

## Crystallization of Solid-State Materials in Nonaqueous Gels. 1. Silver Bromide

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An extraordinary range of physical and chemical properties of materials are dictated to a large extent by crystal form and size, and a remarkable array of techniques have been developed to permit the controlled crystallization of materials in order to alter these properties. A particularly powerful approach involves the diffusion of a reacting solution into an aqueous gel matrix containing a second reactant.<sup>1</sup> The relatively slow diffusion afforded by this gel matrix favors crystal growth over nucleation, often resulting in often large and rather perfect crystals. This approach, in use for over 100 years, has to our knowledge virtually always been carried out using aqueous solutions and gels.<sup>2</sup> In this manuscript, we report a new approach to the preparation of solid-state materials, typified by silver bromide, through analogous "reaction crystallization"<sup>3</sup> in *nonaqueous* aprotic solvent gels. Through use of organic solvent-swollen polymers in place of the aqueous silica or agar gels typically used as the gel phase in aqueous gel crystallizations, we have recruited this simple yet powerful crystallization technique to the nonaqueous milieu, thereby allowing the exploration of solvent and organic additive effects on crystal form and offering the opportunity for designed "adjustment" of crystal form in order to optimize desired solid-state properties.

Alteration of the crystallization solvent in the recrystallization of organic compounds often results in dramatic changes in crystal morphology.<sup>4</sup> We have focused our attention on the crystallization of *inorganic* materials from nonaqueous solvents in order to attempt to exploit such solvent effects for the deliberate modification of their crystal form.<sup>5</sup> Although a growing body of research into the use of soluble metal-organic species to effect such materials syntheses from nonaqueous solvents is developing,<sup>6,7</sup> we focus on the use of simple salt precursors, eliminating the need to synthesize and handle the requisite unstable and often costly and hazardous metal-organic precursors. The silver halides,

for which crystal form so clearly dictates materials properties,<sup>8,9</sup> are prime candidates for such studies. Aqueous gel crystallization techniques have been examined,<sup>10,11</sup> but to our knowledge, no studies of the crystallization of the silver halides (or any other solid-state inorganic materials) in nonaqueous gels have been reported. Although solubility of suitable precursor salts in nonaqueous solvents would appear to present a serious barrier to such studies, it is easily circumvented either by using appropriate salt/solvent combinations or by exploiting the ability of crown ethers and related chelating agents to solubilize inorganic salts even in quite nonpolar media.<sup>5,12</sup>

Simple interdiffusion of dimethyl sulfoxide (DMSO) solutions of AgNO<sub>3</sub> and NaBr results in the rapid formation of microcrystalline aggregates of AgBr displaying no clear crystal form. However, diffusion of DMSO solutions of AgNO<sub>3</sub> and NaBr into a 9% (w/w) gel of poly(vinyl chloride) (PVC) in DMSO in a u-tube arrangement results in slow growth of comparatively large single crystals (ca. 30–50 μm edge length) of AgBr within the gel. In marked contrast to the cubic crystals obtained from aqueous silica gel crystallization,<sup>10</sup> a strong preference for octahedral crystal morphology is evident. X-ray powder diffraction analysis provides a close match with the well-known cubic phase of AgBr.<sup>13</sup> Analogous results are obtained when the chelating agent 1,4,7,10,13,16-hexaoxacyclooctahexadecane (18-crown-6) is added in equimolar amounts to either or both of the reacting salt solutions, with crystal perfection quite high under these growth conditions (Figure 1).

Given the slow growth of crystals in the u-tube configuration, we examined an alternative gel growth procedure in which a solution of one reactant salt diffuses into a polymer gel containing the second reactant salt. Crystal growth was appreciably more rapid, with macroscopic crystals appearing within several days (as opposed to several weeks in the u-tube experiments). In this configuration, using a 9% (w/w) gel of poly(vinyl chloride) in DMSO, the AgBr was produced in the form of oriented octahedral intergrowths (Figure 2), and this crystal morphology was qualitatively the same regardless of which reactant salt was incorporated in the gel. Clear directionality is observed in the crystallization, with initial one-dimensional formation of the oriented intergrowths (up to several mm in length) perpendicular to the gel/solvent interface visually apparent through the translucent gel. Dendritic branching is observed at longer diffusion times and greater distances from the interface. Use of a 7% poly(vinyl chloride) gel in place of the 9% gel affords a more highly dendritic morphology. Formation of the oriented intergrowth/dendritic morphology appears consistent with the higher degree of supersaturation expected under these growth conditions,<sup>14</sup> as opposed to the u-tube experiments, wherein both reacting salts diffuse slowly to "neutral ground" in the gel, maintaining comparatively low salt concentrations in the crystallization zone.

Addition of 18-crown-6 to the two-phase (gel/liquid) growth experiments has a pronounced impact on AgBr crystal form.

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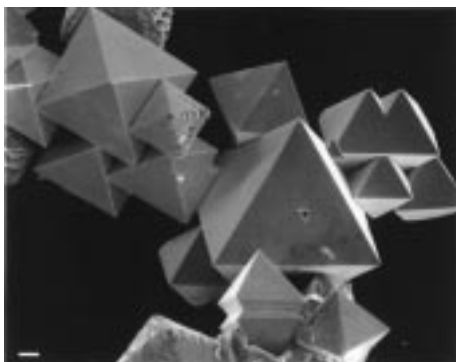
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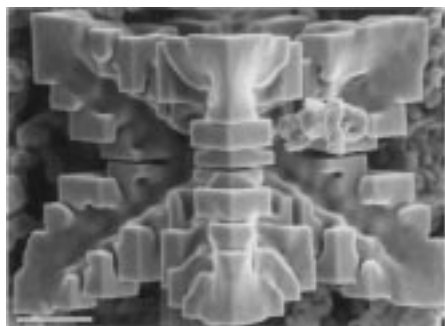
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**Figure 1.** AgBr crystallized from DMSO/9% PVC with 18-crown-6 in the u-tube configuration. Scale bar, 10  $\mu\text{m}$ .



**Figure 2.** AgBr crystallized from DMSO/9% PVC in the two-phase (gel/liquid) configuration. Scale bar, 10  $\mu\text{m}$ .

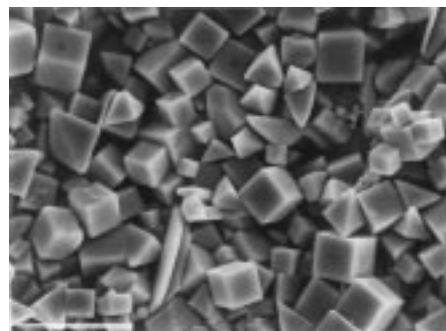


**Figure 3.** AgBr crystallized from DMSO/9% PVC with 18-crown-6 in the two-phase (gel/liquid) configuration. Amorphous material is residual PVC. Scale bar, 10  $\mu\text{m}$ .

Nucleation appears to be dramatically reduced in the presence of this chelating agent, resulting in continued growth of those nuclei which are formed. Thus, even in the 7% gel, crystallinity is appreciably enhanced, as shown by the development of well-faceted crystalline intergrowths, while in the 9% gel, both further growth and the generation of cube-based crystal forms is observed (Figure 3).

Equally dramatic variations of crystal morphology are observed when *N,N*-dimethylformamide (DMF) is used in place of DMSO.<sup>15</sup> In DMF, interestingly, crystal morphology is based upon cubic forms rather than the octahedral forms favored in DMSO (Figure 4). This dramatic change in crystal morphology, effected by a simple solvent change, is perhaps most simply rationalized on the basis of selective interaction of the (coordinating) solvents with surface ions, slowing the growth of specific lattice planes and thus resulting in the expression of these lattice planes in the final crystal form.<sup>16</sup> (Alternatively, it may be argued that

(15) As for DMSO, attempted crystallization of silver bromide from DMF without the use of a gel medium affords polycrystalline aggregates displaying no clear crystal form.



**Figure 4.** AgBr crystallized from DMF/18% PVC in the two-phase (gel/liquid) configuration. Scale bar, 10  $\mu\text{m}$ .

strong solvent interactions lead to surface roughening and increased growth rates for the faces in question.<sup>17</sup>)

Dynamics simulations and energy minimization<sup>18</sup> for the interaction of DMSO with the (111) surface of AgBr predict a significantly stronger interaction with this surface than with the (100) surface. In the minimized geometry for this interaction, the DMSO molecule is in close contact (ca. 3–4 Å) and orients its dipole roughly perpendicular to the surface, with oxygen directed toward silver-containing (111) layers and away from bromide-containing (111) layers, consistent with expectations based on electrostatic grounds. In contrast, DMSO interacts much less strongly and orients its dipole parallel to the (100) surface, with this alignment again consistent with qualitative electrostatic predictions in that it allows simultaneous interaction of the sulfoxide dipole with the alternating silver and bromide ions presented by this crystal surface. DMF also interacts more strongly with the (111) surface than the (100) surface, with similar dipole orientations to those seen for DMSO. Although the simplest possible explanations of habit alteration due to strong solvent interaction with specific crystal surfaces thus are apparently not sufficient to accommodate the experimental observations completely, it is to be noted that DMF displays less discrimination between the two surfaces than does DMSO, supportive of a greater likelihood for expression of (100) surfaces in DMF. Further studies of the interaction of solvents with these crystal surfaces, including the interesting dipole alignments and the issue of relative ability of DMSO and DMF to interfere with step propagation growth mechanisms, are in progress.

These results indicate that gel growth techniques for the crystallization of inorganic materials may be easily extended to the nonaqueous and aprotic milieu, allowing the exploitation of often powerful solvent effects for the alteration of crystal morphology. A number of variables (e.g., experimental apparatus, solvent, presence of chelating agents, type of gel agent, concentration of gel agent) present themselves. Each appears capable of exerting a demonstrable and often dramatic influence on crystal morphology, offering the potential to fine-tune crystal form to optimize desired solid-state properties.

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**Supporting Information Available:** A report of representative experimental procedures and calculational procedures and results for the analysis of solvent interactions with AgBr crystal surfaces (11 pages). See any current masthead page for ordering and Internet access instructions.

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(18) Full details and a sample simulation log file are provided as Supporting Information.