Na₆Sn₃P₄S₁₆: Sn(II)-Chelated PS₄ groups inspired Ultra-strong SHG Response

Chenyao Zhao, Bingbing Zhang, Xinyu Tian, Guoqiang Zhou, Jingjing Xu, Kui Wu

College of Chemistry and Materials Science, Hebei University, Baoding, China

State Key Laboratory of Crystal Materials and Institute of Crystal Materials, Shandong University, Jinan, China

To whom correspondence should be addressed:

E-mail: wukui@sdu.edu.cn (Kui Wu); zhougq1982@163.com (Guoqiang Zhou); zhangbb@hbu.edu.cn (Bingbing Zhang)
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**Table S1.** Property comparison of the reported IR NLO thiophosphates with bandgaps (> 2.50 eV).

<table>
<thead>
<tr>
<th>No.</th>
<th>Compounds</th>
<th>$d_{ij}$($\times$AGS)</th>
<th>$E_g$(eV)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Na$_6$Sn$_3$P$<em>4$S$</em>{16}$</td>
<td>6.6</td>
<td>2.52</td>
<td>this work</td>
</tr>
<tr>
<td>2</td>
<td>AgHgPS$_4$</td>
<td>5</td>
<td>2.63</td>
<td>[1]</td>
</tr>
<tr>
<td>3</td>
<td>KHgPS$_4$</td>
<td>4.15</td>
<td>2.9</td>
<td>[2]</td>
</tr>
<tr>
<td>4</td>
<td>Hg$_3$P$_2$S$_8$</td>
<td>3.6</td>
<td>2.77</td>
<td>[3]</td>
</tr>
<tr>
<td>5</td>
<td>NaHgPS$_4$</td>
<td>3.14</td>
<td>2.78</td>
<td>[2]</td>
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<tr>
<td>6</td>
<td>CuZnPS$_4$</td>
<td>3</td>
<td>3</td>
<td>[4]</td>
</tr>
<tr>
<td>7</td>
<td>Zn$_3$P$_2$S$_8$</td>
<td>2.6</td>
<td>3.12</td>
<td>[5]</td>
</tr>
<tr>
<td>8</td>
<td>KSbP$_2$S$_6$</td>
<td>2.2</td>
<td>2.91</td>
<td>[6]</td>
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<tr>
<td>9</td>
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<td>2.1</td>
<td>4.11</td>
<td>[6]</td>
</tr>
<tr>
<td>10</td>
<td>AgZnPS$_4$</td>
<td>1.8</td>
<td>2.76</td>
<td>[7]</td>
</tr>
<tr>
<td>11</td>
<td>$\alpha$-Ba$_2$P$_2$S$_6$</td>
<td>1.7</td>
<td>4.31</td>
<td>[8]</td>
</tr>
<tr>
<td>12</td>
<td>K$_3$YP$_2$S$_8$</td>
<td>1.4</td>
<td>3.37</td>
<td>[9]</td>
</tr>
<tr>
<td>13</td>
<td>Pb$_2$P$_2$S$_6$</td>
<td>1.4</td>
<td>2.61</td>
<td>[8]</td>
</tr>
<tr>
<td>14</td>
<td>KAg$_2$PS$_4$</td>
<td>1.4</td>
<td>2.92</td>
<td>[10]</td>
</tr>
<tr>
<td>15</td>
<td>AgGa$_2$PS$_6$</td>
<td>1</td>
<td>2.75</td>
<td>[11]</td>
</tr>
<tr>
<td></td>
<td>Compound</td>
<td>a</td>
<td>c</td>
<td>Ref</td>
</tr>
<tr>
<td>-----</td>
<td>------------------</td>
<td>----</td>
<td>------</td>
<td>------</td>
</tr>
<tr>
<td>16</td>
<td>Eu₂P₂S₆</td>
<td>0.9</td>
<td>2.54</td>
<td>[12]</td>
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<tr>
<td>17</td>
<td>LiZnPS₄</td>
<td>0.8</td>
<td>3.38</td>
<td>[7]</td>
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<tr>
<td>18</td>
<td>LiCd₃PS₆</td>
<td>0.8</td>
<td>2.97</td>
<td>[13]</td>
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<tr>
<td>19</td>
<td>α-Ag₄P₂S₆</td>
<td>0.61</td>
<td>2.51</td>
<td>[14]</td>
</tr>
<tr>
<td>20</td>
<td>LiGa₂PS₆</td>
<td>0.5</td>
<td>3.15</td>
<td>[13]</td>
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<tr>
<td>21</td>
<td>AgCd₃(PS₄)S₂</td>
<td>0.45</td>
<td>2.56</td>
<td>[15]</td>
</tr>
<tr>
<td>22</td>
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<td>0.1</td>
<td>3.31</td>
<td>[16]</td>
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<tr>
<td>23</td>
<td>Cs₂Zn₃P₄S₁₃</td>
<td>0.1</td>
<td>3.29</td>
<td>[16]</td>
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</table>

**Table S2.** Crystal data and structure refinement for Na₆Sn₃P₄S₁₆.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>Na₆Sn₃P₄S₁₆</td>
</tr>
<tr>
<td>Formula weight</td>
<td>1130.85</td>
</tr>
<tr>
<td>Crystal system</td>
<td>trigonal</td>
</tr>
<tr>
<td>Space group</td>
<td>R₃m</td>
</tr>
<tr>
<td>Cell parameter a (Å)</td>
<td>19.304(4)</td>
</tr>
<tr>
<td>Cell parameter c (Å)</td>
<td>6.181(2)</td>
</tr>
<tr>
<td>Z, V (Å³) (Volume)</td>
<td>3, 1994.6(11)</td>
</tr>
<tr>
<td>Dₐ (g/cm³) (calculated density)</td>
<td>2.824</td>
</tr>
<tr>
<td>μ (mm⁻¹) (absorption coefficient)</td>
<td>4.388</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>0.998</td>
</tr>
<tr>
<td>R₁, wR₂ (I &gt; 2σ(I))</td>
<td>0.0427, 0.0629</td>
</tr>
<tr>
<td>R₁, wR₂ (all data)</td>
<td>0.0724, 0.0783</td>
</tr>
<tr>
<td>Absolute structure parameter</td>
<td>-0.03(6)</td>
</tr>
</tbody>
</table>

\[ R₁ = \frac{F_o - F_c}{F_o} \text{ and } wR₂ = \left[ \frac{w(F_o^2 - F_c^2)^2}{wF_o^4} \right]^{1/2} \text{ for } F_o^2 > 2\sigma(F_o^2) \]
Table S3. The coordination modes of Sn(II) in the known chalcogenide compounds.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Space group</th>
<th>Link modes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn₂Ga₂S₅</td>
<td>Pna₂₁</td>
<td>SnS₄</td>
</tr>
<tr>
<td>SnGa₄S₇</td>
<td>Pc</td>
<td>SnS₄</td>
</tr>
<tr>
<td>BaSnS₂</td>
<td>P-1</td>
<td>SnS₃</td>
</tr>
<tr>
<td>BaSn₂S₃</td>
<td>P-1</td>
<td>SnS₃</td>
</tr>
<tr>
<td>Ag₄SnGe₂S₇</td>
<td>Cc</td>
<td>SnS₃</td>
</tr>
<tr>
<td>Ag₇Sn(PS₄)₃</td>
<td>P2₁/c</td>
<td>SnS₃</td>
</tr>
<tr>
<td>KSnPS₄</td>
<td>P2₁/c</td>
<td>SnS₃</td>
</tr>
<tr>
<td>CsSnPS₄</td>
<td>P2₁/m</td>
<td>SnS₃</td>
</tr>
<tr>
<td>SnGa₂GeS₆</td>
<td>Fdd₂</td>
<td>SnS₅</td>
</tr>
<tr>
<td>LaSnGa₃S₇</td>
<td>P2₁/n</td>
<td>SnS₅</td>
</tr>
<tr>
<td>Sn₂SiS₄</td>
<td>P2₁/c</td>
<td>SnS₆</td>
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<tr>
<td>SnPS₃</td>
<td>Pn</td>
<td>SnS₈</td>
</tr>
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Table S4. Dipole moment calculation for Na₆Sn₃P₄S₁₆.

<table>
<thead>
<tr>
<th>Species</th>
<th>x(a)</th>
<th>y(b)</th>
<th>z(c)</th>
<th>Magnitude ×10⁴ esu·cm/Å³ Debye</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₆Sn₃P₄S₁₆</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaS₆</td>
<td>-1.89</td>
<td>1.88</td>
<td>11.48</td>
<td>11.79</td>
</tr>
<tr>
<td>SnS₄</td>
<td>-38.03</td>
<td>38.03</td>
<td>-123.76</td>
<td>134.94</td>
</tr>
<tr>
<td>P(1)S₄</td>
<td>38.51</td>
<td>-38.11</td>
<td>-5.38</td>
<td>54.45</td>
</tr>
<tr>
<td>P(2)S₄</td>
<td>57.26</td>
<td>-57.26</td>
<td>19.05</td>
<td>83.19</td>
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<tr>
<td>Unit Cell</td>
<td>55.85</td>
<td>-55.46</td>
<td>-98.61</td>
<td>284.37</td>
</tr>
</tbody>
</table>
2. Figures

**Figure S1.** The overall stacking arrangement of SnS$_4$ units in the unit cell in Na$_6$Sn$_3$P$_4$S$_{16}$.

**Figure S2.** DSC curve of Na$_6$Sn$_3$P$_4$S$_{16}$. 
Figure S3. Band structure and DOS diagram of Na$_6$Sn$_3$P$_4$S$_{16}$.

Figure S4. ELF map of Na$_6$Sn$_3$P$_4$S$_{16}$. 
Figure S5. Experimental SHG intensity of the Na$_6$Sn$_3$P$_4$S$_{16}$ and the standard AgGaS$_2$ at the particle size (200-250 μm).
3. References


