

BRIEF COMMUNICATION

Room-Temperature Synthesis of $\text{Sn}_2\text{P}_2\text{S}_6$

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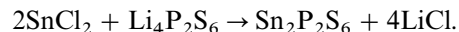
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Twenty-nanometer particles of $\text{Sn}_2\text{P}_2\text{S}_6$ are prepared at room temperature (RT) via a metathesis reaction in aqueous media. Mössbauer and Raman spectroscopy and X-ray diffraction characterization of these powders accord with data on $\text{Sn}_2\text{P}_2\text{S}_6$ synthesized at high temperature (HT). The phase transition and second harmonic generation known to exist in the HT form were not detected in the RT variant, suggesting a critical particle size >20 nm for the occurrence of polar order in $\text{Sn}_2\text{P}_2\text{S}_6$. It is argued that thermal enhancement of the metathesis reaction and growth kinetics should lead to larger, ferroelectric $\text{Sn}_2\text{P}_2\text{S}_6$ crystal-lites. © 1997 Academic Press

Recent years have seen a growing interest in synthesis methods yielding technologically desirable forms of ferroelectric materials. For example, fine homogeneous powders of BaTiO_3 have been prepared hydrothermally (1) and polymer-perovskite composites have been produced by various researchers (2, 3). Relative newcomers to the field of ferroelectrics are the tin thiophosphates $\text{Sn}_2\text{P}_2\text{S}_6$ and SnP_2S_6 , both of which are normally synthesized via high-temperature solid state reactions. The former has a monoclinic three-dimensional (3D) structure and exhibits a second-order ferroelectric–paraelectric transition around 333 K (4) ascribable to T -dependent displacements of the Sn^{II} ions (5). The latter is lamellar and crystallizes within the polar space group $R3$ (6), implying the existence of a spontaneous polarization due to a slight off-centering of the Sn^{IV} ions. Second-harmonic generation (SHG) has been demonstrated in both $\text{Sn}_2\text{P}_2\text{S}_6$ and SnP_2S_6 (7). $\text{Sn}_2\text{P}_2\text{S}_6$, however, remains the more promising compound given its large pyroelectric coefficient and bulk piezo-modulus (8). We thus deemed it worthwhile to prepare $\text{Sn}_2\text{P}_2\text{S}_6$ powders via a soft

chemistry route that may have processing advantages over high temperature methods.

$\text{Sn}_2\text{P}_2\text{S}_6$ may be synthesized at room temperature by a procedure analogous to that developed for amorphous $\text{Ni}_2\text{P}_2\text{S}_6$ (9). The method is based on a metathesis mechanism in aqueous media between the M^{II} metal cations and $(\text{P}_2\text{S}_6)^{-\text{IV}}$ anions. In this work, the cations were furnished by SnCl_2 and the anions by $\text{Li}_4\text{P}_2\text{S}_6$, each salt being used in the form of a 0.1 M water solution. Gradual pouring of the SnCl_2 solution into that of $\text{Li}_4\text{P}_2\text{S}_6$ resulted in a brown gel following a reaction that may be described as



Twice as much SnCl_2 than required by stoichiometry ($\text{Sn}/\text{P} = 2$) was employed in most preparations to favor the reaction of all available $(\text{P}_2\text{S}_6)^{-\text{IV}}$. A few syntheses with Sn/P close to unity were also carried out. Water was eliminated from the gel using a rotary evaporator and the product was subsequently washed in acetone or alcohol. Upon filtration, the solvent and LiCl were removed and a dark brown powder was obtained. The washing and filtration were repeated two to three times to pull out residual water and salt. Finally, the $\text{Sn}_2\text{P}_2\text{S}_6$ powder was dried under vacuum at 120°C.

Scanning electron microscopy showed the various samples to consist of submicrometer particles and 1 to >100 μm aggregates of such. Chemical analysis of representative sections via energy-dispersive spectroscopy (EDS) gave the expected $\text{Sn}_2\text{P}_2\text{S}_6$ formula. SnS_2 and SnP_2S_6 were detected in products prepared with $\text{Sn}/\text{P} \approx 1$. All samples contained 2–3% remnants of Cl ; these were not observed during the other measurements described below.

The oxidation state of tin in our products was determined using ^{119}Sn Mössbauer spectroscopy. Figure 1a displays the Mössbauer resonance for Sn^{II} measured at 298 K from a sample of $\text{Sn}_2\text{P}_2\text{S}_6$ synthesized at room temperature (RT) with $\text{Sn}/\text{P} = 2$. The isomer shift (δ) was refined to 3.91(5) mm/sec relative to CaSnO_3 , and the Lorentzian

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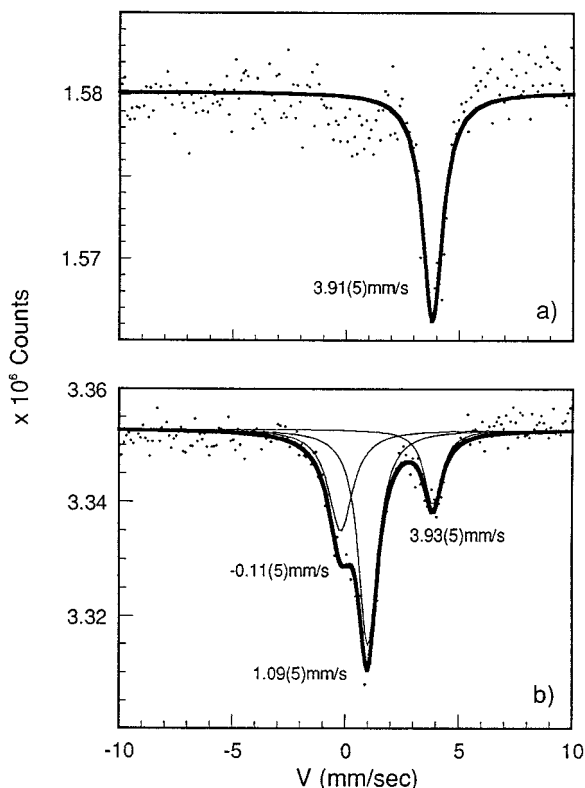


FIG. 1. ^{119}Sn Mössbauer spectrum measured at 298 K for a sample of $\text{Sn}_2\text{P}_2\text{S}_6$ synthesized in solution with (a) $\text{Sn}/\text{P} = 2$ (Sn^{II} resonance at 3.91(5) mm/sec) and, (b) $\text{Sn}/\text{P} \approx 1$ (Sn^{IV} resonance at 1.09(5) and $-0.11(5)$ mm/sec in addition to Sn^{II} signal). Note that because the recoil-free fraction for Sn^{IV} is much larger than for Sn^{II} at 298 K, an inordinately strong Sn^{IV} resonance is observed from the $\text{SnS}_2/\text{SnO}_2$ and SnP_2S_6 impurities.

line-width (Γ) was refined to 0.54(5) mm/sec. These values accord with those obtained from $\text{Sn}_2\text{P}_2\text{S}_6$ synthesized at high temperature (HT): $\delta = 3.96(5)$ mm/sec and $\Gamma = 0.50(5)$ mm/sec. For $\text{Sn}/\text{P} \approx 1$ RT preparations, a resonance for Sn^{IV} in a sulfur environment also appears ($\delta = 1.09(5)$ mm/sec and $\Gamma = 0.59(5)$ mm/sec; see Fig. 1b), in agreement with the EDS evidence for SnS_2 and SnP_2S_6 . This suggests that some $(\text{P}_2\text{S}_6)^{-\text{IV}}$ dissociation and Sn^{II} to Sn^{IV} oxidation occurs in the absence of a large SnCl_2 excess. The absorption at $-0.11(5)$ mm/sec indicates that the Sn^{IV} partly exists as SnO_2 , probably on the surface of SnS_2 particles (10).

The integrity of the $(\text{P}_2\text{S}_6)^{-\text{IV}}$ anions in the soft chemistry products was also checked by Raman spectroscopy. Bands were systematically observed at 187, 244, 277, 380, 556, and 579 cm^{-1} which can be assigned to known vibrational modes of $(\text{P}_2\text{S}_6)^{-\text{IV}}$ (11).

Diffraction studies were performed on selected samples. Figure 2a shows X-ray powder diffractograms for the RT and HT forms of $\text{Sn}_2\text{P}_2\text{S}_6$. The two patterns match and give

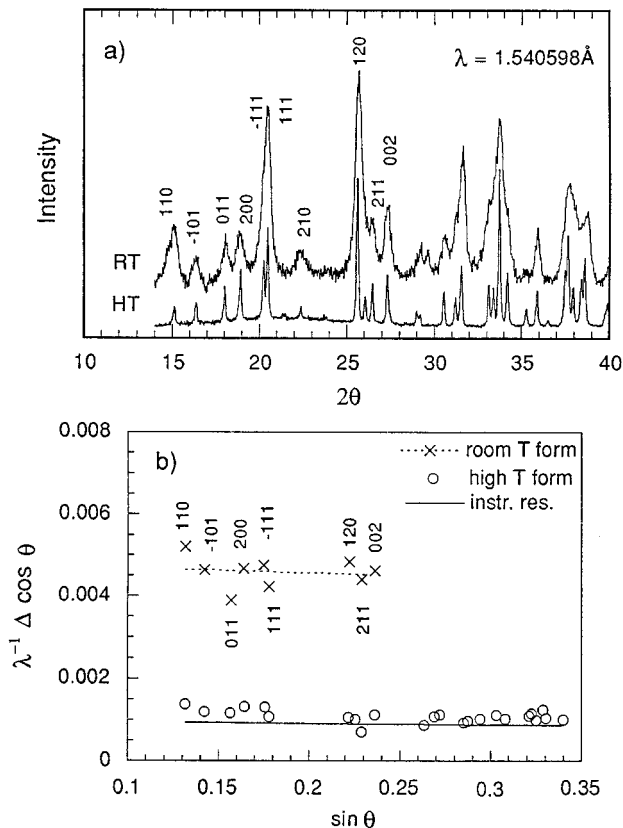


FIG. 2. (a) X-ray powder diffraction patterns for $\text{Sn}_2\text{P}_2\text{S}_6$ prepared at room temperature in solution (RT, top) and $\text{Sn}_2\text{P}_2\text{S}_6$ synthesized at high temperature (HT, bottom). (b) Williamson-Hall plots for lower order reflections from Fig. 2a diffractograms. The solid line represents the instrumental resolution; the dotted curve through the upper data points is a guide for the eye.

consistent cell parameters: $a = 9.37(7)$ Å, $b = 7.450(1)$ Å, $c = 6.51(5)$ Å, $\beta = 91(1)^\circ$ for the first, and, $a = 9.37(1)$ Å, $b = 7.4822(2)$ Å, $c = 6.522(9)$ Å, and $\beta = 91.1(2)^\circ$ for the second. Peak broadening is more visible in the first but occurs in both diagrams. To evaluate its origin, Williamson-Hall plots may be generated following the expression

$$\Delta \cos \theta = \lambda D^{-1} + k\varepsilon \sin \theta,$$

where Δ is the full-width at half-maximum corrected for instrumental resolution, λ is the wavelength, D is the particle size, k is a constant, and ε the elastic strain (12). Figure 2b displays the plots for lower-order reflections from the diagrams of Fig. 2a. The curve for the HT form is essentially flat, implying the absence of strain and anisotropic (hkl -dependent) effects in the crystallites; D is found to be 76 nm which is slightly smaller than the resolution limit (≈ 100 nm) (13). For the RT form, fewer points could be plotted because significant overlap of the higher-order peaks precluded a reliable modeling of their widths.

Figure 2b, however, makes it evident that peak broadening in this case is nearly isotropic and likewise dominated by the particle size which was calculated to be 20 nm.

The above establishes that the soft chemistry product is monoclinic $\text{Sn}_2\text{P}_2\text{S}_6$. A question remains as to whether or not this material is ferroelectric. Differential scanning calorimetry measurements revealed the 333 K ferroelectric–paraelectric transition in the HT but not in the RT samples. Moreover, tests for SHG at 298 K in a RT (HT) sample proved negative (positive). This may be because the particle size accessible via soft chemistry is smaller than required to sustain long-range polar order. For BaTiO_3 , a critical size $D_c = 44$ nm has been predicted by mean-field theory: below this, the length scale of surface disorder becomes comparable with the distance over which polarization fluctuations are correlated so that bulk ferroelectricity is eventually suppressed (14). Our results suggest that $20 < D_c < 76$ nm for $\text{Sn}_2\text{P}_2\text{S}_6$.

Crystallites of $\text{Sn}_2\text{P}_2\text{S}_6$ synthesized at RT are in fact almost an order of magnitude larger than those of similarly prepared $\text{Ni}_2\text{P}_2\text{S}_6$ ($2.5 \times 2.5 \times 4$ nm) (15). A possible explanation would be that the kinetics of $(\text{P}_2\text{S}_6)^{-IV}$ condensation around Ni^{II} ions are slower due to geometric constraints imposed by the octahedral Ni^{II} coordination and the layered $\text{Ni}_2\text{P}_2\text{S}_6$ morphology (9b). $\text{Sn}_2\text{P}_2\text{S}_6$ particles perhaps nucleate and grow more rapidly because higher probabilities are associated with the low-symmetry arrangement of $(\text{P}_2\text{S}_6)^{-IV}$ anions around the Sn^{II} and the 3D interlinking of SnS_8 polyhedra. It is conceivable that $\text{Sn}_2\text{P}_2\text{S}_6$ crystallites large enough to be ferroelectric can be grown with thermal enhancement of the kinetics. Indeed, we find that annealing the RT form of $\text{Sn}_2\text{P}_2\text{S}_6$ for 2 days at 300°C in an evacuated sealed tube yields 37 nm particles. The metathesis route therefore appears to be a reasonable approach to obtaining fine powders of ferroelectric $\text{Sn}_2\text{P}_2\text{S}_6$. We are thus currently studying the optimal reaction and annealing parameters as well as performing hydrothermal variations of the synthesis. Extension of this work to the preparation of SnP_2S_6 should also be straightforward.

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