BRIEF COMMUNICATION

Soft-Chemistry Forms of $Sn_2P_2S_6$ and $CuInP_2S_6$

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We present our attempts to prepare lamellar SnP_2S_6 and $CuInP_2S_6$ by metathesis reactions in aqueous media. Use of a $SnCl_4$ precursor unexpectedly led to the formation of the three-dimensional compound $Sn_2^{II}P_2S_6$ rather than $Sn^{IV}P_2S_6$. The crystallites thus obtained were about 65 nm in size, i.e., much larger than those previously synthesized from $SnCl_2$. We correlate this with the smaller Sn/P ratio (< 1), which implies fewer nucleation sites and probably enhanced particle growth in the present case. The product tested positive for second-harmonic generation (SHG) at room temperature (RT). Initial ^{31}P NMR-MAS spectroscopy data indicate that this material is in an intermediate state between the ferroelectric and paraelectric phases of crystalline $Sn_2P_2S_6$. An analogous solution method readily yielded $CuInP_2S_6$, the first quaternary thiophosphate prepared via this soft-chemistry route. A rather small coherence length $\approx 27\text{Å}$, equivalent to four layers, is found for this product; band broadening is also observed in the Raman spectrum. SHG measurements likewise revealed a signal for this material at RT; a non polar macroscopic state may, however, not be precluded, given the known order-disorder nature of the ferroelectric–paraelectric transition in crystalline $CuInP_2S_6$. © 1998 **Academic Press**

Wet chemistry techniques have received much recent attention as an alternative route to preparing thin films suitable for electronic and optical applications (1). Within this context, there has been some renewed interest in the aqueous chemistry of $M_2P_2S_6$ phases ($M =$ divalent cation) (2). Indeed, dispersed coprecipitates of Mn^{II} with $(P_2S_6)^{4-}$ have been used to cast films of layered $Mn_2P_2S_6$ subsequently employed as intercalation hosts for nonlinear optical chromophores (3). Thin films of other thiophosphates would in themselves be worth synthesizing because of the technological potential indicated by their physical properties. Such is the case for $Sn_2^{II}P_2S_6$ (4), $Sn^{IV}P_2S_6$ (5), and $Cu^IIn^{III}P_2S_6$ (6), which all exhibit acentric structures and remarkable behaviors associated with polarity at room temperature (e.g., piezoelectricity, frequency doubling, and well-defined polarization reversal characteristics). The former has a three-

dimensional (3D) connectivity whereas the latter two are layered. In our effort to obtain new forms of these materials, we had previously prepared $Sn_2P_2S_6$ by reacting water solutions of $SnCl_2$ and $Li_4P_2S_6$ (7). Characterization of this soft-chemistry product brought to light possible relationships between structural anisotropy, growth kinetics, and particle dimension; also raised was the problem of determining the critical size for polar order in this compound. Here, we present our attempts to synthesize SnP_2S_6 and $CuInP_2S_6$ via analogous solution methods and the characterization of the products.

Mixing 0.1 M solutions of $SnCl_4$ and $Li_4P_2S_6$ with ratio $Sn/P = 1/2$ led to a brown suspension. The mixture was centrifuged, the water eliminated, and the product washed in ethanol and acetone. Upon filtering and removal of the solvent and soluble species, a yellow powder was obtained. The washing and filtration were repeated and the powder was dried under vacuum at 120°C. The product composition was checked using energy-dispersive spectroscopy (EDS): it was found to be $Sn_2P_2S_6$ rather than SnP_2S_6. Minority phases were not detected using this technique. A divalent oxidation state for tin was determined using ^{119}Sn Mössbauer spectroscopy, the isomeric shift having been refined to 3.91(4) mm/s relative to $CaSnO_3$ (Fig. 1a), which agrees with that for $Sn_2P_2S_6$ synthesized at high temperature (HT) (7). The Mössbauer spectrum also features a weak resonance at 0.62(4) mm/s consistent with the presence of an impurity containing Sn^{IV} in an oxygen environment.

X-ray diffraction (XRD) revealed a powder pattern corresponding to the known structure of $Sn_2P_2S_6$ with monoclinic cell parameters $a = 9.38(2)$ Å, $b = 7.4564(4)$ Å, $c = 6.53(2)$ Å, and $\beta = 91.2(3)°$. No evidence of the impurity was found. Importantly, the widths of the diffraction peaks for the present product are narrower than those for powders obtained using $SnCl_2$ precursors, although still broader than for the HT form (Fig. 2). The crystallite size estimated here from the Scherrer formula is 65 nm. Our previous work suggested that the critical size D_c for long-range polar order
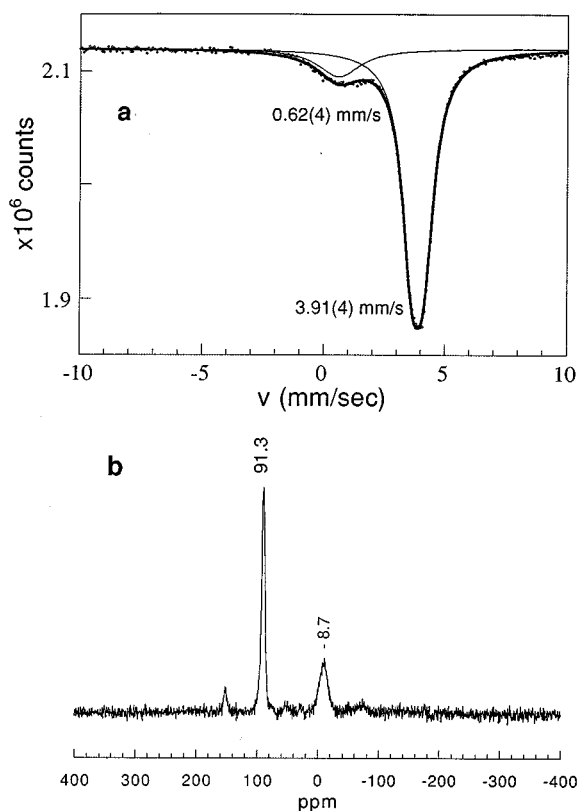
FIG. 1. (a) ^{119}Sn Mössbauer spectrum at 298 K for $Sn_2P_2S_6$ synthesized from $SnCl_4$; the resonances at 0.62 and 3.91 mm/s have Lorentzian line widths of 1.1(4) and 0.51(4) mm/s, respectively. (b) Corresponding ^{31}P NMR-MAS spectrum.

in $Sn_2P_2S_6$ is $20 < D_c < 76$ nm (7). The soft-chemistry form of $Sn_2P_2S_6$ prepared from $SnCl_4$ could then have some polar character. Indeed, a second-harmonic generation signal has been measured from this product at room temperature (RT), albeit over 10^2 weaker than found for the HT
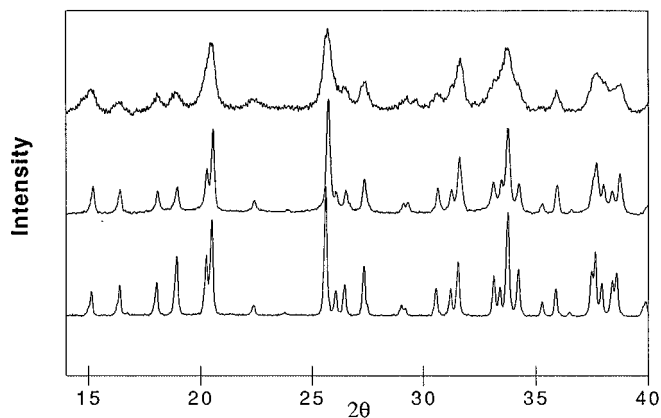
FIG. 2. XRD powder patterns (Cu$K\alpha_1$) at 298 K for $Sn_2P_2S_6$ synthesized by HT solid-state reaction (bottom) and by the solution method using $SnCl_4$ (middle) and $SnCl_2$ (top) precursors.

form. No transition for $150 < T < 390$ K could be detected from the present sample by differential scanning calorimetry (DSC). In the HT form, the second-order, displacive ferroelectric–paraelectric transition occurs around 333 K (4). The negative DSC result here may be due to an appreciable enthalpy decrease with particle size (8). Initial ^{31}P NMR-MAS spectroscopy data obtained at RT on our product (Fig. 1b) show a signal with chemical shift $\delta = 91.3(1)$ ppm, a value smaller than found for the HT form in the paraelectric phase and close to the average position of the two bands in the ferroelectric phase (9,10). Moreover, the peak in Fig. 1b is at least eight times broader than the signals from the HT form (10). This suggests that at RT the present soft-chemistry variant of $Sn_2P_2S_6$ is in an intermediate state between the ferroelectric and parelectric phases of the HT form: either it is in midtransition (10) or it exhibits a modulated phase (11). The NMR spectrum of Fig. 1b also contains a peak at $-8.7(1)$ ppm indicative of an impurity containing oxygen-coordinated phosphorus; this peak is broader than the main signal, implying a less crystalline second phase.

Given the minority signals in the spectra of Fig. 1, the impurity is conceivably SnP_2O_7. The reaction would then be

$$4SnCl_4 + 3Li_4P_2S_6 + 14H_2O \rightarrow Sn_2P_2S_6 + 2SnP_2O_7$$

$$+ 12LiCl + 12H_2S + 4HCl.$$
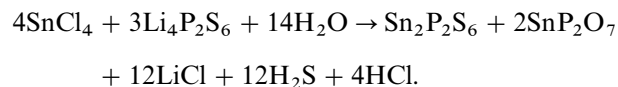
Tetravalent tin phosphate presumably forms more easily than $Sn^{IV}P_2S_6$ and facilitates the $Sn^{IV} \rightarrow Sn^{II}$ reduction that leads to $Sn_2P_2S_6$. The formation of lamellar SnP_2S_6 is probably hindered by slower kinetics for $(P_2S_6)^{4-}$ condensation around Sn^{IV} ions in a planar geometry. While the starting $Sn/P = 1/2$, the foregoing reaction involves $Sn/P = 2/3$. This is less than used in our previously reported synthesis (7) of $Sn_2P_2S_6$ from $SnCl_2$ ($Sn/P \geq 1$). More recent preparations using dichloride precursors and $Sn/P < 1$ show that products of smaller Sn/P mixtures exhibit narrower difffraction peaks, i.e., bigger particle sizes. A decreased Sn/P signifies fewer Sn^{II} seeds for condensation and this apparently favors particle growth. Last, the detection of the impurity as a minority rather than a majority phase as in the proposed reaction may be rationalized by assuming that SnP_2O_7 remains mostly dissolved.

To obtain $CuInP_2S_6$, 0.1 M solutions of $CuCl$, $InCl_3$, and $Li_4P_2S_6$ with ratio $Cu/P = In/P = 1/2$ were used. Following the procedure described earlier, a brownish yellow powder was isolated. Chemical analysis by EDS gave an almost perfect $CuInP_2S_6$ stoichiometry. To our knowledge, this is the first quaternary thiophosphate to be prepared by a solution method. The XRD pattern for this product is consistent with that for $CuInP_2S_6$ synthesized at HT but exhibits pronounced peak broadening (Fig. 3). Similar observations have been made for soft-chemistry forms of layered $Ni_2P_2S_6$
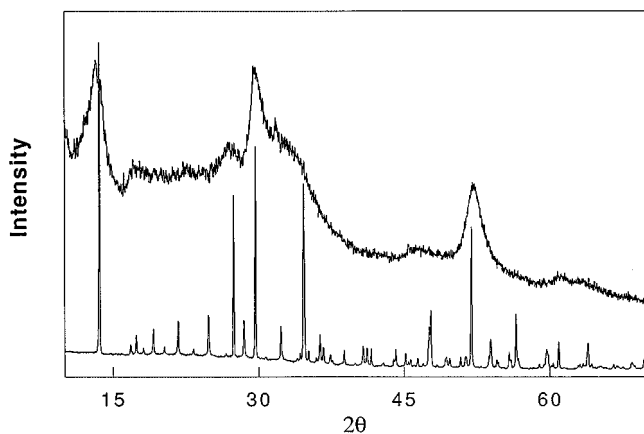
FIG. 3. XRD powder patterns ($CuK\alpha_1$) at 298 K for $CuInP_2S_6$ synthesized by HT solid-state reaction (bottom) and by the solution method (top).

(12) and $Mn_2P_2S_6$ (3). A full-pattern profile fit to the product's diffractogram led to monoclinic cell parameters close to those of the HT form (6): $a = 6.1(1)$ Å, $b = 10.5(1)$ Å, $c = 13.5(1)$ Å, and $\beta = 107(1)°$. Applying the Scherrer formula to the (002) and (060) peaks yields a coherence length of ≈ 27 Å in either direction. This implies $CuInP_2S_6$ crystallites that are non-platelike and much smaller than the corresponding $Sn_2P_2S_6$ particles. The size difference may be due to faster growth kinetics associated with low-symmetry, 3D arrangements in the latter (7). The inferred aspect ratio (≈ 1) reflects a limit to lateral layer dimensions attainable via the solution method. DSC scans on the present product detected no anomalies for $150 < T < 390$ K. On the other hand, a SHG signal was observed at RT although $\approx 10^3$ less intense than found for a crystal. Because the ferroelectric–paraelectric transition in $CuInP_2S_6$ is of the order–disorder type (i.e., the paraelectric phase is microscopically polar), the positive SHG test does not preclude a nonpolar macroscopic state. There is also some evidence that the transition temperature $T_c \approx 315$ K in $CuInP_2S_6$ (6) decreases with sample thickness normal to the layer (13). It would be of interest to determine if the $CuInP_2S_6$ particles prepared here can support long-range polar order because their thickness (≈ 4 layers) probably represents an experimental lower limit.

The Raman spectrum of the soft-chemistry product $CuInP_2S_6$ closely resembles that of the HT form (Fig. 4). The $(P_2S_6)^{4-}$ libration, deformation, and stretching modes are clearly present in the 90–120, 140–340, and 360–600 cm^{-1} ranges, respectively. The lower wavenumber bands at 30 and 62 cm^{-1} are consistent with Cu^I and In^{III} oscillations observed for the HT variant, implying similar cation environments in the two forms. The band broadening is reminiscent of that in the spectrum for crystalline $CuInP_2S_6$ in the paraelectric phase (14).

To complete the characterization, we are currently carrying out T-dependent NMR-MAS, vibrational spectroscopy, SHG, and EXAFS measurements on the soft-chemistry forms of $Sn_2P_2S_6$ and $CuInP_2S_6$. Doing so should reveal the degree of polar order in these materials at various temperatures. We shall also be casting or spray painting thin films from dispersions of these products. Physical measurements shall be performed on these with the ultimate goal of optimizing the synthesis to obtain technologically useful films.
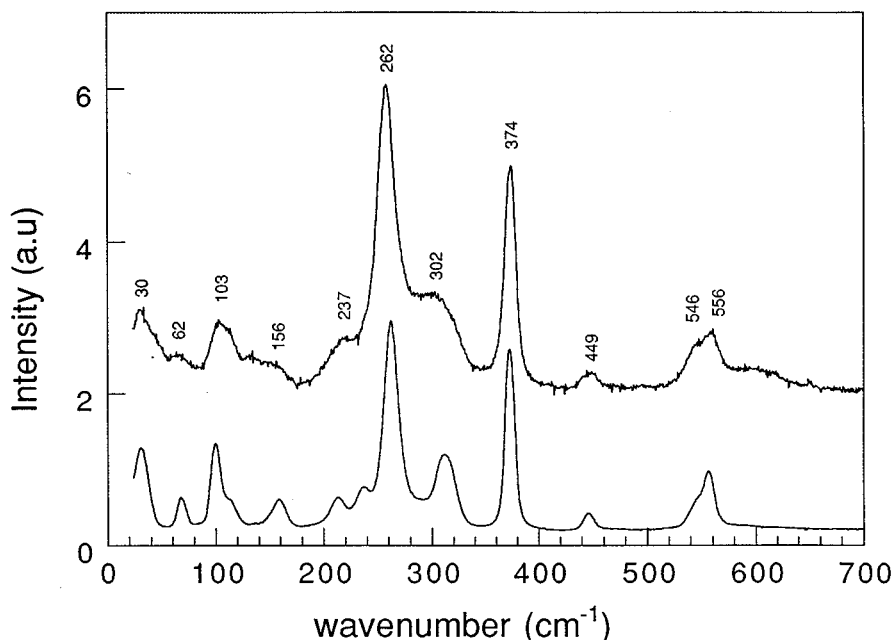

FIG. 4. Raman spectra at 298 K for the HT (bottom) and soft-chemistry (top) form of $CuInP_2S_6$.

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