

## Thallium selenate (Tl<sub>2</sub>SeO<sub>4</sub>) in a paraelastic phase by X-ray powder diffraction

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The structure of thallium selenate, Tl<sub>2</sub>SeO<sub>4</sub>, in a paraelastic phase (above 661 K) has been analysed by Rietveld analysis of the X-ray powder diffraction pattern. Atomic parameters based on the isomorphous K<sub>2</sub>SO<sub>4</sub> crystal in the paraelastic phase were used as the starting model. The structure was determined in the hexagonal space group *P*6<sub>3</sub>/*mmc*, with *a* = 6.2916 (2) Å and *c* = 8.1964 (2) Å. From the Rietveld refinement it was found that two orientations are possible for the SeO<sub>4</sub> tetrahedra, in which one of their apices points randomly up and down with respect to [001]. One Tl atom lies at the origin with  $\bar{3}m$  symmetry, the other Tl and one of the O atoms occupy sites with *3m* symmetry, the Se atom is at a site with  $\bar{6}m2$  symmetry and the remaining O atom is at a site with *m* symmetry. Furthermore, it was also found that the Tl atoms display anomalously large positional disorder along [001] in the paraelastic phase.

### Comment

The *M*<sub>2</sub>*XO*<sub>4</sub>-type compounds (where *M* = K, Rb, Cs, NH<sub>4</sub> or Tl, and *X* = Se or S) exhibit interesting characteristics, such as ferroelectricity, ferroelasticity and structural incommensurate modulation (Matthias & Remeika, 1956; Aiki *et al.*, 1969; Aizu, 1974; Iizumi *et al.*, 1977; Matsuo *et al.*, 1996, 2000). It is known that the Tl<sub>2</sub>SeO<sub>4</sub> crystal, which is one of a family of *M*<sub>2</sub>*XO*<sub>4</sub>-type compounds, shows ferroelasticity at room temperature and undergoes a ferroelastic phase transition at 661 K (Matsuo *et al.*, 1996). At room temperature, the Tl<sub>2</sub>SeO<sub>4</sub> crystal structure is orthorhombic, *Pnma*, which is the same as the space group in β-K<sub>2</sub>SeO<sub>4</sub>-type crystals (Fábrý & Breczewski, 1993; Matsuo *et al.*, 1996). Recently, it has been reported that Tl<sub>2</sub>SeO<sub>4</sub> is hexagonal in the paraelastic phase, *P*6<sub>3</sub>/*mmc* (Matsuo *et al.*, 1996), which is the same space group as that in the paraelastic phase of the isomorphous K<sub>2</sub>SO<sub>4</sub> crystal structure. However, there are no reports of the crystal structure of this phase of Tl<sub>2</sub>SeO<sub>4</sub>. Moreover, it is also known that in the paraelastic phase of the isomorphous compound

K<sub>2</sub>SO<sub>4</sub>, the SO<sub>4</sub> tetrahedra randomly show two orientations, in which the apices of the tetrahedra point up and down along [001] (van den Berg & Tuinstra, 1978; Miyake *et al.*, 1980; Arnold *et al.*, 1981). This anomalously large degree of disorder may be a characteristic feature in the paraelastic phase of *M*<sub>2</sub>*XO*<sub>4</sub>-type compounds. However, there are no comprehensive viewpoints for this feature in *M*<sub>2</sub>*XO*<sub>4</sub>-type crystals. In order to summarize the characteristic features of the ferroelastic phase transition in *M*<sub>2</sub>*XO*<sub>4</sub>-type compounds, it is important to clarify the crystal structure of Tl<sub>2</sub>SeO<sub>4</sub> in the paraelastic phase. Therefore, we have measured the X-ray diffraction pattern of Tl<sub>2</sub>SeO<sub>4</sub> and have determined the crystal structure in the paraelastic phase using Rietveld analysis, with the atomic parameters of the isomorphous compound K<sub>2</sub>SO<sub>4</sub> in its paraelastic phase as the starting model.

Selected geometric parameters are given in Table 1. The fitted diffraction profile for Tl<sub>2</sub>SeO<sub>4</sub> is shown in Fig. 1 and the crystal structure of the paraelastic phase of the Tl<sub>2</sub>SeO<sub>4</sub> crystal is shown in Fig. 2.

The structure of Tl<sub>2</sub>SeO<sub>4</sub> consists of isolated SeO<sub>4</sub> tetrahedra with Tl atoms distributed between them. It is also evident that the SeO<sub>4</sub> tetrahedra have two orientations, with the apices pointing in opposite directions along [001], as

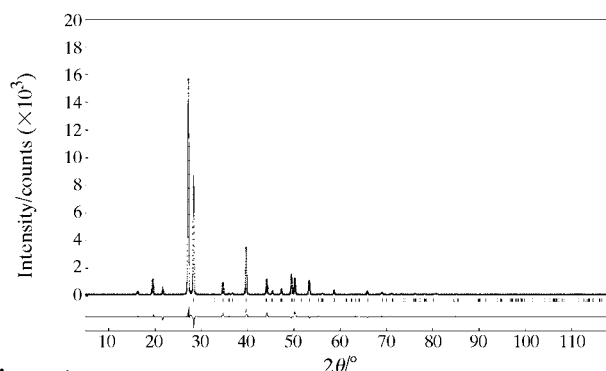


Figure 1

The fitted diffraction profile for Tl<sub>2</sub>SeO<sub>4</sub>, showing the calculated (line), observed (solid circle) and difference (lower) profiles.

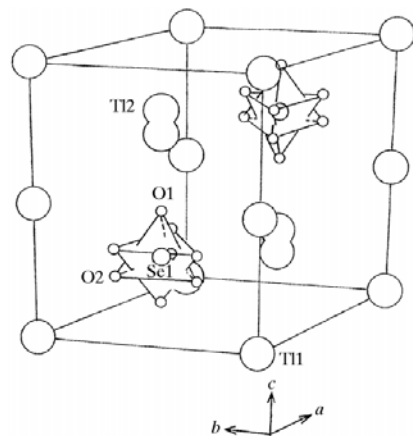


Figure 2

A view of the unit cell of the crystal structure of Tl<sub>2</sub>SeO<sub>4</sub>. The Tl2 atom statistically occupies two equivalent positions, with 50% probability. There are two orientations of the SeO<sub>4</sub> tetrahedra, with the apices pointing either up or down along [001].

shown in Fig. 2. Moreover, it can be clearly seen that one of the Tl atoms (Tl2) occupies two stable positions along [001]. The distance between these positions is 0.786 Å. Thus, the crystal structure of the paraelastic phase is characterized by the existence of the large disordered rotation of the SeO<sub>4</sub> tetrahedra and the anomalously large positional disorder of the Tl2 atoms along [001]. This structure is similar to that of the K<sub>2</sub>SO<sub>4</sub> crystal in the high-temperature paraelastic phase (Arnold *et al.*, 1981). On the other hand, in the ferroelastic phase of Tl<sub>2</sub>SeO<sub>4</sub>, it is noted that the disorder of the Tl2 atoms and the orientational disorder of the SeO<sub>4</sub> tetrahedra are not observed (Fábry & Brezowski, 1993).

The phase transition at 661 K is accompanied by a structural change from *P6<sub>3</sub>/mmc*, with lattice parameters *a* = 6.2916 (2) Å and *c* = 8.1964 (2) Å, to *Pnma*, with lattice parameters *a* = 7.927 (2) Å, *b* = 6.086 (2) Å and *c* = 10.934 (3) Å (Fábry & Brezowski, 1993). From these results, it is deduced that the ferroelastic phase transition of Tl<sub>2</sub>SeO<sub>4</sub> is closely related to the appearance of the order–disorder motion of Tl2 atoms and SeO<sub>4</sub> tetrahedra with the increase in temperature.

### Experimental

Crystals of Tl<sub>2</sub>SeO<sub>4</sub> were grown by slow evaporation of a saturated aqueous solution of Tl<sub>2</sub>SeO<sub>4</sub> at 313 K, after several recrystallizations for purification.

#### Crystal data

Tl <sub>2</sub> SeO <sub>4</sub>	Cu Kα radiation
<i>M<sub>r</sub></i> = 551.78	<i>T</i> = 683 K
Hexagonal, <i>P6<sub>3</sub>/mmc</i>	Specimen shape: flat sheet
<i>a</i> = 6.2916 (2) Å	15 × 20 × 1 mm
<i>c</i> = 8.1964 (2) Å	Specimen prepared at 100 kPa
<i>V</i> = 280.98 (1) Å <sup>3</sup>	Specimen prepared at 313 K
<i>Z</i> = 2	Particle morphology: plate-like,
<i>D<sub>x</sub></i> = 6.52 (2) Mg m <sup>-3</sup>	white

#### Data collection

Rigaku RINT-2000 diffractometer	<i>T</i> = 293 K
Specimen mounting: packed powder pellet	<i>h</i> = 0 → 3
Specimen mounted in reflection mode	<i>k</i> = 0 → 5
Scan method: step	<i>l</i> = 0 → 8
	2θ <sub>min</sub> = 5.0, 2θ <sub>max</sub> = 119.0°
	Increment in 2θ = 0.01°

#### Refinement

Refinement on <i>I</i> <sub>net</sub>	Profile function: pseudo-Voigt
<i>R<sub>p</sub></i> = 0.060	42 reflections
<i>R<sub>wp</sub></i> = 0.094	69 parameters
<i>R<sub>exp</sub></i> = 0.076	(Δσ) <sub>max</sub> = 0.01
<i>R<sub>B</sub></i> = 0.059	Extinction correction: none
<i>S</i> = 1.32	Preferred orientation correction:
Wavelength of incident radiation:	March–Dollase function, axis
1.54184 Å	(001) (Dollase, 1986)
Excluded region(s): none	

**Table 1**

Selected geometric parameters (Å, °).

Se1–O1 <sup>i</sup>	1.42 (2)	Tl1–O2 <sup>ii</sup>	4.75 (1)
Se1–O2 <sup>ii</sup>	1.40 (2)	Tl2–O1 <sup>i</sup>	3.06 (3)
O1–O2 <sup>ii</sup>	2.27 (2)		
O1–Se1 <sup>i</sup> –O2 <sup>ii</sup>	106.97 (6)	O2–Se1 <sup>iii</sup> –O2 <sup>iv</sup>	111.85 (6)

Symmetry codes: (i) *x, y, z*; (ii) *x, y + 1, z*; (iii) *x, y, z + 1*; (iv) *–y, x – y, z*.

It is known that K<sub>2</sub>SO<sub>4</sub> undergoes a ferroelastic phase transition from the low-temperature ferroelastic phase to the high-temperature paraelastic phase at 860 K (Shiozaki *et al.*, 1977). The structure is hexagonal, *P6<sub>3</sub>/mmc*, in the paraelastic phase and monoclinic, *Pnma*, in the ferroelastic phase. The Tl<sub>2</sub>SeO<sub>4</sub> crystal also undergoes a ferroelastic phase transition at 661 K (Matsuo *et al.*, 1996), with the symmetry change at this transition being the same as that of the isomorphous compound K<sub>2</sub>SO<sub>4</sub>. Therefore, the starting model for the determination of the structure of the Tl<sub>2</sub>SeO<sub>4</sub> paraelastic phase was based on the isomorphous *P6<sub>3</sub>/mmc* K<sub>2</sub>SO<sub>4</sub> crystal structure. In the analysis of the crystal structure, we have used both single- and split-atom models for the Tl2 atoms. The result was strongly in favour of truly split-atom positions (goodness-of-fit factor *S* = 1.32; in the single model, *S* = 2.08). Therefore, the single-atom model for the Tl2 atom (*z* =  $\frac{3}{4}$ ) was rejected and the split-atom model was used in the refinement. Refinements were also carried out using a range of occupancies for atoms O1 and O2 in the disordered tetrahedra. However, the goodness-of-fit factor was lowest for 50% occupancy. The profile shape was represented by a pseudo-Voigt function. In addition to the profile, lattice and structure parameters, the zero-point shift, ten background parameters and the scale factor were determined with corrections for preferred orientation along [001] (the crystal shape is plate-like). Rietveld analysis was carried out with the *RIETAN2000* program (Izumi & Ikeda, 2000). Isotropic thermal vibrations were assumed. The interatomic distances and bond angles were calculated using *ORFFE* (Busing *et al.*, 1964) and *ORTEP-3* (Farrugia, 2001).

Data collection: *RINT Server Software* (Rigaku, 1994); cell refinement: *RIETAN2000* (Izumi & Ikeda, 2000); data reduction: *RINT Server Software*; program(s) used to solve structure: *RIETAN2000*; program(s) used to refine structure: *RIETAN2000*; molecular graphics: *ORTEP-3* (Farrugia, 2001); software used to prepare material for publication: *RIETAN2000*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TY1005). Services for accessing these data are described at the back of the journal.

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