

## Phase Transitions and Second-Harmonic Generation in Sodium Monothiophosphate

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Oxythiophosphate compounds, which contain anions comprised of oxidized phosphorus bound to oxygen and sulfur, are scarce and, in general, poorly characterized. Although  $\alpha$ - $\text{Na}_3\text{PO}_3\text{S}$  has been known for over 60 years, little has been revealed about this compound. Here we present thermal analysis and second-harmonic-generation (SHG) efficiency of  $\alpha$ - $\text{Na}_3\text{PO}_3\text{S}$ . Details about its transformation to the high-temperature  $\beta$  phase are discussed. Under vacuum,  $\alpha$ - $\text{Na}_3\text{PO}_3\text{S}$  undergoes one endothermic event at 553 °C upon heating and two exothermic events at 504 and 467 °C upon cooling.  $\beta$ - $\text{Na}_3\text{PO}_3\text{S}$  can be trapped upon quenching  $\text{Na}_3\text{PO}_3\text{S}$  from high temperature. We have observed that the  $\beta$  phase converts back to the  $\alpha$  phase at room temperature. Interestingly, relative humidity has been determined to catalyze this phase transformation.  $\alpha$ - $\text{Na}_3\text{PO}_3\text{S}$  oxidizes at 315 °C in air to produce  $\text{Na}_4\text{P}_2\text{O}_7$  and  $\text{Na}_2\text{SO}_4$ . Upon exposure to 1064-nm incident radiation, noncentrosymmetric  $\alpha$ - $\text{Na}_3\text{PO}_3\text{S}$  produces an SHG efficiency 200 times that of  $\alpha$ -quartz and is nonphase-matchable (type 1).

Metal oxythiophosphates<sup>1</sup> are compounds that contain metals bound to anions comprised of oxidized phosphorus bonded to oxygen and sulfur. There are few oxythiophosphates reported in the literature, with less than 30 compounds published, to date.<sup>2–6</sup> Considering the outstanding structural diversity and myriad of useful applications that exist for the related metal phosphates and thiophosphates, such as ion exchange,<sup>7</sup> catalysis,<sup>8</sup> batteries,<sup>9</sup> and nonlinear optics,<sup>10</sup> it is imperative to develop the almost nonexistent class of oxythiophosphates.

Although the crystal structure of  $\alpha$ - $\text{Na}_3\text{PO}_3\text{S}$  has been solved using neutron powder methods,<sup>11</sup> recent solid-state NMR experiments have introduced the possibility of disorder in this structure.<sup>12</sup> Although no direct structural information is offered in this paper, indirect evidence confirming the noncentrosymmetry of the structure (see Figure 1) is offered by the determination of the second-harmonic-generation (SHG) properties of the material. The thermal stability of the material in air as well as in vacuo is also presented.

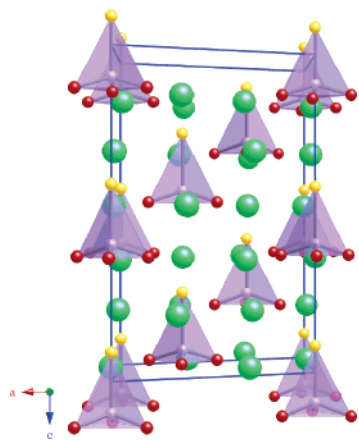
$\beta$ - $\text{Na}_3\text{PO}_3\text{S}$ , previously reported by Jansen et al., can be trapped by the quenching samples of  $\text{Na}_3\text{PO}_3\text{S}$  from high temperature.<sup>12</sup> We present the first report of a phase transition from the  $\beta$  phase back to the  $\alpha$  phase at room temperature. Interestingly, this transition is catalyzed by atmospheric water, even though neither form of the material is hydrated.

Phase transitions catalyzed by atmospheric water are well-known in the pharmaceutical literature.<sup>13</sup> These transitions most often involve conversions between anhydrous and hydrated states. A few transitions among anhydrous glasses and anhydrous crystalline states have also been reported. In these processes, adsorbed water acts as a plasticizing agent, which lowers the glass transition temperature, enhancing the molecular mobility to an extent that rapid recrystallization

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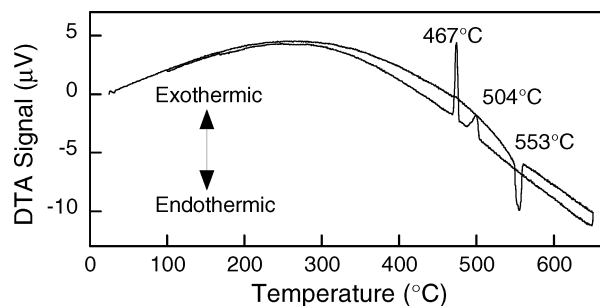
**Figure 1.** Structure of  $\alpha$ - $\text{Na}_3\text{PO}_3\text{S}$  viewed down the crystallographic  $b$  axis. It is easy to see that the structure is noncentrosymmetric because all of the tetrahedra point in the same direction along the  $c$  axis. Sodium atoms are green, phosphorus atoms are purple, oxygen atoms are red, and sulfur atoms are yellow.

occurs.<sup>13a,b</sup> This Communication represents the first report, to our knowledge, of a phase transition between two anhydrous inorganic, crystalline phases catalyzed by relative humidity (RH).

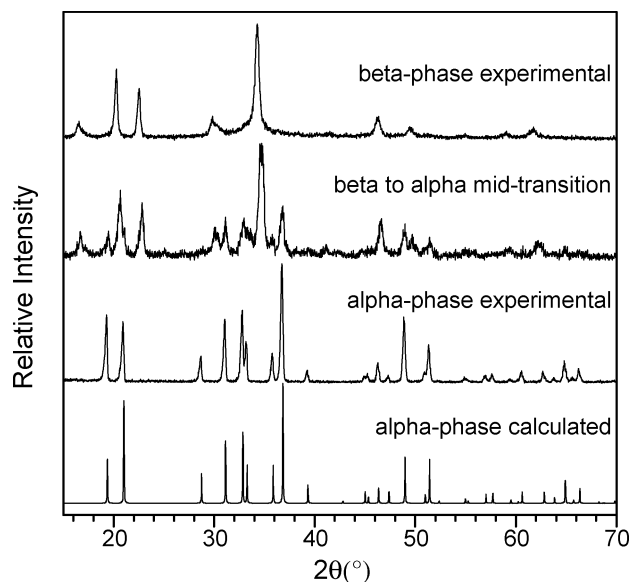
Initially, we planned to use  $\alpha$ - $\text{Na}_3\text{PO}_3\text{S}$  as a starting material to form new metal oxythiophosphates. We attempted to prepare  $\alpha$ - $\text{Na}_3\text{PO}_3\text{S}$  using solid-state reactions in which the reactants were combined in stoichiometric proportions and heated ( $\leq 800$  °C).<sup>14</sup> Although  $\alpha$ - $\text{Na}_3\text{PO}_3\text{S}$  formed, there were also impurities present as determined by powder X-ray diffraction (PXRD). Later, following the preparation method outlined by Yasuda and Lambert,<sup>15</sup> a pure, white microcrystalline material was obtained by a solution reaction to form the hydrate, which was subsequently dehydrated.

Differential thermal analysis (DTA) under vacuum revealed that  $\text{Na}_3\text{PO}_3\text{S}$  undergoes no irreversible structural changes from room temperature to 650 °C (see Figure 2). Three reversible thermal events were observed during the experiment: an endothermic event at 553 °C upon heating and two exothermic events at 504 and 467 °C upon cooling. PXRD of the DTA residue indicated the presence of  $\alpha$ - $\text{Na}_3\text{PO}_3\text{S}$ , as well as a minor amount of the  $\beta$  phase.

Jansen et al. have reported the endothermic event to be a melting point;<sup>11,16</sup> however, observation of the material at high temperature and observation of the morphology of the material after quenching would tend to disagree with this assessment. At temperatures greater than 553 °C, the sample appears as a sintered solid and has never been observed to take the shape of its container. The possibility that this endotherm may correspond to a transition to a  $\gamma$  phase cannot be excluded. It is clear to us that the two exotherms correspond to the crystallization of the  $\beta$  and  $\alpha$  phases, respectively, based on the following data. Quenching  $\text{Na}_3\text{PO}_3\text{S}$  in an ice–water bath from 490 °C demonstrated that the  $\beta$  phase exists between 504 and 467 °C. Slow cooling



**Figure 2.** DTA diagram obtained for  $\text{Na}_3\text{PO}_3\text{S}$  under vacuum.



**Figure 3.** PXRD patterns of  $\text{Na}_3\text{PO}_3\text{S}$ . The patterns containing the  $\beta$  phase were obtained relatively quickly in order to minimize exposure to ambient humidity and therefore appear noisier. The calculated PXRD pattern for the  $\alpha$  phase was obtained from data in ref 11.

of the sample ( $<10$  °C/min) yields only the  $\alpha$  phase. Quenches from temperatures between 600 and 650 °C did not reveal the presence of a  $\gamma$  phase by PXRD; only the  $\beta$  phase could be observed. This suggests that if there is a  $\gamma$  phase, it is highly unstable.

The first observation of a room-temperature phase transition from  $\beta$ - to  $\alpha$ - $\text{Na}_3\text{PO}_3\text{S}$  occurred serendipitously.  $\text{Na}_3\text{PO}_3\text{S}$  was quenched from 600 °C into ice water, ground, and a PXRD pattern of the trapped  $\beta$  phase was obtained (see Figure 3).<sup>17</sup> After the PXRD pattern was obtained, the sample was left on the countertop. The next morning slight changes in the sample color and granularity were observed; therefore, another PXRD pattern was obtained, revealing that the sample was now mostly  $\alpha$ - $\text{Na}_3\text{PO}_3\text{S}$  after only 16 h in ambient conditions. Subsequent experiments led to samples that converted from the  $\beta$  phase to the  $\alpha$  phase at various times scales, 16 h to 8 days (see Figure 3).

The realization that atmospheric water played a role in this transformation came to light because the phase transformation was observed to occur at especially high rates on days when it rained. This was later confirmed by producing

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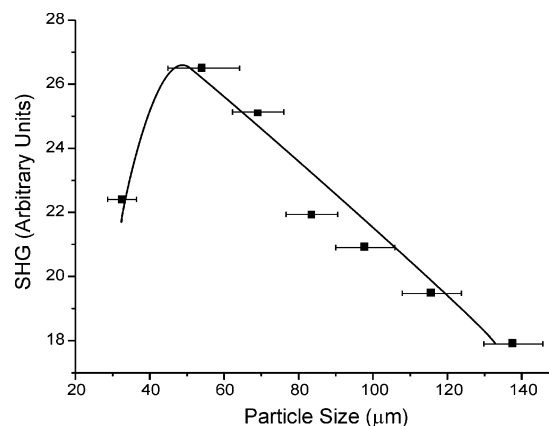
(17) Attempts to reproduce this quench were often met with difficulty. Usually the PXRD pattern of the product was observed to contain a small amount of the  $\alpha$  phase in addition to the  $\beta$  phase.

a sample of the  $\beta$  phase and dividing it into two aliquots, one that was stored in a desiccator and one that was exposed to ambient conditions.<sup>18</sup> The desiccated sample was observed to persist as the  $\beta$  phase for much longer than the sample exposed to ambient relative humidities. The cause of this transition is likely similar to anhydrous glass to anhydrous crystalline transitions found in the literature.<sup>13</sup> In these processes, a thermodynamically unfavorable phase is transformed to a more thermodynamically stable phase by the increased molecular mobility afforded by a small amount of adsorbed water.<sup>13a,b</sup>

A series of humidity-controlled chambers were prepared using saturated salt solutions in order to determine the rate of the phase transition as a function of relative humidity.<sup>19</sup> At a relative humidity of 6.6%, the  $\beta$  phase remained unaffected. The material never fully converted to the  $\alpha$  phase when stored under 33.1% RH. In the case of 54.5 and 69.9% RH, hydrated forms of the material formed so rapidly so as not to afford any observation of the  $\beta$ - to  $\alpha$ -phase transition, if indeed the conversion took place by this path ( $\beta \Rightarrow \alpha \Rightarrow \text{hydrate}$ ). The sample stored under 54.5% RH formed what we believe to be a hydrated form of sodium monothiophosphate, although its PXRD pattern could not be indexed to anything in the available literature. The PXRD pattern of the sample stored under 69.9% RH indexed to  $\text{Na}_3\text{PO}_3\cdot 12\text{H}_2\text{O}$ .<sup>20</sup> The current data suggest that there may be a minimum relative humidity necessary for the transition ( $33.1 < x < 54.5\%$  RH). Thus far, attempts to determine the rate of the phase transition as a function of the relative humidity have been qualitative. In situ diffraction studies under controlled humidity conditions will be forthcoming.<sup>21</sup>

Because the  $\alpha$  phase is relatively stable under normal laboratory conditions ( $\sim 40\%$  RH), further characterization of this material was possible. DTA and thermogravimetric analysis (TGA) of  $\alpha\text{-Na}_3\text{PO}_3\text{S}$  in air indicate that the material is stable up to  $\sim 315$  °C, when an exothermic oxidative decomposition to  $\text{Na}_4\text{P}_2\text{O}_7$ ,  $\text{Na}_2\text{SO}_4$ , and some volatile form of sulfur occurs. The decomposition is accompanied by a weight gain of 13.23%. The calculated weight gain is 13.31%. This result disagrees with the findings of Lambert and Yasuda, who observed decomposition at 120–125 °C.<sup>15</sup>

$\alpha\text{-Na}_3\text{PO}_3\text{S}$  crystallizes in a noncentrosymmetric space group,  $R3c$  (see Figure 1). The lack of an inversion center leads to a second-order, nonlinear optical (NLO) property known as second-harmonic generation (SHG).<sup>22</sup> SHG of a powdered sample of  $\alpha\text{-Na}_3\text{PO}_3\text{S}$  was measured using a modified Kurtz NLO system<sup>23</sup> with a Nd:YAG laser, as



**Figure 4.** Results of the  $\alpha\text{-Na}_3\text{PO}_3\text{S}$  phase-matching experiment. The line is superimposed to guide the eye and is not a fit to the data.

described elsewhere.<sup>24</sup> The incident light of 1064 nm was converted to 532 nm with an efficiency of  $\sim 200$  times that of  $\alpha$ -quartz. Because  $\alpha\text{-Na}_3\text{PO}_3\text{S}$  was SHG-active, a phase-matching experiment was performed in which the material was found to be nonphase-matchable (type 1). In a nonphase-matchable material, the SHG response goes to zero with an increase in the particle size.  $\langle d_{\text{eff}} \rangle$  is calculated to be 7.8 pm/V.<sup>24</sup>

Recently, oxythiophosphate materials have proven to be selective and recyclable in the remediation of toxic heavy-metal ions.<sup>5</sup> Also, the properties of oxythiophosphates, such as ionic conductivity, have been demonstrated to be tunable by varying the anionic composition.<sup>3b,11,25</sup>  $\text{Na}_3\text{PO}_3\text{S}$  presents us with another glimpse of the interesting physicochemical properties possible in oxythiophosphates. We have shown sodium monothiophosphate to be a remarkable phase-change material, as well as an SHG-active compound. This wide variety of properties supports the prediction that further work in this field is warranted and should lead to the discovery of new and interesting materials.

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**Supporting Information Available:** Additional synthetic details, elaborated experimental procedures, PXRD pattern after DTA in vacuo, PXRD patterns monitoring the room-temperature  $\beta$ - to  $\alpha$ -phase transition, PXRD pattern of sodium monothiophosphate stored under 69.9% RH, DTA and TGA diagrams obtained in air, and PXRD patterns obtained after thermal analysis in air. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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