddlesden–Popper phases to form A-site defective cubic perovskites.

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 reactor. Once hot, the reactants thermally become directly susceptible to microwave heating and instantaneously form products. Assisted-microwave methods are appealing for a wide variety of high-temperature solid-state reactions, resulting in reaction temperatures of 1000 °C and above. Among the many advantages that are the direct volumetric heating associated with microwaves allows for rapid reaction times while employing significantly less energy than conventional furnace-based preparation. Thermoreactive times and selective heating permit volatile reactants to be incorporated stoichiometrically in the product. Undesirable reactions with containers or crucibles 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 and soft-gel based processing of complex oxides, or sensitive intermediates, and transition metal chalcogenides.

INTRODUCTION

Over the past few decades, microwave-based methods have been extensively employed for solution chemistry including organic synthesis, polymerization reactions, and hydrothermal processing. 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 provided questions on whether an alleged “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 microwaves.1 In regard to the solid state, there is a relatively long history of microwave being employed for the processing of ceramics,2,3 where they are understood to display distinct advantages over conventional heating for annealing (homogenization) and sintering (densification) due to the heat being delivered, as will be discussed below.4 In a similar vein, Roy et al. demonstrated fully dense adherent metallic parts in just 10 to 30 min using microwaves.5

The use of microwave ovens for the preparation of inorganic solids was given widespread currency by Baghramian and Mingers in 1984, when they discovered certain oxides coupled well to microwaves and could exceed temperatures of 700 °C in less than a minute using a 2.45 GHz domestic microwave oven.6 They prepared ternary oxides and the superconductor YBa2Cu3O7, using the high-attenuating reactant species to heat reactants that did not couple well to microwaves.7,8 An early report of microwave methods involving metal powders was in 1992, when Whittaker and Mingers prepared metal chalcogenides from elemental starting materials.9 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.10 Increased understanding of the interaction between microwaves and materials, especially metal powders, as well as the factors in experimental devices that affect reactions, has allowed the use microwave ovens for high-temperature reactions. Building on this, microwave reactions have been used to prepare inorganic materials including battery materials,11 chalcogenides,12 intermetallics,13 and oxides.14 An assortment of techniques such as solvothermal synthesis of metal-organic frameworks15 and soft-gel synthesis of nanoparticles16 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 initiate heat reactions. Once hot, the reactants couple directly to the microwaves (i.e., 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.17 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.

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Active Crystal Growth Techniques for Quantum Materials

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Abstract
We review recent advances in crystal growth techniques, focusing on the development of novel quantum materials. Recent progress in instrumentation design, opening new avenues in bulk crystal growth of oxide and intermetallic compounds, is highlighted. Specifically, we illustrate leading techniques that allow for the active control of crystal nucleation/growth and provide platforms for the realization of single crystals with ultrahigh purity and minimized defects. Advances in the postgrowth manipulation of crystals, as well as the impact of purification techniques on the stabilization of delicate quantum phases, are also discussed. Throughout, we highlight new scientific avenues opened by access to high-purity single-crystal samples.

Chemistry of precious metal oxides relevant to heterogeneous catalysis

Joshua A. Kurzman,∗ab Lauren M. Mischab and Ram Seshadriab,c

The platinum-group metals (PGMs) are widely employed as catalysts, especially for the mitigation of automotive exhaust pollutants. The low natural abundance of PGMs and increasing demand from the expanding automotive sector necessitates strategies to improve the efficiency of PGM use. Conventional catalysts typically consist of PGM nanoparticles dispersed on high surface area oxide supports. However, high PGM loadings must be used to counter sintering, agglomeration, and deactivation of the catalyst such that sufficient activity is maintained over the operating lifetime. An appealing strategy for reducing metal loading is the substitution of PGM ions into oxide hosts: the use of single atom (sola) catalysts; active sites represents a highly atom-efficient alternative to the use of nanoparticles. This review addresses the crystal chemistry and reactivity of oxo compounds of precious metals that are, or could be relevant to developing an understanding of the role of precious metal ions in heterogeneous catalysis. We review the chemical conditions that facilitate stabilization of the notoriously oxophilic precious metals in oxide environments, and survey complex oxide hosts that have proven to be amenable to reversible redox cycling of PGMs.

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Joshua A. Kurzman graduated in 2007 from Reed College in Portland, Oregon, with a BA in Chemistry. At Reed, he was introduced to solid-state chemistry by Professor Margaret Gault-Schmitz, under whose guidance he carried out research on short-lived phases. His doctoral thesis, defended in 2011 at the University of California, Santa Barbara, was on the topic of Solid State Chemistry of Platinum Group and Noble Metal Oxo: Implications for Heterogeneous Catalysis. Dr Kurzman is currently a post-doctoral fellow at the Université de Versailles St. Quentin, in France, where he researches in the group of Prof. Jean-Marc Tarascon.

Lauren M. Misch graduated in 2009 from Indiana University in Bloomington, Indiana, with a BS in Chemistry. At Bloomington, she carried out research on the surface chemistry of particles exposed to moving flow; working under the guidance of Prof. Reginald Lingua, her doctoral research at the University of California, Santa Barbara is supervised by Professors Glenn Stucky and Ram Seshadri and focuses on redox-containing oxides for heterogeneous catalysis.

Ram Seshadri has been on the faculty of the University of California, Santa Barbara since 2001, where he is currently Professor of Materials and Professor in the Department of Chemistry and Biochemistry, in addition to co-Directing the Materials Research Laboratory. The research carried out in his group combines aspects of physics, chemistry, and materials science, within the broad theme of crystal chemistry, and crystal-structure-property relations in functional inorganic materials. Functions of current interest include heterogeneous catalysis, solid-state lighting, magnetism, thermoelectricity, and energy storage.

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The Preparation Science of Solids: Noble Metals
The simple oxides are pretty unstable.

In complex oxides, the added stability is provided by electropositive cations.

Rapid Microwave Preparation and ab Initio Studies of the Stability of the Complex Noble Metal Oxides La$_2$BaPdO$_5$ and La$_2$BaPtO$_5$

Lauren M. Misch, Jakob Brgoch, Alexander Birkel, Thomas E. Mates, Galen D. Stucky, and Ram Seshadri

The crystal structure for La$_2$BaMO$_5$ ($M = \text{Pd or Pt}$) projected nearly down (a) the $c$ axis and (b) the $b$ axis. The larger dark gray spheres are Ba, the smaller light gray spheres are La. Square planes of (Pd/Pt)O$_4$ are also depicted.
The Preparation Science of Solids: Stabilizing Noble Metal Oxides

Thermogravimetric analysis of the decomposition of final product achieved after microwave heating.

La$_2$BaPdO$_5$ and La$_2$BaPtO$_5$ are expected to lose 2.6% and 2.3%, respectively, indicated with dashed lines.

DFT energetics shows the significant stabilization induced by the addition of the electropositive cations.

Calculated using, for example:

$$\Delta E = E_{La_2BaMO_5} - E_{La_2O_3} - E_{BaO} - E_M - \mu_0 - \frac{1}{2} E_{O_2}$$
Absolute energetics DFT (vacuum reference rather than $E_F$) facilitates comparisons of the levels.
Rapid preparation and magnetodielectric properties of trirutile $\text{Cr}_2\text{WO}_6$

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Dense pellets of >99% purity trirutile $\text{Cr}_2\text{WO}_6$ were prepared in one step from starting oxides using spark plasma sintering, leading to simultaneous reaction and consolidation in 3 min at 1473 K. The reducing environment during processing may be partly responsible for the rapid reaction time in these oxides, with partial reduction of $\text{Cr}^{3+}$ and the associated oxygen vacancies allowing rapid diffusion of cations. The low-temperature physical properties of $\text{Cr}_2\text{WO}_6$ were examined, and a new transition at $T \approx 5.8 \text{K}$ was observed as an anomaly in the temperature-dependent dielectric permittivity and a corresponding anomaly in the specific heat. A strong enhancement of the magnetoelectric response is observed below this transition temperature at $T \approx 5.8 \text{K}$ and may be associated with a change from collinear spin order to more complex spin order. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4905466]

I. INTRODUCTION

The preparation of complex oxides with multiple metal ions frequently involves cycles of intimate grinding of the starting oxide powders and annealing at high temperatures in a process that can take multiple days. The long heating times are a consequence of the slow rate of solid-state diffusion for most ions in oxide environments. This is particularly true in the case of $\text{Cr}_2\text{WO}_6$ (Ref. 1 and 2)—the compound of interest here—as $\text{Cr}^{3+}$ is quite inert and diffuses rather slowly, a property that is responsible for its protective properties as one of the primary protective oxides in engineering materials, such as steels. There are frequently other complications as well. Notably for this material class, $\text{WO}_3$ is a volatile solid, making it challenging to obtain single-phase materials using the extended reaction times required to enable $\text{Cr}^{3+}$ mobility. Moreover, the resulting materials after traditional solid-state reaction are powders or low density sintered bodies that require consolidation and/or densification to achieve dense bodies suitable for physical property measurement. This can be accomplished by hot-pressing at elevated temperatures for extended times (generally several hours), though this introduces further challenges, including the potential for decomposition, or, in this case, volatilization. This contribution describes the use of spark plasma sintering (SPS), more accurately described as current-assisted, pressure-activated densification (CAPAD), to rapidly prepare multi-gram quantities of high purity, dense samples of $\text{Cr}_2\text{WO}_6$, in a single processing step that takes less than an hour. The rapid processing times and simultaneous reaction and consolidation overcome many of the common pitfalls of traditional ceramic methods. Further, we describe how the rapid reaction times followed by this processing ($\leq 3 \text{ min}$ at 1473 K for $\text{Cr}_2\text{WO}_6$) may be related to fundamental rates of well-understood models of ligand exchange in apogean molecular metal complexes.

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FIG. 1. $\text{Cr}_2\text{WO}_6$, prepared and studied here as a candidate magnetoelectric material. $\text{Cr}_2\text{WO}_6$ adopts an inverse trirutile-type crystal structure (Figure 1) and was proposed to have potential magnetoelectric properties by Homsy, 4 and more recent work has investigated the magnetoelectric coupling in $\text{Cr}_2\text{WO}_6$ near the antiferromagnetic ordering temperature at $\approx 45 \text{K}$. The coupling of magnetic and electric properties is of great interest for next generation information storage, where an electric field may control and interrogate the magnetic state of a memory storage device. Complete characterization of magnetoelectric materials is imperative to

The Preparation Science of Solids: Reduction/SPS

Sintered pellet of clean product in minutes


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The mean residence time of water molecules in metal hexaaqua complexes may be a useful proxy to understand solid state reactions of oxides. Inert cations, such as Cr$^{3+}$, lie on the left, while reactive cations with labile ligands lie towards the right, such as Cr$^{2+}$.

While ions of lower charge/radius ratio are expected to react more quickly (for example, the series of Al$^{3+}$, Ga$^{3+}$, and In$^{3+}$), the crystal field stabilization energy dominates the reactivity of transition metal ions.

The reducing conditions in SPS processing may lead to partial reduction of Cr$^{3+}$ and creation of oxygen vacancies, and may explain the unexpectedly rapid reaction times possible with SPS (<3 min).

Structure and Magnetism in CrTaO₆: A Trirutile Oxide Based on Cr²⁺

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Introduction

Oxides with the trirutile structure of composition MÖ₆ [1], which exist for various combinations of divalent perovskite ions, for example, M = Y, Ce, Y, Fe, Co, and Ni and B = Ta and M = Co, Ni, and Cu for B = Sb (1-11). All crystallographic data for Pnma or Pn2₁/a, when M is a John-Taylor species such as Cr³⁺ or Cu²⁺. The crystallographic ordering between M and B. Fig. 1, results in a M substituent of B26 symmetry, the same as that found for the magnetic sublattice of K₂NiF₄ structure materials, which are considered to be among the best examples of two-dimensional antiferromagnets [12]. The two dimensionality arises due to a combination of factors including a more complex interlayer exchange pathway and also a symmetry cancellation effect between antiferromagnetically coupled square planar layers at 0 and c = 1/2, which can be regarded as a form of geometric frustration. The ligand positions within the square planar layers, Fig. 2, allow 180° M-O-M superexchange between nearest neighbors (nn) and thus a large negative JMN results and the condition JMN > JAA applies. In addition, JMN > JAA due to the aforementioned frustration. The above relationships result in a set of magnetic properties for K₂NiF₄ materials characterized by extensive short-range, two-dimensional correlations followed by a crossover to three-dimensional, long-range order. For the MnO₂ trirutiles, in contrast, intraplanar ligand positions, also shown in Fig. 2, do not favor a dominant JMN. Rather, JMN > JAA is more likely due to the long bond distances and large bond angles involved in JMN while a favorable 180° M-O-M pathway is available for JAA. Note also that the two possible JMN pathways are not equivalent, which suggests a dimensionality of one-dimensional, short-range correlations. Two dimensionality is expected for JMN > JAA. It is noteworthy that for this condition a form of intraplanar magnetic frustration will result as illustrated in Fig. 3. Evidence for short-range magnetic correlations in the MnO₂ materials is clear from the observation of broad susceptibility maxima at temperatures significantly higher than the critical temperature for three-dimensional order, Tc. In fact, a measure of the importance of short-range correlations in these materials is afforded by the ratios, F(A)F(T)/F(T), and values for the MnO₂ group are collected in Table 1. A wide variation is seen from large ratios for NBO₄O₂ and CS₅O₂ to much smaller values for V₂O₅ and Fe₂O₃. A detailed analysis of susceptibility data indicates one-dimensional, short-range order (SRO) for the Ni and Cu. Lanthanides with JMN values of -4K and -4K, respectively (8,11). For the Cu material, JMN - JMN = 10⁻⁴, supporting the linear chain model. On the other hand, Co₃O₄ has been analyzed in terms of square planar SRO with JMN - JMN = 80 (8). In the long-range ordered state, two magnetic structures are found with propagation vectors, in a combination of factors including a more complex interlayer exchange pathway and also a symmetry cancellation effect between antiferromagnetically coupled square planar layers at 0 and c = 1/2, which can be regarded as a form of geometric frustration. The ligand positions within the square planar layers, Fig. 2, allow 180° M-O-M superexchange between nearest neighbors (nn) and thus a large negative JMN results and the condition JMN > JAA applies. In addition, JMN > JAA due to the aforementioned frustration. The above relationships result in a set of magnetic properties for K₂NiF₄ materials characterized by extensive short-range, two-dimensional correlations followed by a crossover to three-dimensional, long-range order. For the MnO₂ trirutiles, in contrast, intraplanar ligand positions, also shown in Fig. 2, do not favor a dominant JMN. 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