Crystallization of Solid-State Materials via Decomplexation of Soluble Complexes

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A variety of compounds which are at best sparingly soluble in aqueous media may be readily brought into solution through the formation of soluble coordination complexes. Modification of experimental conditions through, e.g., dilution or slow removal of the complexing agent, leads to supersaturation and, consequently, crystallization of the original solid-state phase. This technique of decomplexation crystallization, both of simple inorganic coordination complexes and of complexes with macrocyclic organic chelating agents, offers the opportunity both to effect the recrystallization of sparingly soluble species and to modify their crystal morphology. Similarly, precursors for solid-state materials may be solubilized in nonaqueous solvents through the formation of soluble complexes and then allowed to undergo reaction crystallization, allowing the examination of both solvent effects and chelation effects on the morphology and phase of the resulting solid-state materials. These effects are often dramatic, and such "complexation-mediated crystallization" approaches offer promise for the facile preparation of metastable phases from simple precursors under ambient conditions.

Contents

Introduction

Crystallization represents a key processing step for a wide array of solid-state materials, ranging from the preparation of bulk crystalline hosts for laser applications to the synthesis of nanocrystalline semiconductors.[1] Given the central importance of crystallization, numerous methods have been developed to permit the preparation of solid-state materials in crystalline form. Perhaps the most generally applied techniques are growth from the melt (e.g., the Czochralski method)[2] and crystallization from high-temperature fluxes.[3] Each of these suffers, however, from the general requirement of rather high temperatures, often eliminating the possibility of accessing metastable phases. In addition, cooling of single crystals from the high temperature of their formation to ambient temperatures not infrequently interjects an additional complication in the form of various phase transitions. Thus, as but one example, whereas dysprosium molybdate [$Dy_2(MoO_4)_3$] may be prepared in single crystalline form through Czochralski growth, cooling of the resulting crystals to room temperature affords material displaying multiple domains corresponding to different ferroelectric orientations.[4,5] Thus, the development of techniques for the crystallization of solid-state materials under ambient conditions remains an issue of ongoing importance. Crystallization from solution offers a number of advantages, including the possibility of low-temperature operation and the ability to control crystal morphology through variation of solvent, but is applicable, of course, only to those materials which display reasonable solubility. As a result, although solvent effects on the crystallization of organic compounds are well-known,[6] reports of analogous effects for salts and inorganic materials are comparatively scarce. One of the conceptually simplest approaches to ambient solution crystallization is the use of reaction crystallization,[7] wherein two (or more) precursors species react, generally under diffusion control, to afford a desired insoluble phase. Although this technique may be used in some cases to prepare large and rather perfect crystals, particularly when carried out in gelatinous media[8] rather than homogeneous solution, the high nucleation rate often seen for very insoluble phases generally leads to the formation of microcrystalline products.[8] Many technological applications, of course, require smaller crystals, and the preparation of small, uniformly sized particles of highly insoluble phases through, e.g., the technique of double jet precipitation, is well-precedented.[9−11]

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This review presents an overview of two related approaches to the solution crystallization of highly insoluble phases under ambient conditions.[12−14] One approach exploits the slow generation of target phases through the decomplexation of soluble, reversibly formed precursor complexes, either simple inorganic coordination complexes[15] or complexes with organic chelating agents ("complexation-mediated crystallization").[16] The other focuses on complexation-mediated reaction crystallizations wherein soluble complexes of one or more of the reactant species (rather than of the product phase) are used both to allow control over nucleation through reduction of supersaturation and to allow the more general use of nonaqueous solvents.

Decomplexation Crystallization

Whereas many solid-state inorganic materials display at best negligible solubility in water or other solvents, they frequently undergo reversible reactions with either neutral molecules (e.g., NH_3) or anions to afford complexes displaying much higher solubility. Simple perusal of compendia of solubility data[17−19] reveals examples of such behavior—e.g., it is well-known that whereas silver halides are virtually insoluble in water, they dissolve readily in aqueous ammonia[20] and in aqueous solutions of alkali metal halides.[21,22] The volatility of ammonia led to the early discovery that slow evaporation of ammoniacal silver halide solutions affords convenient access to crystalline materials, while only more recently was it noted that dilution of silver halide/alkali metal halide solutions should and does result in the crystallization of the silver halide. Translation of these decomplexation crystallization techniques, which have been treated theoretically,[15] to the milieu of aqueous gel matrixes[8] has often permitted the formation of large crystals displaying comparatively low impurity and defect concentrations.[23] Despite the availability of a potentially large number of solid-state phases through such simple decomplexation crystallization approaches, surprisingly few materials have received attention. Reported results for those materials which have been examined are summarized below.

Silver Halides

Decomplexation crystallization of silver iodide has been studied for well over 100 years. Early reports focused on the solubility of silver iodide in concentrated aqueous hydrogen iodide, forming $[AgI_2]^-$.[24,25] Diffusion of hydrogen iodide from such solutions into an absolute ethanol overlayer resulted in a slow reduction in the iodide concentration and, ultimately, the deposition of hexagonal plates of silver iodide with edge lengths of up to 5 mm. Replacement of preformed silver iodide with silver metal, which is slowly oxidized to silver iodide under the crystallization conditions, afforded hexagonal pyramids rather than plates.

Although the hydrogen halide assisted crystallizations demonstrated some promise for habit modification through alteration of experimental conditions, they were largely supplanted by the development of techniques for the crystallization of silver halides from aqueous ammonia. Dissolution of silver halides in 15% aqueous ammonia, forming $[Ag(NH_3)_2]^+X^-$ ($X = Cl, Br$), and slow evaporation (over the course of 3−5 days) afforded crystalline halides with grain sizes in the range 50−100 μm,[26] a size range appropriate for photographic applications.[26,27] Cooling of ammoniacal solutions of silver chloride or silver bromide, in contrast, afforded much larger single crystals, up to 3 mm in width, which appear to display more regular structures, generally octahedral or truncated tetrahedral forms, than those obtained by the evaporative route.[20]

Most recently, attention has been focused on the crystallization of silver iodide from aqueous potassium iodide solutions. Whereas induction of crystallization through the concentration of aqueous silver iodide/potassium iodide solutions afforded a crystalline *complex*,[22] dilution of such solutions decreases the silver iodide solubility, and the ternary phase diagram for this mixture[18] suggests that even a small change in concentration can lead to a dramatic decrease in the solubility of silver iodide. In the event, slow diffusive dilution of solutions of silver iodide in concentrated aqueous potassium iodide at room temperature afforded single crystals of silver iodide.[28] After 6−8 weeks, a mixture of hexagonal prisms (up to 20 mm × 2 mm) and small hexagonal dipyramids (3 mm × 1.5 mm) was obtained. This material, which contained ca. 2 ppm potassium, in general displayed appreciably higher crystal quality than that obtained by the hydrogen iodide route. In a modification of this procedure exploiting the inverse temperature dependence of the solubility of silver iodide in aqueous potassium iodide, circulation of an aqueous solution through a lower temperature (23 °C) saturation zone and a higher temperature (40 °C) growth chamber afforded only the hexagonal prismatic habit.[21] Although potassium impurity levels were higher, crystal growth required less than half the time of the dilution approach.

Whereas simple reaction crystallization of silver halides in aqueous starch[29] or agar[30] gels affords microcrystalline material in the form of Liesegang rings, adaptation of the decomplexation routes to gelatinous media offers additional promise for control of crystal morphology. Each of the approaches used for decomplexation crystallization from homogeneous solution, described above, has been adapted to the gel environment. Although an early report suggested that gelatin was incorporated in silver bromide crystals prepared by evaporation of gelatin-containing ammoniacal silver bromide,[20] silicate-based gels do not appear to be incorporated. Thus, silver bromide and silver iodide were obtained in nicely crystalline form (1-mm cubes and 10−12-mm hexagonal platelets, respectively) when their solutions in the corresponding aqueous hydrogen halides were layered over silicate gels containing lower concentrations of hydrogen halide.[31] These diffusional dilution crystallizations afforded observable crystals within 1 h; 8−10 days were required to obtain maximum crystal dimensions. Silver chloride was also obtained in this manner, but the resulting crystals were brittle, and better material was obtained through the use of ammoniacal silver chloride. Silver iodide has also been crystallized from aqueous potassium iodide solutions in silicate gels.[32] Crystal size and form were noted to depend on both the concentration of potassium iodide and the temperature. Small hexagonal platelets were obtained when lower concentrations were used at 45 °C, while crystallization at room temperature afforded small (ca. 50 μm) pyramidal and prismatic crystals within the gel matrix as well as larger (to 5 mm) hexagonal pyramids in the supernatant aqueous phase. These results have been generalized to silver chloride and silver bromide and to other halide sources as well (KX, NaX, NH_4X, CaX_2).[33] Variation of countercation appears to offer some promise for size and/or habit modification, with 3-mm octahedral crystals of silver bromide obtained from ammonium bromide solution and 2-mm cubic crystals from potassium bromide solution, although silver iodide and silver chloride gave comparable crystal forms regardless of the identity of the countercation.

In each of these silver halide crystallizations, the thermodynamically favored phase is exclusively obtained. Given the crystallization conditions, it is not surprising that phase selectivity is dictated by thermodynamic considerations, as kinetic formation of a metastable phase would presumably be "corrected" through redissolution through soluble complex formation. Access of metastable phases (vide infra), in general, will require either a more abrupt change in conditions, an approach not necessarily offering good control over crystal size or form, or essentially irreversible deposition of the solid-state phase.

Copper(I) Halides

Numerous reports of the decomplexation crystallization of copper(I) halides have also appeared, although the range of techniques brought to bear on these materials is quite limited in comparison with that reported for the silver halides. Crystallization from homogeneous solution has been effected through the formation of a soluble chloride complex[34] in aqueous hydrogen chloride at 40−45 °C followed by slow cooling to ca. 20 °C.[35] Although seed crystals were provided, they were apparently consumed before crystallization ensued; comparatively large (up to 7 mm) transparent, tetrahedral crystals displaying partial blue coloration were obtained with cooling rates of 0.5 °C/day.

Copper(I) chloride has also been crystallized from aqueous hydrogen chloride in silicate gels, both by diffusion of CuCl/HCl solutions into hydrogen chloride-free gels,[36−39] in which case the more rapid diffusion of HCl through the gel leads to crystallization of CuCl behind the diffusion front, and by diffusive dilution of CuCl/HCl solutions with water.[40−46] The impact of such variables as acid concentration, temperature, gel pH, and crystallizer configuration, as well as of ambient light, has been assessed. Given the focus of all these studies on one particular decomplexation reaction for the crystallization of copper(I) chloride, it is perhaps not surprising that only qualitative differences were observed in the crystalline products obtained, which were generally found to be well-formed tetrahedra. Optimization of apparatus and crystallization conditions has allowed the growth of crystals approaching edge lengths of 1 cm,[37] although 3-mm tetrahedra are more routinely obtained. One report noted the formation of long needles, oriented perpendicular to the gel/solution interface, when diffusion was carried out at 22 °C into a gel formed at 50 °C; analogous examples in which the gel was formed at lower temperatures (22, 30, 40 °C) all afforded the more typical tetrahedral crystals. Given the key role the gel plays, going beyond simple control of diffusion rates (as seen, e.g., in the formation of "cusps" around growing crystals),[23] it is possible that continued exploration of the effect of gel structure on crystallizations may lead to additional dramatic examples of morphology modification.

Copper(I) bromide has also been crystallized in silicate gels through diffusive dilution of its solutions in aqueous hydrobromic acid. Optimized conditions, using an apparatus providing large excesses of feed solution and water so as to permit establishment of pseudo-steady-state growth conditions, afforded tetrahedral crystals with edge lengths of up to 6 mm after ca. 3 weeks.[43,45]

Mercury(II) Iodide

Mercury(II) iodide, itself sparingly soluble in water, is readily solubilized by various iodide salts, including potassium iodide,[19] as well as by hydrogen iodide, through the formation of complex polyiodides, $[HgI_3]^-$ and $[HgI_4]^{2-}$.[47−49] Evaporation or slow cooling generally results in the crystallization of mercury(II) iodide,[47,48] although an early report noted the inhibition of crystal growth due to the adsorption of polyiodide complexes.[49] Such adsorption, of both $[HgI_3]^-$ and potassium ion, has also been suggested to be a source of habit modification in the decomplexation crystallization of mercury(II) iodide.[47] Evaporation of HgI_2/HI solutions in a vacuum desiccator over sodium hydroxide, serving to remove HI from solution, afforded thin platelets of α-HgI_2 up to ca. 2 mm in size, while slow cooling of aqueous HgI_2/KI solutions from 80 °C affords small pyramidal crystals of the same phase.[48] Layering a potassium iodide solution over a silicate gel containing mercury(II) acetate also afforded crystalline α-HgI_2, although difficulty in removing the gel limited the utility of this reaction crystallization approach.[48]

Mercury(II) iodide is unique among the materials for which decomplexation crystallization has been examined in that it is quite soluble in a number of organic solvents, including alcohols, nitriles, ketones, esters, halides, and aromatic solvents. Simple recrystallization from pure organic solvents gives rise to significant modifications of both habit and phase—e.g., crystallization from 1,2-dibromoethane affords large crystals of α-HgI_2, while use of diiodomethane affords large (to several cm) plates of β-HgI_2, and crystallization from alcohols affords mixtures of both phases.[49] Use of iodide sources, including alkali metal iodides and various ammonium iodides, enhances the solubility of mercury(II) iodide in a number of organic solvents and appears to allow further control of crystal morphology.[47] In the majority of these cases, various soluble solvates are presumably formed, and recrystallization of HgI_2 from such solutions thus represents a type of decomplexation crystallization. This has been discussed in detail for the recrystallization of α-HgI_2 from dimethyl sulfoxide solution.[50] A comprehensive examination of the intermediacy of solvates in the recrystallization of solid-state materials, however, is beyond the scope of this review.

Lead(II) Iodide and Cadmium(II) Chloride

Lead(II) iodide and cadmium(II) chloride have also been crystallized through intermediate formation of soluble iodide complexes with potassium iodide or hydrogen iodide.[48] These materials both display reasonable solubility in pure water, and the best crystallization results were in fact obtained through direct recrystallization (slow cooling from 80 °C for PbI_2, evaporation at room temperature for CdI_2) rather than decomplexation methods.

Mercury(II) Sulfide

The solubility of mercury(II) sulfide in water is dramatically increased in the presence of sodium sulfide.[51,52] Decomplexation crystallization of mercury(II) sulfide from such solutions may be achieved via either exposure to atmospheric oxygen, which serves to slowly reduce the sulfide concentration by oxidation,[53] or by taking advantage of the negative temperature dependence of HgS solubility in sulfide-containing solutions, allowing crystallization to occur in a warm zone of a flow crystallizer.[54] In each case, growth of α-HgS (cinnabar) was observed, although this was perhaps preordained by the use of either α-HgS or structurally related CdS as seed material. Formation of mosaic crystals was observed in each case, although adjustment of the thermal gradient approach to allow slower growth rates ($\Delta T = 20$ °C, growth rate 15 μm/day) did allow for the preparation of relatively high quality single crystals. Hydrothermal growth of α-HgS from aqueous sulfide solution has also been reported,[55,56] in some cases affording very large single crystals of good quality. Interestingly, sodium hydrogen sulfide may also be used to effect crystallization of α-HgS under hydrothermal growth conditions,[57] whereas it has been reported that HS^- does not add to HgS to afford soluble complexes under ambient conditions.[53]

Gel growth techniques have also been applied to the decomplexation crystallization of mercury(II) sulfide. Thus, diffusion of sulfide-solubilized HgS into a silicate gel resulted in the precipitation of β-HgS (metacinnabar) in crystalline form (up to ca. 0.5 mm). Longer reaction times resulted in conversion to α-HgS, which was also obtained in crystalline form (up to ca. 0.5 mm). Both crystal size and the conversion rate were reported to increase with increasing temperature.[33] Others have found the phase conversion to be unreliable and have generally obtained only β-HgS from silicate gels.[58,59] Use of a cross-linked aqueous acrylamide gel afforded a microcrystalline precipitate of β-HgS and, in a distinct region of the gel, irregular but euhedral (i.e., displaying defined faces) crystals of α-HgS (ca. 0.1−0.15 mm).[58]

Selenium

Under hydrothermal growth conditions, elemental selenium is solubilized by sodium sulfide in aqueous solution through the formation of Se_2S^{2-}, allowing recrystallization in the form of single crystals up to nearly 1 cm in length. Higher temperatures favored prismatic crystal morphologies, while needles were formed at lower temperatures.[60]

Lead(II) Oxide

Slow cooling of solutions of lead(II) oxide in concentrated aqueous alkali afforded three distinct crystal morphologies, thin yellow needles (≤2 mm), blocky red crystals (ca. 1 mm), and yellow laths (8 × 1 × 0.1 mm). The latter form appeared to be kinetically unstable, undergoing conversion to the red form after several days.[61]

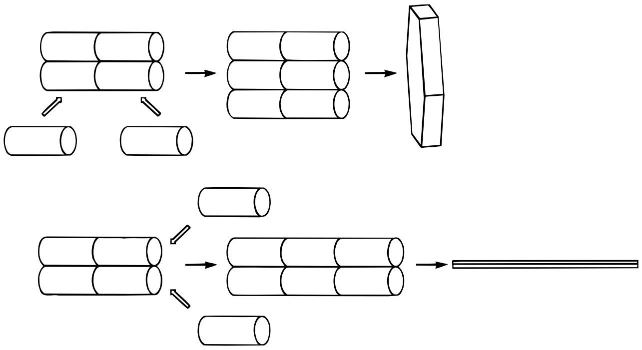

Figure 1. Schematic depiction of results of selective solvation on the crystallization of sodium acetate trihydrate, leading to plates from aqueous solution (top) due to selective hydration of the hydrophilic "caps" of the growing crystal and to needles from cyclohexane solution (bottom) due to selective solvation of the comparatively hydrophobic sides.

Complexation-Mediated Recrystallization

Precipitation of salts with relatively high lattice energies (e.g., fluorides, carbonates) upon attempted crystallization of their complexes with macrocyclic ("crown") polyethers was noted in the earliest reports of the synthesis and properties of the crown polyethers.[62] This phenomenon has nearly universally been viewed as a problem to be avoided but more recently has been developed as a general tool for the recrystallization of inorganic and organic salts from solvents which afford at best extremely limited solubility of the salt in the absence of a chelating agent.[16] This technique of "complexation-mediated crystallization", taking advantage of the rapidly growing body of information regarding specific molecular and ionic recognition phenomena,[63] permits the analysis of both solvent and chelating agent effects on the morphology and phase of resulting crystalline materials.

Crystallization of sodium acetate trihydrate from cyclohexane solution, mediated by the formation of the 15-crown-5 complex of sodium acetate,[16] afforded long slender prismatic crystals whose long axes were perpendicular to the dominant faces of the platelike crystals obtained by conventional aqueous crystallization.[64] This morphology change was rationalized on the basis of selective solvation of specific crystal faces, with the hydrocarbon environment slowing growth in the *a* and *b* crystallographic directions relative to their growth in aqueous solution, consistent with the comparatively hydrophobic nature of these crystal surfaces (Figure 1).

Complexation-mediated crystallization appears generally applicable to a wide range of salts and is particularly attractive in that it offers a number of variables for alteration. In a systematic study of the recrystallization of potassium hydrogen tartrate,[65] the role of the chelating agent was demonstrated through the generation of a distinct crystal morphology when 18-crown-6 was used in place of 15-crown-5 (Figure 2). Observation of {001} crystal faces from the 18-crown-6

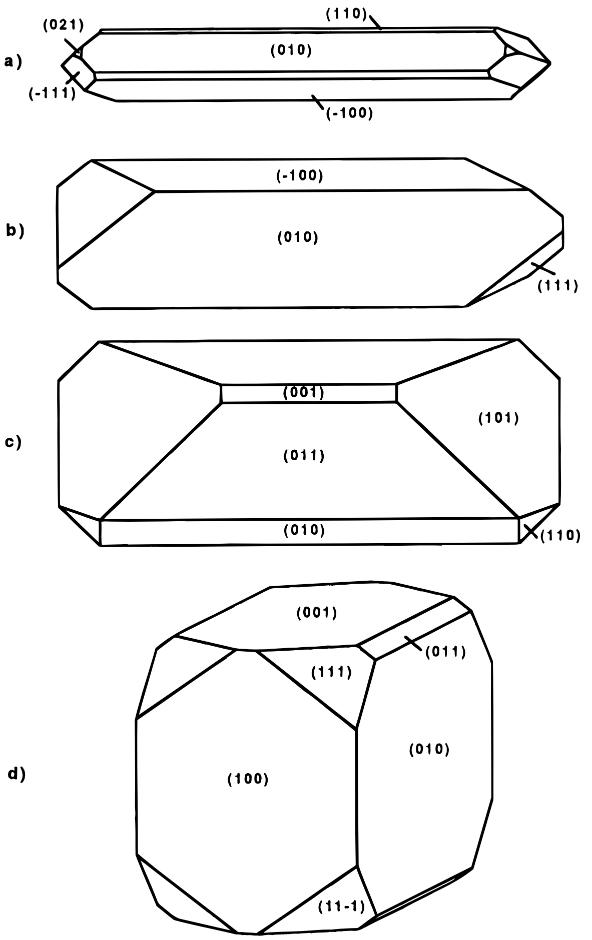

Figure 2. Crystal forms of potassium hydrogen tartrate obtained from (a) H_2O (>50 °C), (b) CH_2Cl_2/15-crown-5, (c) CH_2Cl_2/18-crown-6, and (d) CCl_4/18-crown-6 showing progressive expression of {001} surfaces.

mediated crystallization is consistent with stronger adsorption of this chelating agent to surface-bound potassium ions, slowing growth in the (001) and (00$\bar{1}$) directions, comprised of alternating sheets of intermolecularly hydrogen bonded hydrogen tartrate moieties and potassium ions (Figure 3).[66] Use of carbon tetrachloride in place of dichloromethane as the crystallization solvent gave rise to further development of the {001} faces (Figure 2), as anticipated given the lower solubility of the potassium complex of 18-crown-6 in this nonpolar solvent, resulting in stronger adsorption to the {001} faces and further slowing crystal growth in this direction.

Ammonium salts are also amenable to complexation-mediated crystallization, and ammonium nitrate has been successfully crystallized from a number of organic solvents in a variety of crystal morphologies.[67] Fibrous morphologies dominate, but suitable choice of solvent and chelating agent has led to the generation of both prismatic and dendritic forms. Given the comparatively low lattice energy of ammonium nitrate, care must be taken to avoid crystallization of its complexes; use of 15-crown-5 in place of 18-crown-6 reduces the likelihood of complex crystallization due to its intrinsically lower affinity toward ammonium ion, while use of poly(ethylene glycol) appears to eliminate complex crystallization entirely.

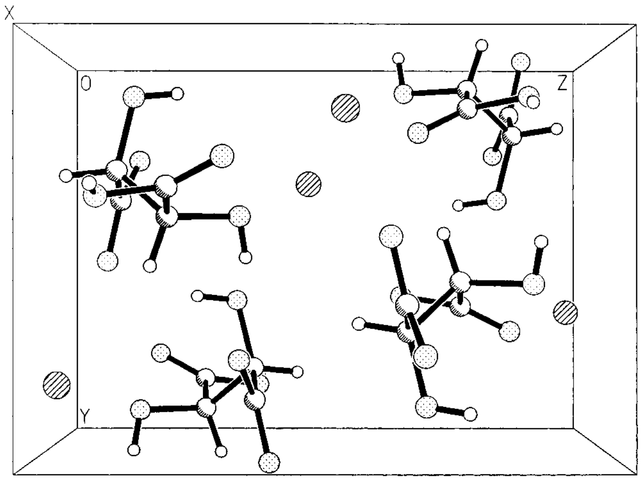

Figure 3. Perspective view of the crystallographic unit cell of potassium hydrogen tartrate, showing alternating sheets of hydrogen tartrate ions and potassium ions along the crystallographic *c*-axis.

The ammonium nitrate complexes obtained, while not of direct interest with regards to the preparation of crystalline ammonium nitrate, display a number of interesting structural features of relevance to molecular recognition studies of ammonium ion complexation.[68] In a similar vein, although occasionally other complexes are obtained instead of the anticipated uncomplexed salt, these complexes are of general interest from this perspective. Thus, for example, an attempted recrystallization of dipotassium tartrate afforded a potassium complex of 18-crown-6 displaying a highly unusual coordination number and geometry.[69]

Hydrothermal Crystallization

Hydrothermal crystal growth through the use of mineralizers,[70−73] such as the crystallization of bismuth silicate ($Bi_{12}SiO_{20}$) from aqueous sodium hydroxide[74] and the well-known crystallization of quartz from aqueous alkali solutions,[75] clearly involves the formation of soluble complexes, and in some cases the nature of these intermediate complexes is quite well established. Several examples of hydrothermal growth are presented above (HgS, PbO, Se), but comprehensive coverage of hydrothermal crystallization is beyond the scope of this review.

Reaction crystallization, particularly of metal oxides, has also been effected from aqueous solution in the presence of additives such as triethanolamine, nitrilotriacetic acid, gluconic acid, and (ethylenedinitrilo)tetraacetic acid (EDTA).[76−78] Although these reactions presumably involve intermediate complexes, they generally involve higher temperature processing steps and thus are beyond the coverage of this review.

Complexation-Mediated Reaction Crystallization

In addition to simple recrystallization, complexation-mediated crystallization has been exploited as a powerful tool for the alteration of both crystal form and phase of products of salt metathesis reactions. Such reactions, wherein two soluble salts react to produce at least one insoluble phase, are most often carried out in aqueous

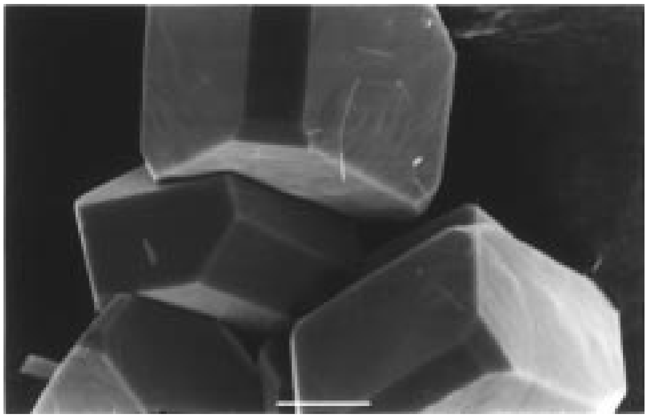

Figure 4. Scanning electron micrograph of calcite as obtained from aqueous solution after 36 days at 21 °C. Bar = 10 μm.

solution in order to dissolve the reactant salts. However, the use of chelating agents allows them to be effected in nonaqueous environments, and dramatic solvent and chelating agent effects on both crystal morphology and phase have been noted. Although the approach is conceptually very simple, it offers a wide variety of variables for exploration, including the identity of the solvent, the chelating agent, and the counterions, the crystallizer configuration, and the reaction medium (e.g., homogeneous solutions, immiscible liquid/liquid systems, and gels).

Three anhydrous phases of calcium carbonate ($CaCO_3$) have been identified. Precipitation of calcium carbonate from aqueous solution under ambient conditions affords calcite, the thermodynamically most stable phase (Figure 4).[79] Under some conditions, kinetic formation of a metastable phase, vaterite, is also observed,[80] and at higher temperatures, a third polymorph, aragonite, becomes the thermodynamic phase.[81] Interestingly, each of the anhydrous calcium carbonate polymorphs is a so-called biomineral, with calcite forming the basis of many marine shells, aragonite serving as the principal component of coral reefs, and vaterite appearing in several marine tunicates.[82] The mechanism by which nature effects both the phase selective synthesis of calcium carbonate and the alteration of its morphology remains an open question. Astoundingly, precipitation of calcium carbonate from methanolic solutions of calcium chloride, itself quite soluble in this solvent, and sodium bicarbonate, completely insoluble in methanol but readily solubilized with 1 equiv of 18-crown-6, affords calcite initially, but aging results in the quantitative conversion of this kinetic precipitate to vaterite.[83] This seemingly contrathermodynamic result is clearly due to surface solvation and/or chelation effects which overcome the intrinsic bulk stability of calcite.[84] These interactions are made sufficiently stabilizing by the formation of vaterite in essentially nanocrystalline form (Figure 5), presenting very high surface area. The conversion from calcite to vaterite is made kinetically feasible by the initial precipitation of microcrystalline calcite—bulk crystalline calcite, as obtained from aqueous precipitation, is not converted to vaterite in methanolic 18-crown-6 on a kinetically accessible time scale.

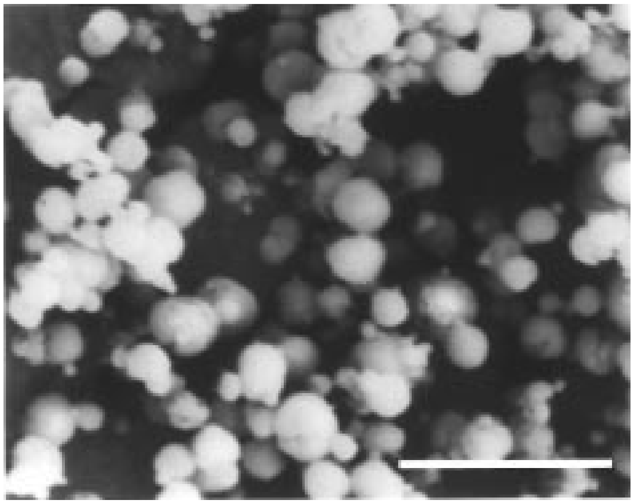

Figure 5. Scanning electron micrograph of vaterite as obtained from methanol after 36 days at 21 °C. Bar = 10 μm.

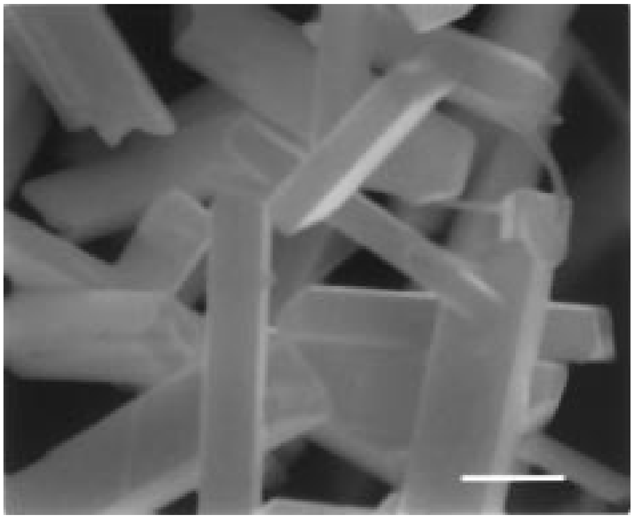

Figure 6. Scanning electron micrograph of monoclinic $PbCrO_4$ as obtained from aqueous solution. Bar = 1 μm.

Lead chromates (lead chromium oxides), serving as prototypes for the broad and technologically significant class of ternary metal oxides, also yield to the technique of complexation-mediated crystallization.[85] Thus, whereas the salt metathesis reaction between lead(II) acetate and potassium chromate in aqueous solution affords monoclinic $PbCrO_4$ (crocoite) (Figure 6), the same reaction in methanol, using 2 equiv of 18-crown-6 to solubilize the potassium chromate, affords a metastable orthorhombic polymorph of $PbCrO_4$. Use of an additional chelating agent, tris(methoxyethoxyethyl)amine, to kinetically sequester the lead ion predictably leads to the formation of larger crystals of orthorhombic $PbCrO_4$ (Figure 7) by slowing the process of nucleation relative to the growth of already-formed nuclei. Attempted use of the same chelating agent in aqueous preparations yields a metastable lead oxide-rich phase, $PbO{\cdot}PbCrO_4$ (phoenicochroite), previously prepared only from the corresponding element oxides at elevated temperatures. This phase results from initial precipitation of hydrous lead oxide, also effected by simply adding triethylamine to aqueous lead(II) acetate, followed by nucleation of $PbO{\cdot}PbCrO_4$ on this initial precipitate, as indicated by the ability of this hydrous lead oxide to nucleate formation of $PbO{\cdot}PbCrO_4$ from methanolic solutions.

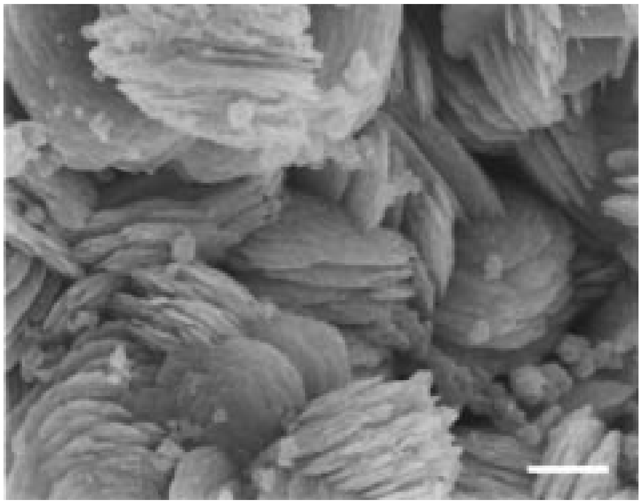

Figure 7. Scanning electron micrograph of orthorhombic $PbCrO_4$ as obtained from methanol solutions of K_2CrO_4·2(18-crown-6) and $Pb(OAc)_2$·$3H_2O$·[tris(methoxyethoxyethyl)amine]. Bar = 1 μm.

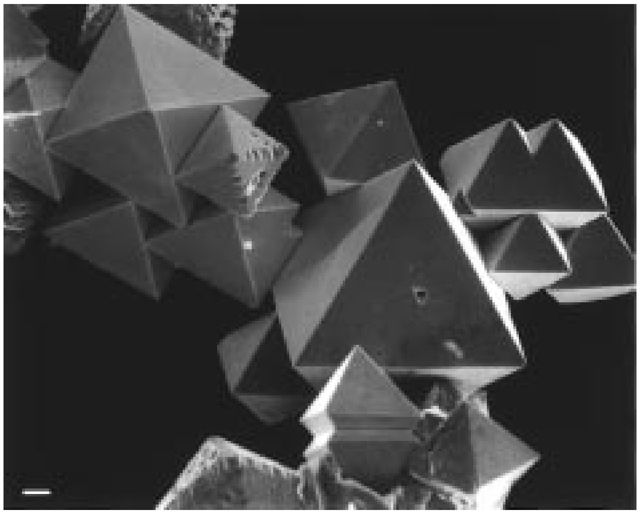

Figure 8. Scanning electron micrograph of AgBr as obtained from DMSO/9% poly(vinyl chloride) in a U-tube (liquid/gel/liquid) configuration with 18-crown-6. Bar = 10 μm.

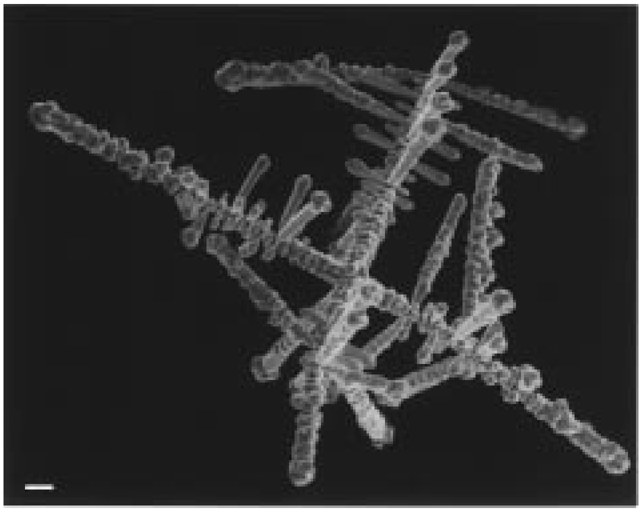

Figure 9. Scanning electron micrograph of AgBr as obtained from DMSO/9% poly(vinyl chloride) in a two-phase (gel/liquid) configuration. Bar = 10 μm.

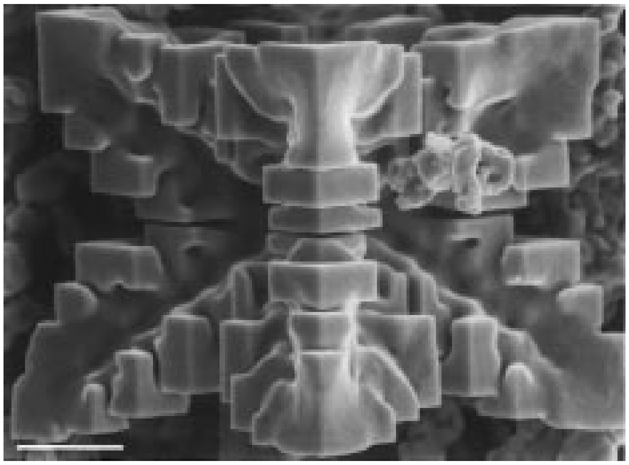

Figure 10. Scanning electron micrograph of AgBr as obtained from DMSO/9% poly(vinyl chloride) with 18-crown-6 in a two-phase (gel/liquid) configuration. Bar = 10 μm.

Crystallization of silver bromide from nonaqueous solvents has also been explored.[86] The solubility of both silver nitrate and alkali metal bromides in polar aprotic solvents such as *N*,*N*-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) permitted analysis of the effects of solvent on crystal morphology even in the absence of chelating agents, with cubic AgBr formed from DMF solution and octahedral AgBr from DMSO solution. This system permitted the analysis of several factors pertaining to the use of nonaqueous gels for the reaction crystallization of solid-state phases, opening the door for wide-scale recruitment of the powerful technique of gel growth to nonaqueous preparations. Both the identity and the concentration of the gel have pronounced impacts on the morphology of the crystalline silver bromide obtained. Gels affording additional chelation sites [poly(methyl methacrylate) vs poly(vinyl chloride)] and higher gel concentrations led to larger and more perfect crystals (Figure 8), apparently by slowing the rate of nucleation relative to the growth rate, while lower concentrations of nonchelating gels afforded oriented intergrowths of octahedral crystals (Figure 9). Introduction of 18-crown-6 further reduced the nucleation rate, leading to the development of quite large crystals displaying very unusual growth features (Figure 10).

Complexation-mediated reaction crystallization of metal sulfides can be problematic, in that many simple salt precursors (e.g., Na_2S) are sparingly soluble in most organic solvents even in the presence of an excess of a crown ether. However, several modifications of the technique have been successfully applied even for such sparingly soluble salts. Introduction of aqueous sodium sulfide to an organic solution of mercuric chloride containing dibenzo-18-crown-6 afforded both β-HgS (metacinnabar) and α-HgS (cinnabar), the latter in the form of complex twinned crystals up to several millimeters in diameter.[59] Alternatively, simply stirring the solid reactant salts as a suspension in an anhydrous organic solvent containing dibenzo-18-crown-6 can also afford crystalline products, with the crown ether essentially serving a catalytic role.[87] In the most dramatic example, cubic-phase lead sulfide (galena) was obtained in nicely crystalline form from tetrahydrofuran (Figure 11), whereas precipitation from water or other organic

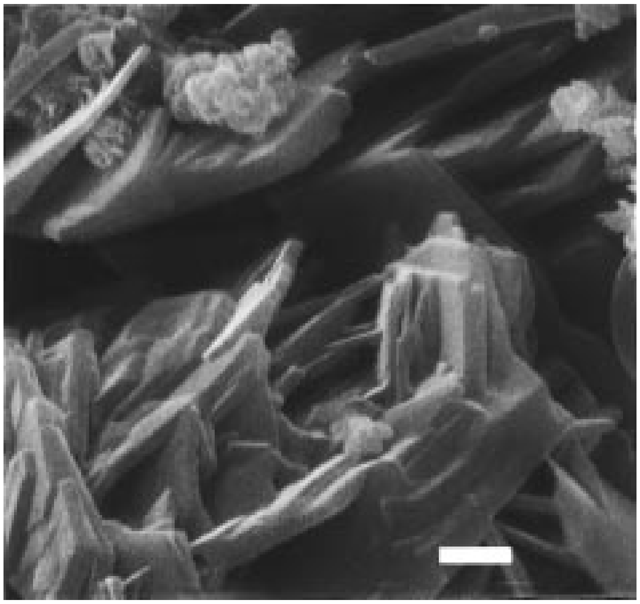

Figure 11. Scanning electron micrograph of PbS as obtained from anhydrous tetrahydrofuran/dibenzo-18-crown-6 under catalytic solubilization conditions. Bar = 1 μm.

solvents under similar conditions afforded largely amorphous material.

As in the case of the simple complexation-mediated recrystallization of ammonium nitrate and potassium tartrate noted above, complexes rather than simple inorganic phases are occasionally obtained. Given the ongoing global attention macrocyclic complexation phenomena are receiving, the structural analysis of such complexes is generally quite rewarding. Two zinc complexes of 18-crown-6 were obtained in the course of studies of the complexation-mediated crystallization of zinc sulfide, one containing a zinc ion directly coordinated to the crown ether, the other displaying supramolecular complexation of hexaaquo zinc(II) via hydrogen bonding to the crown ether.[88] Similar coordination modes appear to exist for yttrium(III).[89] Lead(II) acetate forms a sparingly soluble complex with dibenzo-18-crown-6 in which the lead ion, bearing two bidentate acetate groups and coordinated to each of the crown ether oxygens, displays a coordination number of 10.[87,89]

Clearly, dramatic alteration of both crystal morphology and crystal phase is accessible through the use of complexation-mediated crystallization. Consideration of crystal packing and selective solvent and/or chelating agent interactions with specific crystal faces affords a plausible level of understanding of the observed effects, particularly for the complexation-mediated recrystallization of salts of organic compounds, but a more quantitative understanding of these interactions is required in order to develop predictive capability. Initial calculational studies[86] of the interaction of single solvent molecules with the (100) and (111) surfaces of silver bromide were suggestive, showing DMF to display a relatively higher preference for binding to the (100) surface than does DMSO, which strongly favors binding to the (111) surface. In addition, the geometries of interaction of these solvents with both the (100) and the (111) surface are consistent with those qualitatively anticipated on simple electrostatic grounds (e.g., Figure 12), suggesting that chemical intuition can provide helpful insights even in these more complex reaction crystallizations. Additional calculational analyses, complemented by appropriate experimental studies, are clearly warranted.

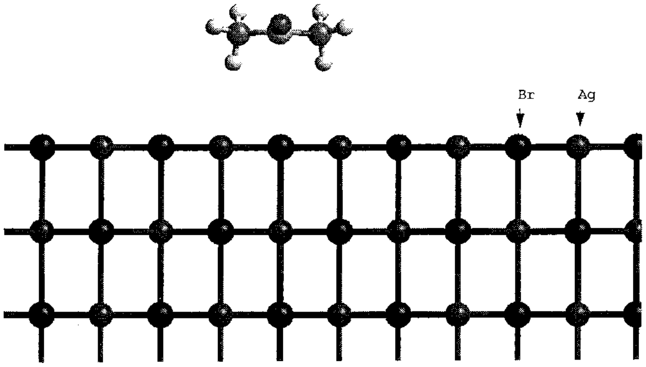

Figure 12. Calculated optimum geometry for interaction of DMSO with the (100) surface of AgBr. Note the orientation of the dipole parallel to the surface, allowing interaction with both silver and bromide ions.

Summary

A variety of compounds which are at best sparingly soluble in aqueous media may be readily brought into solution through the formation of soluble coordination complexes. Modification of experimental conditions through, e.g., dilution or slow removal of the complexing agent, leads to supersaturation and, consequently, crystallization of the original solid-state phase. This technique of decomplexation crystallization, both of simple inorganic coordination complexes (e.g., AgI_2^-) and of complexes with macrocyclic organic chelating agents (e.g., sodium acetate/15-crown-5), offers the opportunity to effect the recrystallization of sparingly soluble species and to modify their crystal morphology. Similarly, precursors for solid-state materials may be solubilized in nonaqueous solvents through the formation of soluble complexes and then allowed to undergo reaction crystallization, allowing the examination of both solvent effects and chelation effects on the morphology and phase of the resulting solid-state materials. These effects are often dramatic, and such "complexation-mediated crystallization" approaches offer promise for the facile preparation of metastable phases from simple precursors under ambient conditions.

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