

**MS15-2-4 The crystal structures of Sn<sub>6</sub>TO<sub>8</sub> (T = Si or Ge): tin(II)-cluster containing zinc blende structural analogues**  
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**Abstract**

A cubic tin(II) silicate,  $\alpha$ -Sn<sub>6</sub>SiO<sub>8</sub>, and a cubic tin(II) germanate,  $\alpha$ -Sn<sub>6</sub>GeO<sub>8</sub>, have been synthesised by hydrothermal methods and the crystal structures of these materials have been elucidated by Rietveld refinement of synchrotron PXRD data.<sup>[1][2]</sup> The crystal structures are analogous to the zinc blende structure: comprising a face-centred cubic array of [Sn<sub>6</sub>O<sub>8</sub>]<sup>4-</sup> anionic clusters with Si<sup>4+</sup> or Ge<sup>4+</sup> cations occupying half of the tetrahedral holes, giving rise to a 3-dimensional framework of clusters joined by bridging orthosilicate or orthogermanate moieties. The crystal structure of the cubic tin(II) germanate is depicted in Figure 1.

Applying variable temperature PXRD studies to both the tin(II) silicate and tin(II) germanate have revealed thermal decomposition and oxidation to tin(IV) occurs at ca. 600°C and 675°C, respectively.<sup>[1][2]</sup> Thermal decomposition is observed at significantly higher temperatures than for tin(II) oxide,  $\alpha$ -SnO, which decomposes over the range 300 – 500°C,<sup>[3]</sup> demonstrating the superior stability of the framework structures of the silicate and germanate. Variable temperature PXRD has also revealed the formation of a tetragonal polymorph upon cooling the tin(II) silicate to 170 K. The crystal structure of the tetragonal tin(II) silicate polymorph,  $\gamma$ -Sn<sub>6</sub>SiO<sub>8</sub>, has also been elucidated by Rietveld refinement of synchrotron data. While a phase transition occurs upon cooling the tin(II) silicate, no such transition occurs upon cooling the tin(II) germanate and the cubic structure is instead retained at 100 K. By comparing the crystal structures of  $\alpha$ -Sn<sub>6</sub>SiO<sub>8</sub>,  $\gamma$ -Sn<sub>6</sub>SiO<sub>8</sub> and  $\alpha$ -Sn<sub>6</sub>GeO<sub>8</sub> (at both ambient temperature and 100 K), a structural argument based on strain is presented for why a transition occurs in the silicate system upon cooling but not in the germanate system. In this poster, the crystal structures of the cubic and tetragonal tin(II) silicate and the cubic tin(II) germanate are presented, along with structural explanations for the temperature behaviour of these materials.

**References**

<sup>[1]</sup> D. S. Parsons, S. N. Savva, W-C. Tang, A. Ingram and J. A. Hriljac, *Inorg. Chem.*, 2019, **58**, 16313 – 16316.

<sup>[2]</sup> D. S. Parsons, A. Nearchou and J. A. Hriljac, manuscript in preparation.

<sup>[3]</sup> M. S. Moreno, R. C. Mercader and A. G. Bibiloni, *J. Phys.: Condens. Matter*, 1992, **4**, 351 - 355.

The crystal structure of  $\alpha$ -Sn<sub>6</sub>GeO<sub>8</sub>.

