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Where Do New Materials Come From? Neither the Stork nor the Birds and the Bees! In Search of the Next “First Material”

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Where Do New Materials Come From? Neither the Stork nor the Birds and the Bees! In Search of the Next “First Material”

Abstract

Materials discovery and optimization has driven the rapid technological advancements that have been observed in our lifetimes. For this advancement to continue, solid-state chemists must continue to develop new materials. Where do these new materials come from? In this review, we discuss the approaches used by the zur Loye group to discover the next “First Material”, a new material exhibiting a desired or not previously observed property that can be optimized for use in the technologies of tomorrow. Specifically, we discuss several crystal growth techniques that we have used with great success to synthesize new materials: the flux growth method, the hydroflux method, and the mild-hydrothermal method.

Keywords

Crystal Growth, Flux Growth, Hydroflux, Hydrothermal Method

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Materials discovery and optimization has driven the rapid technological advancements that have been observed in our lifetimes. For this advancement to continue, solid-state chemists must continue to develop new materials. Where do these new materials come from? In this review, we discuss the approaches used by the zur Loye group to discover the next “First Material”, a new material exhibiting a desired or not previously observed property that can be optimized for use in the technologies of tomorrow. Specifically, we discuss several crystal growth techniques that we have used with great success to synthesize new materials: the flux growth method, the hydroflux method, and the mild-hydrothermal method.

INTRODUCTION

In our complex lives of the 21st Century we rely on technology and technological devices that work because they contain advanced materials that exhibit specific properties to perform specific functions. For example, many of us carry a smart phone that is powered by a lithium ion battery. This battery works because of cathode and anode materials that were developed for the express purpose of constructing a battery that can power an electronic device, such as a cell phone, for days. The cell phone itself contains a microwave dielectric material that enables the phone to make contact with the nearest cell tower and to rapidly send and receive voice, text, or data files. Over time we, of course, expect technology to improve and our phones to become smaller and lighter, to send and receive data faster, and the battery charge to last longer. This can only happen if advances are made in the materials that are contained within the phone or any other device that we come to rely on. The switch from incandescent light bulbs to compact fluorescent to LED based lights is one example where a series of material developments allowed us to create, and to use, more energy efficient light sources. This transformation took place, in part, because of the development of a large number of new materials, efficient and color pleasing phosphors, that convert short wavelength ultra violet (compact fluorescent) or deep blue (LED) light into visible light and moreover, emit multi-wavelength light that closely mimics the optical emission spectrum of the sun.

So, where do these impressive materials come from? How were they discovered? By accident or by design? Can one really “plan” improved function? How about plan a property that doesn't even exist yet? In all of this we rely on both the synthesis and the discovery of new materials whose properties are better than those of current materials or whose properties are unprecedented. While the former is hard and takes a lot of planning, the latter is exceptionally difficult – in part because we have already discovered many materials with impressive properties. One might fear that there is nothing new under the sun, however, those fears are unfounded and each discovery of a material exhibiting a new phenomenon or behavior confirms this. We are lucky that over the past centuries scientists have strived and succeeded to create new materials, to discover new properties and phenomena, and we reap the benefit. Of course, it may not seem to be impressive technology if one grows up with it! So, it is up to us to find the next awesome materials that will change the world of the future and improve the lives of its inhabitants.

So, what have we experienced in the past 25 years? The increase in hard drive storage capacity due to new giant magneto-resistive

materials, the ever-shrinking cell phone due to improved microwave dielectric materials, the enhancement in lithium battery storage capacity due to new intercalation materials, and the improved capacitor due to new ferroelectric materials are all excellent examples of materials that were developed only recently. We should not for one second believe, however, that these materials were discovered and used without further optimization, since all of the ones mentioned above went through countless iterations to optimize their properties and functions. In all cases, however, there was a “First Material” that exhibited the *heretofore never observed property or phenomenon*. After all, there always is a first! And the first is usually followed by a second and a third and so on. But how do we go about finding this “First Material”, this archetype in which the phenomenon is first observed, whose composition is almost impossible to predict? After all, where would one start?

In the zur Loye research group we utilize crystal growth as a process to discover new materials. It is certainly not the only approach; however, exploratory crystal growth is an extremely rewarding as well as aesthetically pleasing approach that results in beautiful single crystals having novel chemical compositions. By coupling this synthesis approach with modern instrumentation that allow us to use single crystals to determine the atomic structure of the materials and to characterize their intrinsic properties, we can rapidly prepare a large number of new materials and, if we are lucky, find that next ‘first material.’

In this paper, several crystal growth approaches are described with an emphasis on how and why they – versus some other method – are used and how they enable the preparation of new materials. An attempt is made to realistically portray the strategies and planning that goes into the experiments that aim to create new crystals with new compositions that hopefully exhibit the desired behavior, or that, by serendipity, exhibit something different but perhaps even more exciting.

Crystal Growth

Many crystal growth approaches are available to the solid-state chemist. Crystal growth differs from the traditional solid state or ceramic method in its ability to grow high quality single crystals. In the ceramic method, intimately mixed powder precursors are heated and solid state diffusion is responsible for the formation of the products. As diffusion in the solid state is slow, high temperatures, long dwell times, and intermittent grindings of the sample are required to form a desired phase. Unfortunately, these growth conditions almost always result in polycrystalline, powder samples as opposed to single crystals. Crystal growth approaches overcome the challenges of solid state diffusion by conducting the

reaction in a liquid or gas phase, typically through the use of a solvent. The use of a solvent allows for reactions to be conducted at lower temperatures and often in shorter times and, importantly, allows for the growth of single crystals.

Crystal growth generally occurs through a series of several steps.¹ First, the precursors are dissolved in the solvent. This step often includes heating to increase the solubility. The concentration of the resulting solution is then increased until it becomes supersaturated. This can be done by either cooling the solution or by evaporating off some of the solvent. After supersaturation is achieved, nucleation, the precipitation of small crystallites out of solution, and growth, the precipitation of material onto crystallites to increase their size, can take place. Ideally, a small number of nucleation sites and a large amount of growth will occur, leading to large single crystals.

While many crystal growth methods are available, we have primarily focused on a handful of methods, shown on a temperature-pressure scale in Figure 1, with the majority of our work utilizing the flux, hydroflux, and mild hydrothermal growth methods. In the flux growth method,² a molten salt, for example an alkali halide, is used as a solvent to dissolve the higher melting reactants. As these reactions must be performed above the melting point of the flux, flux growth reactions are typically heated to between 600 - 1000 °C. Along with molten salts, another common solvent is water. Reactions utilizing water as the solvent can be broken down into three types depending on the temperature used. At temperatures below 100 °C, reactions can be performed in aqueous solution, with supersaturation and crystal growth typically being achieved by evaporation of the water. If instead, the reaction is performed in a sealed system and heated to above 100 °C, pressure is built up as liquid water is converted to water vapor. At a certain critical temperature, 374 °C for water, the liquid and gas phases become one phase called a supercritical fluid. Crystal growth conducted in supercritical water are referred to as hydrothermal reactions,³ whereas those performed at intermediate temperatures, 100 °C < T < 374 °C, are referred to as mild hydrothermal reactions.⁴⁻⁵ One final crystal growth approach, the hydroflux method,⁶⁻⁷ uses a wet hydroxide as a solvent and is intermediate between an aqueous solution and a flux, reaching higher temperatures than an aqueous solution without the pressure build up that occurs in hydrothermal and mild hydrothermal conditions.

Each crystal growth approach has different strengths and excels at growing different classes of materials. For example, in some cases the solvent may become incorporated into the crystals and for this reason, salt fluxes are ideal for forming salt-inclusion compounds,⁸ aqueous solutions and mild hydrothermal reactions are ideal for forming hydrated materials,⁹ and hydroflux reactions often result in the formation of hydroxides⁶ and oxyhydroxides.¹⁰

One of the challenges of exploratory crystal growth is growing new, as opposed to known, compounds. After all, how do you target something that you don't know exists? In the infancy of solid state chemistry, this was often achieved by working with a new combination of elements, often referred to as a phase space. However, little unexplored phase space remains for simple compositions, supporting the use of modern exploratory crystal growth methods for the discovery of new materials with complex compositions. In the zur Loye group, we have utilized two approaches to continue to target new compounds.

The first approach is to target phases which can be predicted to exist but have not been prepared. One family of materials where this method can be applied successfully is the perovskites, where known guiding principles enable the accurate prediction of new compositions that will form in this well-known structure type.¹¹ Using this approach, we have synthesized a large number of new

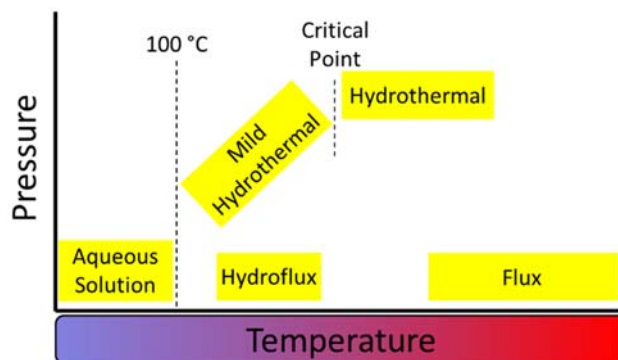


Figure 1. Temperature-pressure scale showing the various crystal growth techniques used in the zur Loye group.

noble metal containing perovskites and perovskite-related compounds.¹²

The second approach is to develop new synthetic methods that allow for new classes of compounds to be grown within already explored phase space. Our development of an enhanced flux growth technique has enabled us to grow a series of new salt-inclusion uranyl silicates.^{8, 13-14} The hydroflux crystal growth technique, developed in the zur Loye group, has led to the discovery of the first all transition-metal framework zeotype.¹⁰ Another approach, the two-step reduction method, has led to the synthesis of multiple new reduced transition metal containing oxides.^{5, 15}

Flux Growth Approach

As previously mentioned, flux growth is an intermediate temperature synthetic technique available to solid state chemists to produce potentially new materials with interesting properties.² Flux growth as a synthetic technique is typically conducted in a vessel that is inert to the compounds placed inside it, such as an alumina¹⁶⁻¹⁷ or silver crucible¹⁸⁻²⁰ or a quartz²¹⁻²³ or silver tube.^{12, 24} Often, these reaction vessels are covered with a lid or sealed shut to minimize evaporation of the flux. Minimizing flux evaporation can be important for the success of these reactions because if too much of the supersaturated molten flux evaporates, the dissolved starting materials will come out of solution before reacting to produce new materials. In other cases, the evaporation of the flux is required to produce the supersaturation that leads to nucleation and crystal growth.²⁵

One class of compounds whose synthesis lends itself especially well to the flux growth technique is the perovskites. The perovskite structure type, shown in Figure 2a, has the formula ABX_3 where A is a large cation, B is a smaller cation, and X is an anion, often oxygen. Along with the basic perovskite, many other perovskite and perovskite-related structure types exist including the $A_2BB'X_6$ double perovskites, Figure 2b, and the $A_4B_3X_9$ 2H-hexagonal perovskite-related oxides, Figure 2c.²⁶ Based on charge balance and radius ratios of the constituent elements, one can readily predict what combinations of A, B and X will form perovskite structures and which of the many variants of the perovskite structure they will adopt.¹¹

Using the flux growth technique, the zur Loye group has been able to grow a large number of noble metal containing perovskite and perovskite-related oxides.^{12, 26-34} For example, using the predictive nature of the perovskite structure types, we were able to design a series of double perovskites with the formula Ln_2MfO_6 ($Ln = La, Pr, Nd, Sm-Gd$; $M = Mg, Ni$).¹² These compounds were

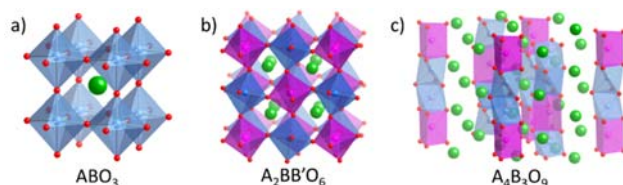


Figure 2. Structures of select perovskite and perovskite-related compounds showing (a) the basic ABO_3 perovskite, (b) the $A_2BB'O_6$ double perovskite, and (c) the $A_4B_3O_9$ 2-H hexagonal perovskite-related compound. In each structure the A atom is in green, the B polyhedra are in blue and pink and the oxygen atoms are in red.

grown by reaction of Ln_2O_3 , NiO or MgO, and Ir metal in a KOH flux, where the oxidizing nature of the hydroxide flux readily oxidized the iridium from Ir^0 to Ir^{4+} . Using the ability to tune which element occupies the A, B and B' sites, we were able to form compounds where only the B' site is magnetic, where the A and B' sites are magnetic, where the B and B' sites are magnetic, and where all three sites are magnetic. This allowed us to investigate the various magnetic interactions within the structure.¹²

Typically, when flux growth reactions are performed in open vessels, the resulting compounds are pure oxides, i.e. oxygen is the only anion in the structure. Mixed anion compounds containing both oxygen and another anion can also be grown if the reaction is conducted in a sealed system in the presence of mixed anions.³⁵ For example, if UO_3 is heated with a CsCl flux in a sealed, evacuated fused silica tube, an oxyhalide $CsUO_3Cl$ can be grown.³⁶ While sealed systems can lead to mixed anion compounds, the limited availability of oxygen can often make the growth of oxygen containing compounds difficult.³⁷

We have developed a modified flux growth method for the targeted growth of mixed-anion systems.⁸ By decreasing the surface area to volume ratio of the reaction and using metal halide as opposed to metal oxide precursors, the availability of oxygen in the reaction melt can be limited, making the inclusion of other anions favorable. At the same time, the reaction remains open to the atmosphere, avoiding the difficulties of sealed flux reactions. When this is combined with structural considerations, the targeted growth of salt-inclusion compounds is possible. Salt-inclusion compounds, which had previously been predominately grown serendipitously, consist of a covalent metal oxide framework which contains voids occupied by a simple salt-lattice. For example, $[Cs_3F][(UO_2)(Si_4O_{10})]$ was grown from UF_4 and SiO_2 in a CsCl/CsF flux contained in an open silver tube covered with a lid. This compound, shown as part of Figure 3, consists of a uranyl silicate framework which contains channels filled by a Cs_3F salt.⁸

Hydroflux Approach

Hydroflux reactions are a niche area between molten flux reactions and aqueous solution methods.^{7, 38} Relative to other salt fluxes, alkali metal hydroxides have low melting points, for example NaOH melts at 318 °C. Commercial hydroxides have an even lower melting point compared to their anhydrous counterparts because of the presence of water in these compounds. The melting point of these compounds can be further lowered to below 200 °C by the intentional addition of even more water. This forms a low temperature melt which has a very high water content but is not an aqueous solution and is termed as a hydroflux.

We have used the hydroflux method for the exploratory crystal growth of new phases.^{6-7, 38-39} There are several positive aspects to this technique, such as the use of relatively low temperatures (230

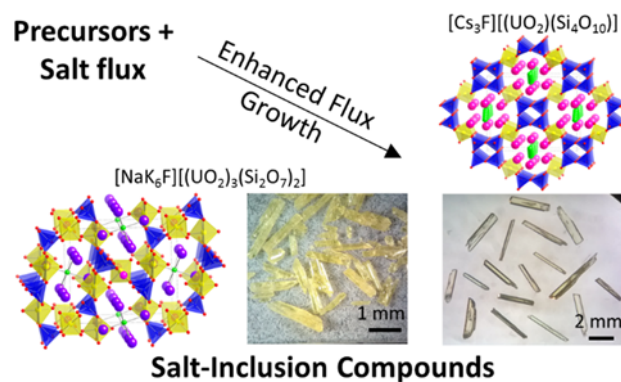


Figure 3. Enhanced flux method for the synthesis of salt-inclusion compounds showing the structures and crystal pictures of two salt-inclusion uranyl silicates. In the structures, uranium polyhedra are shown in yellow, silicon polyhedra in blue, sodium and cesium atoms in pink, potassium atoms in purple, fluorine atoms in green, and oxygen atoms in red.

°C), a shorter reaction time (often 24 h), and the lack of need for any specialized equipment.³⁸ They can be carried out in a simple polytetrafluoroethylene (PTFE) lined stainless steel autoclave, because a closed vessel is only needed to prevent dehydration.

Notably, the development of the hydroflux technique allowed for the discovery of the first ferrolite, a zeolitic compound with an all iron framework.¹⁰ A zeolite is a porous compound composed of an aluminosilicate framework. Zeolites have found many industrial applications including being used as gas adsorbents, catalysts, and ion exchange media.⁴⁰ The first ferrolite, $Ba_8(Fe_{12}O_{24})Na_3(OH)_6 \cdot xH_2O$, was grown using $Fe(NO)_3$ and $Ba(OH)_2$ in a NaOH/ H_2O hydroflux. The brown/black crystals were isolated after sonicating the resulting mixture in methanol to remove the residual flux. Iron in this framework is found in a tetrahedral coordination environment and FeO_4 tetrahedra link to four other tetrahedral to form Fe_4O_4 rings and puckered Fe_6O_6 rings that are arranged to form channels and internal cavities which resembles the sodalite structure (Figure 4). The sodium, barium, hydroxide ions and the water molecules provide the charge balance to the framework and are found in the cavities. Further work is underway to find new synthetic methods for the development of iron based zeolites in other structure types. These materials are a start to a new class of material and they can be potentially used for a wide variety of applications ranging from catalysis to new magnetic materials to sodium ion batteries for stationary power storage.¹⁰

Hydrothermal Approach

One extremely versatile method of discovering the so-called “First Material” is the hydrothermal method of crystal growth. The hydrothermal growth technique takes its name from undersea hydrothermal vents where extreme temperatures and pressures create conditions that favor materials impossible to synthesize under what we would consider normal conditions. The hallmark of hydrothermal vents is the presence of water that exists above its critical point: 374 °C and 218 atm of pressure. Scientists have been able to utilize the unique properties of supercritical water such as its ability to dissolve solids like a liquid, yet flow with next to no viscosity like a gas to synthesize many interesting and new materials.

While not one of our primary crystal growth techniques, we have on occasion utilized the hydrothermal method at the lower

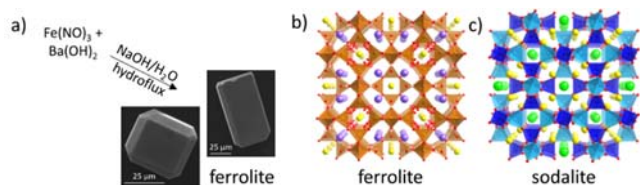


Figure 4. Hydrothermal flux growth of $\text{Ba}_8(\text{Fe}_{12}\text{O}_{24})\text{Na}_9(\text{OH})_6 \cdot x\text{H}_2\text{O}$ showing (a) electron microscopy images of representative crystals, (b) the structure of the ferrolite, and (c) the sodalite structure for comparison. Fe polyhedra are shown in orange, barium atoms in purple, sodium atoms in yellow, oxygen atoms in red, silicon polyhedra in dark blue, aluminum polyhedra in light blue, and chlorine atoms in green.

supercritical region of water, 400 °C. For example, by combining water, uranium oxide, and highly concentrated KOH at this temperature, the phase $\text{K}_5\text{U}_5\text{O}_{17}\text{OH}$ was formed. This is an interesting three-dimensional layered structure with a rare uranyl sheet topology. The structure can be seen in Figure 5.

Mild Hydrothermal Approach

Even though scientists are able to routinely create the supercritical conditions required for hydrothermal growths using furnaces and high-pressure vessels, the set up and operation of these reactions are quite expensive. To get around the expense issue associated with the supercritical conditions, in the zur Loye lab we make use of a milder approach to the hydrothermal method. This mild approach involves staying well below the critical point of water, yet still heating the vessel above the normal boiling point. By keeping the reaction sealed, we are able to keep water in its liquid state well above the point where it would normally have boiled off, and as long as we avoid the critical point the pressures needed for this approach are much more manageable.

In the zur Loye group we use PTFE-lined autoclaves in order to contain these kinds of reactions. The PTFE liners provide an excellent container for crystal growth as they are chemically inert and thus unlikely to react and corrupt our reaction. We use the mild hydrothermal approach as a versatile platform to create many different materials including oxides,⁴¹ fluorides,^{4, 42-43} mixed anion systems,⁴⁴ and metal-organic compounds.^{5, 15}

Reduced Fluorides

In particular, we have seen great success using organic reducing agents, specifically acetates, to create interesting new reduced uranium fluorides, which grow as small, intensely green crystals. In order to synthesize fluorides, an effective fluorinating agent must be used. Although a very hazardous chemical, dilute hydrofluoric acid provides an excellent way to incorporate the fluoride ion into many structures. At the same time, the reducing nature of the HF combined with acetate ligands allow for the reduction of U(VI) down to U(IV) within the reaction. This *in situ* reduction technique allows us to overcome many of the traditional problems associated with growing reduced uranium crystals, including limited solubility in many different solvents. For example, by combining $\text{UO}_2(\text{CH}_3\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}$, NaF, a transition metal or main group oxide or fluoride, H_2O and HF, we were able to synthesize a series of quaternary uranium fluorides $\text{Na}_x\text{MU}_6\text{F}_{30}$ ($M = \text{Al}^{3+}, \text{Ga}^{3+}, \text{Ti}^{3+}, \text{V}^{3+}, \text{Cr}^{3+}, \text{Fe}^{3+}, \text{Mn}^{2+}, \text{Co}^{2+}, \text{Ni}^{2+}, \text{Cu}^{2+}, \text{Zn}^{2+}$).^{4, 43} Representative crystal pictures and images of the structures are shown in Figure 6.

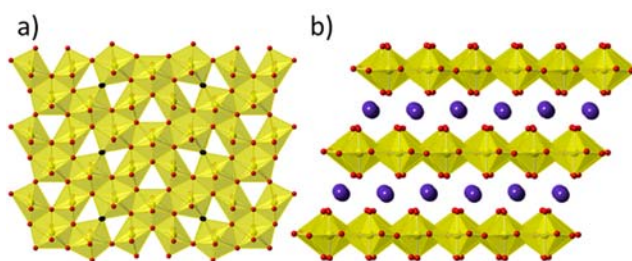


Figure 5. Structure of $\text{K}_5\text{U}_5\text{O}_{17}\text{OH}$ showing (a) the uranyl sheet and (b) the overall structure. Uranium polyhedra are shown in yellow, potassium atoms in purple, non-hydroxide oxygen atoms in red, and hydroxide ions in black (hydrogens are omitted).



Figure 6. Mild hydrothermal crystal growth of $\text{Na}_x\text{MU}_6\text{F}_{30}$ showing the structures and representative crystal pictures for each compound.

Other fluorides can also be grown under mild hydrothermal conditions including the complex anti-perovskite material $[\text{Cu}(\text{H}_2\text{O})_4]_3[\text{MF}_6]_2$ where $M = \text{V}, \text{Cr}, \text{Mn}, \text{and Fe}$.⁹ A picture of this structure can be seen in Figure 7. This material grows as large rectangular prism crystals that show excellent chemical stability, even in concentrated nitric acid. These materials were made by combining the appropriate transition metal fluorides with copper acetate, water, and hydrofluoric acid in a PTFE lined autoclave; then heating it to 200 °C for 24 hours. This allows all of the starting materials to dissolve. After heating, the autoclave is slowly cooled down to room temperature, which allows for the crystals to form and grow.⁹

Reduced Oxides

Our group has established a new synthetic route to grow high quality single crystals of reduced systems by using a low temperature two-step hydrothermal method. In general, reduction can be performed in two different ways: starting with metals in the desired low oxidation state or using a reducing agent to carry out an *in situ* reduction. Although it is very convenient to use a metal precursor with the lower oxidation state, maintaining the oxidation state throughout the reaction can be difficult. On the other hand, a fully oxidized metal precursor can instead be used in combination with an organic reducing agent, including, oxalic acid, tartaric acid, polyols, and acetates, or an inorganic reducing agent, including, HF, Zn amalgam, and HI. This is very useful as the lower oxidation state can be maintained during the entire process due to the presence of the reducing agent.

While an in-situ reduction step offers certain advantages, such as making it easier to maintain the lower oxidation state and more readily available precursors, in some instances, instead of reduced compounds being grown, only fully oxidized products form. The reason behind this is that the reduction of the metal cation is kinetically slow when compared to the time it takes for the fully oxidized reactants to react and form fully oxidized phase(s). To prevent this, we have developed a two-step mild hydrothermal

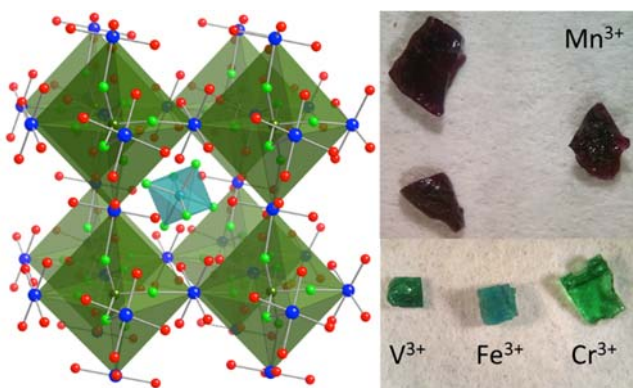


Figure 7. Structure of $[\text{Cu}(\text{H}_2\text{O})_4]_3[\text{MF}_6]_2$ and pictures of crystals of each analogue.

method that divides this process into two separate steps. In the first step, the metal cation is reduced using the organic reducing agent and in the second step, the remaining reactants are added to lead to the crystallization of the desired reduced compounds.

Using our new two-step hydrothermal method, we were able to synthesize high quality single crystals of multiple compounds including $\text{Cs}_2\text{V}_3\text{O}_8$,⁴¹ $\text{Ba}_3[(\text{VO})_2(\text{C}_2\text{O}_4)_5(\text{H}_2\text{O})_6] \cdot (\text{H}_2\text{O})_3$,⁵ and $\text{A}_2[(\text{VO})_2(\text{C}_4\text{H}_2\text{O}_6)_2(\text{H}_2\text{O})_2] \cdot (\text{H}_2\text{O})_2$ ($\text{A} = \text{K}, \text{Rb}, \text{and Cs}$),¹⁵ Figure 8. Either PTFE-lined autoclaves or thick walled Pyrex tubes can be used as reaction vessels for these types of reactions, as they provide the necessary redox neutral environment. We used naturally occurring carboxylic acids, such as oxalic acid and tartaric acid, as reducing agents in an aqueous reaction environment. Both oxalic acid and tartaric acids are known to be mild reducing agents, which have the ability to reduce V^{5+} to V^{4+} . Vanadium exhibits multiple oxidation states in solution, yellow (V^{5+}), blue (V^{4+}), green (V^{3+}), and purple (V^{2+}). Although oxalic acid or tartaric acid are strong enough to reduce vanadium to V^{4+} , stronger reducing agents, such as Zn, are needed to achieve the lower oxidation states, V^{3+} and V^{2+} .

Blue color single crystals of $\text{Ba}_3[(\text{VO})_2(\text{C}_2\text{O}_4)_5(\text{H}_2\text{O})_6] \cdot (\text{H}_2\text{O})_3$ were synthesized using oxalic acid as the reducing agent at 160°C . Isolated VO_6 octahedra present in the structure are connected to each other via oxalate ligands to form V_2O_{12} dimers. These dimers connect with each other via Ba atoms and form the extended structure, Figure 9. Water molecules present in $\text{Ba}_3[(\text{VO})_2(\text{C}_2\text{O}_4)_5(\text{H}_2\text{O})_6] \cdot (\text{H}_2\text{O})_3$ can be selectively removed by heating and, interestingly, the initial structure transforms to $\text{Ba}_3[(\text{VO})_2(\text{C}_2\text{O}_4)_5(\text{H}_2\text{O})_4] \cdot (\text{H}_2\text{O})_2$, and $\text{Ba}_3[(\text{VO})_2(\text{C}_2\text{O}_4)_5(\text{H}_2\text{O})_2]$ at 50°C and 100°C , respectively, while retaining its single crystal nature.⁵

Conclusion

The continuing improvement of technology is dependent on the ability of solid state chemists to produce better, more efficient materials. To achieve this, it is important to discover new “First Materials,” initial compounds which then can be further developed to optimize the desired properties. In the zur Loye group, we have utilized exploratory crystal growth to produce new crystalline compounds with the goal of discovering the next “First Material.” Through our development of new synthetic techniques, such as our enhanced flux growth method, the hydroflux method, and the two step mild hydrothermal method, we have had great success in discovering new compounds.

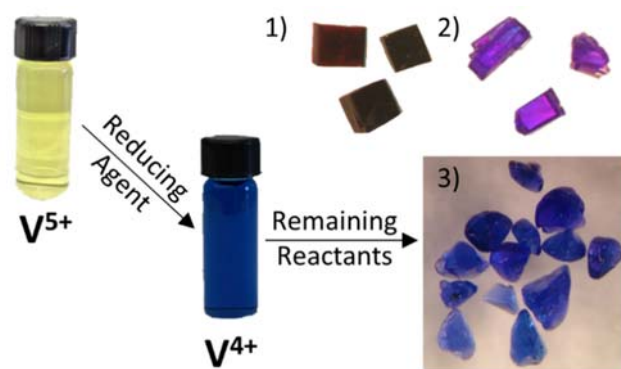


Figure 8. Two-step mild hydrothermal synthesis of reduced vanadium compounds including (1) $\text{Cs}_2\text{V}_3\text{O}_8$, (2) $\text{K}_2[(\text{VO})_2(\text{C}_4\text{H}_2\text{O}_6)_2(\text{H}_2\text{O})_2] \cdot (\text{H}_2\text{O})_2$ and (3) $\text{Ba}_3[(\text{VO})_2(\text{C}_2\text{O}_4)_5(\text{H}_2\text{O})_6] \cdot (\text{H}_2\text{O})_3$.

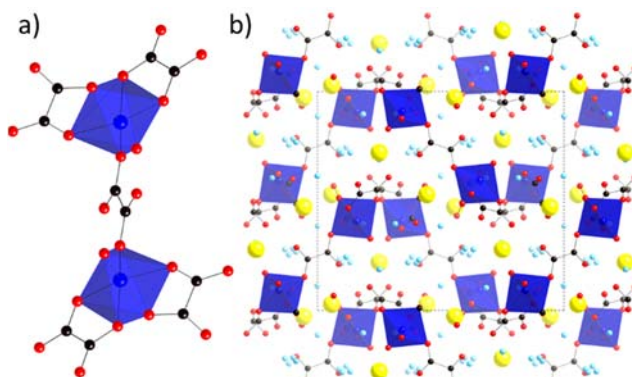


Figure 9. Structure of $\text{Ba}_3[(\text{VO})_2(\text{C}_2\text{O}_4)_5(\text{H}_2\text{O})_6] \cdot (\text{H}_2\text{O})_3$ showing the (a) $(\text{VO})_2(\text{C}_2\text{O}_4)_5$ unit and (b) the overall structure. V polyhedra are shown in dark blue, barium atoms in yellow, carbon atoms in black, non-water oxygen atoms in red, and water molecules in light blue (hydrogens are omitted).

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