

# Communications

## Hydrothermal Dehydration of Precipitates: Convenient Synthesis Method for Solids

Benjamin L. Clark and Douglas A. Keszler\*

Department of Chemistry, Oregon State University, 153 Gilbert Hall, Corvallis, Oregon 97331-4003

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Among reactions in aqueous solutions, most chemists are generally introduced first to the precipitation reaction. In many cases, these reactions can be readily executed to produce simple anhydrous, crystalline solids with formulations ranging from  $\text{BaSO}_4$  to  $\text{PbI}_2$ . As such, precipitation can be considered to be a convenient, low-temperature synthesis method. Success in the production of an anhydrous, crystalline product, however, rests on the feeble acidities and basicities of the aqua ions involved in the reaction. If the values of the hydrolysis constants  $\text{p}K_a$  and  $\text{p}K_b$  of the aqua ions are sufficiently small or negative, extensive hydrolysis occurs, and the solid precipitates as a hydroxo species. Attempts to dehydrate such products at modest temperatures invariably lead to the production of undesirable, amorphous products. Of course, these products can subsequently be crystallized by heating at temperatures of a few to several hundred degrees above their dehydration points. To achieve truly low-temperature preparation of materials, a variety of procedures, including sol–gel techniques<sup>1</sup> and hydrothermal methods,<sup>2</sup> have been devised and adapted for the production of crystalline solids. Sol–gel and related techniques generally involve multiple steps, varying levels of complexity, and moderate to high reagent costs.

The production of an amorphous material in the drying process of a hydrated, hydroxo precipitate is associated with the kinetic stabilization that occurs in the absence of nucleation centers. After all, the thermodynamically favored products in these systems are generally the crystalline inorganic material and water. To prevent the formation of an amorphous product, the dehydration process should be done under conditions that provide an opportunity for nucleation and grain growth. As we describe here for the preparation of crystalline  $\text{Zn}_2\text{SiO}_4$  and  $\text{SnSiO}_3$ , this result can be achieved by conducting the dehydration under hydrothermal conditions at temperatures near 473 K and lower.

$\text{Zn}_2\text{SiO}_4$  is a common phosphor host, and its preparation by both low- and high-temperature methods has been extensively studied.<sup>3</sup> On mixing solutions of  $\text{ZnSO}_4(\text{aq})$  and  $\text{Na}_4\text{SiO}_4(\text{aq})$ ,<sup>4</sup> a precipitate forms.<sup>5</sup> Since  $\text{p}K_b$  for  $\text{SiO}_4^{4-}(\text{aq})$  is approximately  $-8$ ,

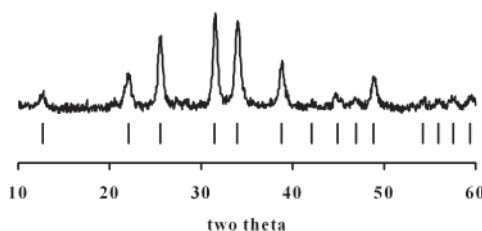


Figure 1. Powder X-ray pattern for  $\text{Zn}_2\text{SiO}_4$ . Ticks represent calculated peak positions.

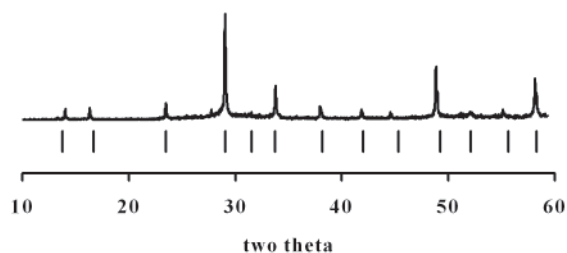


Figure 2. Powder X-ray diffraction pattern for  $\text{SnSiO}_3$ . Ticks represent previously reported peak positions.

the precipitate is a hydroxylated product, and dehydration of the material in air at 473 K leads to the production of an amorphous product. If the precipitate, however, is collected by filtration and placed in a Teflon-lined high-pressure reaction vessel at 473 K for a period of 12 h, a highly crystalline product is formed. In fact, on opening the reaction vessel beads of water are completely separated from the solid product. The sharpness of the lines in the X-ray diffraction pattern (Figure 1) of the material is consistent with the high crystallinity of the sample.<sup>6</sup>

Because  $\text{Zn}_2\text{SiO}_4$  may be prepared at low temperatures by a variety of methods, it does not represent a particularly rigorous test of the hydrothermal dehydration method. The preparation of  $\text{SnSiO}_3$  represents a better case study. The general solid-state chemistry of oxides containing  $\text{Sn}^{2+}$  is largely undeveloped, in part, because of the loss of  $\text{O}_2(\text{g})$  that occurs on heating  $\text{SnO}$ :



Here, a general low-temperature synthesis method could provide an attractive means for the development of a more extensive oxide chemistry of  $\text{Sn}^{2+}$ . In their original determination of the phase diagram, Slonimskii and Tseidler characterized the system  $\text{SnO}-\text{SiO}_2$  as a simple eutectic, i.e., no compound formation was

a Teflon-lined high-pressure reaction vessel (Parr Instruments) at 473 K for 12 h. The resulting product was a dehydrated, fine crystalline powder; approximately 1–2 mL of clear water was present in the Teflon container.

(6) The diffraction pattern of  $\text{Zn}_2\text{SiO}_4$  was obtained on a Philips diffractometer equipped with  $\text{Cu K}\alpha$  radiation.

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(4) The material commonly marketed as  $\text{Na}_4\text{SiO}_4$  is a mixture of  $\text{NaOH}$  and  $\text{Na}_2\text{SiO}_3$ .

(5)  $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$  (1.79 g) (Aldrich, 99.9%) and 0.92 g of  $\text{Na}_4\text{SiO}_4$  (Alfa-Aesar, reagent grade) were each dissolved separately in 20 mL of deionized  $\text{H}_2\text{O}(\text{l})$ . A precipitate forms on mixing these solutions; the resulting mixture was stirred and heated (338 K) for 30 min. The wet, white precipitate was collected by filtration and immediately placed in

detected.<sup>7</sup> Later, Carbó Nover and Williamson annealed the glass composition 1SnO:1SiO<sub>2</sub> and produced small crystalline spherulites embedded in the glass matrix that were determined by electron microprobe analysis to have the same composition as the glass, i.e., SnSiO<sub>3</sub>.<sup>6</sup> Clearly, heating mixtures of SnO and SiO<sub>2</sub> and annealing the aforementioned glass are not practical synthesis methods.

A precipitation reaction involving Sn<sup>2+</sup>(aq) and SiO<sub>4</sub><sup>4-</sup>(aq) would appear to offer a low-temperature route to the production of a crystalline product, but the small values of *pK* associated with these aqua ions result in the precipitation of a hydroxylated product. Attempts to dehydrate the precipitate under normal conditions lead to amorphous products. If the dehydration, however, is conducted under hydrothermal conditions, a well-crystallized product is obtained that exhibits diffraction peaks (Figure 2) consistent with those previously reported for SnSiO<sub>3</sub>.<sup>8,9</sup> Importantly, no reaction is observed by direct interaction of SnO and SiO<sub>2</sub> at various pH levels under the same hydrothermal conditions.

We have recently produced single crystals of the tin silicate by a low-temperature vapor transport method. The crystal structure

of this phase as well as some more general considerations and applications of the hydrothermal dehydration of precipitates to the production of powders, thin films,<sup>10</sup> and luminescent materials will appear in forthcoming contributions.

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- (8) CuSO<sub>4</sub>·5H<sub>2</sub>O (1.25 g) was dissolved in 20 mL of deionized water. N<sub>2</sub>(g) was bubbled through the solution, which was heated to 338 K; approximately 3 g of Sn powder (Aesar, 99.8%, 325 mesh) was added, and the mixture was stirred for 30 min. Na<sub>2</sub>SiO<sub>4</sub> (0.92 g) was dissolved in 20 mL of deionized H<sub>2</sub>O. The SnSO<sub>4</sub>(aq) solution was then filtered (removing the Cu metal) directly into the Na<sub>2</sub>SiO<sub>4</sub>(aq) solution, resulting in the formation of an off-white precipitate. The mixture was stirred for 30 min, and the wet solid was subsequently collected by filtration and placed in a Teflon-lined, high-pressure reaction vessel at 473 K for 12 h. The resulting product was a dehydrated, fine crystalline, green-yellow powder; approximately 1–2 mL of clear water was also present in the reaction container. The diffraction pattern of SnSiO<sub>3</sub> was obtained on a Siemens D-5000 diffractometer equipped with Cu K $\alpha$  radiation.
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