Single crystals of SnTe₃O₈ in the millimetre range grown by chemical vapor transport reactions

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Tin(IV) trioxidotellurate(IV), SnTe₃O₈, is a member of the isotypic M⁴⁺Te⁴⁺O₈ (M = Ti, Zr, Hf, Sn) series crystallizing with eight formula units per unit cell in space group Ia₃. In comparison with the previous crystal structure model of SnTe₃O₈ based on powder X-ray diffraction data [Meunier & Galy (1971). Acta Cryst. B27, 602–608], the current model based on single-crystal X-ray data is improved in terms of precision and accuracy. Nearly regular [SnO₆] octahedra (Sn site symmetry 3.) are situated in the voids of an oxidotellurate(IV) framework built up by corner-sharing [TeO₄] bisphenoids (Te site symmetry 2.). A quantitative structural comparison revealed a very high degree of similarity for the structures with M = Ti, Zr, Sn in the M⁴⁺Te₃O₈ series.

1. Chemical context

The crystal chemistry of oxidotellurates(IV) is dominated by the presence of the 5s² electron lone pair that, in the majority of cases, is stereochemically active, thus enabling one-sided coordination spheres around the Te⁴⁺ atom (Christy et al., 2016). This peculiar building block often results in compounds with non-centrosymmetric structures or structures with polar directions exhibiting interesting physical properties (Ra et al., 2003; Kim et al., 2014). In this context, the microwave dielectric properties of M⁴⁺Te₃O₈ (M = Sn, Zr) ceramics were investigated some time ago (Subodh & Sebastian, 2008).

The crystal structure of the isotypic series M⁴⁺Te₃O₈ was originally determined for M = Ti from a single crystal in space group Ia₃ using photographic Weissenberg X-ray data, whereas for M = Sn, Zr and Hf, the crystal structures were refined from powder X-ray data (Meunier & Galy, 1971). In subsequent studies, crystal-structure refinements on the basis of single-crystal X-ray data were reported for the mineral winstanleyite with composition (Ti₀.₀₉Fe₀.₀₁)Te₃O₈ (Bindi & Cipriani, 2003), and for the synthetic compound ZrTe₃O₈ (Noguera et al., 2003; Lu et al., 2019). A powder X-ray study of the solid solution Sn₀.₅⁹Ti₀.₄₁Te₃O₈ crystallizing in the M⁴⁺Te₃O₈ structure type has also been reported (Ben Aribia et al., 2008).

Single-crystal growth of oxidotellurates(IV) can be accomplished through various crystallization methods including, for example, experiments under hydrothermal conditions (Weil et al., 2018), cooling from the melt (Stöger et al., 2009), from salt melts as fluxing agents (Weil, 2019), or from chemical vapor transport reactions (Missen et al., 2020). The latter method (Binnewies et al., 2012) is particularly suitable for growing large crystals of high quality and was the
Displacement ellipsoids are as in Fig. 1; \([\text{TeO}_4]\) numbers of the oxide anions are two and three: O1 coordinates to two Te1 atoms at the shorter of the two Te1—O distances whereas O2 coordinates to three Te1 atoms at the longer of the two Te1—O distances.

In the crystal structure of SnTe3O8, the \([\text{SnO}_6]\) octahedra are isolated from each other and arranged in rows running parallel to [100]. Each of the \([\text{TeO}_6]\) bisphehnoids shares corners (O2) with other \([\text{TeO}_4]\) bisphehnoids to form a three-dimensional oxidotellurate(IV) framework. The \([\text{SnO}_6]\) octahedra are situated in the voids of this framework, thereby sharing each of the six corners with an individual \([\text{TeO}_4]\) bisphenoid. The crystal structure of SnTe3O8 is depicted in Fig. 2.

The unit-cell parameter \(a\) from the previous powder X-ray study, 11.144 (3) Å, as well as interatomic distances of Sn1—O1 = 2.032 Å (6 \(\times\)), Te1—O1 = 1.850 Å (2 \(\times\)), Te1—O2 = 2.124 Å (2 \(\times\)), and angles O1—Te1—O1' = 102.9°, and O2—Sn1 and Te1 at the shorter of the two Te1—O distances whereas O2 coordinates to three Te1 atoms at the longer of the two Te1—O distances.

Notes: (a) \(a = 10.956 (3) \text{ Å}\); Meunier & Galy (1971); (b) \(a = 10.965 (1) \text{ Å}\); Bindi & Cipriani (2003); (c) \(a = 11.308 (1) \text{ Å}\); Noguera et al. (2003); (d) \(a = 11.340 (4) \text{ Å}\); Lu et al. (2019).
The relation of the isotypic crystal structures of $M^{IV}$Te$_3$O$_8$ compounds with that of the fluorite structure has been discussed previously for TiTe$_3$O$_8$ (Meunier & Galy, 1971; Wells, 1975). The unit-cell parameter $a$ of cubic TiTe$_3$O$_8$ is $\sim 2a$ of cubic CaF$_2$, whereby the ordered distribution of the cationic sites leads to a doubling of the unit cell and also to a considerable distortion of the respective coordination environments.

The original cubic coordination around the Ca$^{II}$ cation in the fluorite structure is changed to an octahedral coordination of Sn$^{IV}$ and a fourfold coordination of Te$^{IV}$ in the superstructure. Sn$^{IV}$ and a fourfold coordination of Te$^{IV}$ in the superstructure. SnO$_2$ (71 mg, 0.47 mmol) and TeO$_2$ (225 mg, 1.40 mmol) were thoroughly mixed in the molar ratio 1:3 and placed in a silica ampoule. The silica ampoule was then evacuated and torch-sealed, placed in a two-zone furnace using a temperature gradient 973 K (source) $\rightarrow$ 873 K (sink) for three days. Cubic, canary-yellow crystals had formed in the millimetre size range.

A quantitative structural comparison of the $M^{IV}$Te$_3$O$_8$ structures where single crystal data are available ($M = Ti, Zr, Sn$) was undertaken with the program compstru (de la Flor et al., 2016) available at the Bilbao Crystallographic Server (Aroyo et al., 2006).

Table 3

| Crystal data                  | SnTe$_3$O$_8$         |
|------------------------------|-----------------------|
| Chemical formula             | $M$                   |
| Crystal system, space group  | $\text{Cubic, Ia} \overline{3}$ |
| Temperature (K)              | 296                   |
| $a$ ($\text{Å}$)             | 11.1574 (4)           |
| $V$ ($\text{Å}^3$)           | 1388.96 (15)          |
| $Z$                          | 8                    |
| Radiation type               | Mo $K\alpha$         |
| $\mu$ (mm$^{-1}$)            | 16.04                 |
| Crystal size (mm)            | 0.06 $\times$ 0.06 $\times$ 0.01 |

Data collection

Diffractometer: Bruker APEXII CCD

Absorption correction: Multi-scan (SADABS; Krause et al., 2015)

$T_{\text{min}}, T_{\text{max}}$ 0.452, 0.748

No. of measured, independent and observed $|I > 2\sigma(I)|$ reflections 14087, 735, 697

$R_{\text{int}}$ 0.048

(sin $\theta$/$\lambda)_{\text{max}}$ (Å$^{-1}$) 0.907

Refinement

$R[F^2 > 2\sigma(F^2)], wR(F^2), S$ 0.014, 0.030, 1.07

No. of reflections 735

No. of parameters 21

$\Delta$R$_{\text{max}}$, $\Delta$R$_{\text{min}}$ (e Å$^{-3}$) 1.27, −0.86

Acknowledgements

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Figure 3

Photograph of Sn$_3$TeO$_8$ single crystals grown by chemical vapor transport reactions.

3. Synthesis and crystallization

Reagent-grade chemicals were used without further purification. SnO$_2$ (71 mg, 0.47 mmol) and TeO$_2$ (225 mg, 1.40 mmol) were thoroughly mixed in the molar ratio 1:3 and placed in a silica tube to which 50 mg of TeCl$_4$ were added as the transport agent. The silica ampoule was then evacuated and torch-sealed, placed in a two-zone furnace using a temperature gradient 973 K (source) $\rightarrow$ 873 K (sink) for three days. Cubic, canary-yellow crystals had formed in the millimetre size range in the colder sink region as the only product (Fig. 3). Powder X-ray diffraction of the remaining material in the source region revealed SnTe$_3$O$_8$ as the main phase and SnO$_2$ as a side phase. For the single-crystal diffraction study, a fragment was broken from a larger crystal.

4. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. Atomic coordinates and the labelling scheme were adapted from isotypic TiTe$_3$O$_8$ (Meunier & Galy, 1971).
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Computing details
Data collection: APEX3 (Bruker, 2018); cell refinement: SAINT (Bruker, 2018); data reduction: SAINT (Bruker, 2018); program(s) used to solve structure: coordinates from previous refinement; program(s) used to refine structure: SHELXL (Sheldrick, 2015); molecular graphics: ATOMS (Dowty, 2006); software used to prepare material for publication: publCIF (Westrip, 2010).

Tin(IV) trioxidotellurate(IV)

Crystal data
SnTe₃O₈
Mr = 629.49
Cubic, Ia₃
a = 11.1574 (4) Å
V = 1388.96 (15) Å³
Z = 8
F(000) = 2160
Dₐ = 6.021 Mg m⁻³

Mo Kα radiation, λ = 0.71073 Å
Cell parameters from 5266 reflections
θ = 3.7°–38.9°
μ = 16.04 mm⁻¹
T = 296 K
Plate, light yellow
0.06 × 0.06 × 0.01 mm

Data collection
Bruker APEXII CCD
diffractometer
ω– and φ–scans
Absorption correction: multi-scan
(SADABS; Krause et al., 2015)
Tₘᵩᵣᵩ = 0.452, Tₘᵩᵧ = 0.748
14087 measured reflections

735 independent reflections
697 reflections with I > 2σ(I)
Rₑₘᵡᵩ = 0.048
θₑₘᵩᵩ = 40.2°, θₑₘᵩᵪ = 3.7°
h = −18→20
k = −20→20
l = −19→20

Refinement
Refinement on F²
Least-squares matrix: full
R[F² > 2σ(F²)] = 0.014
wR(F²) = 0.030
S = 1.07
735 reflections
21 parameters
0 restraints

w = 1/[σ²(F₀²) + 0.0127P² + 1.9293P]
where P = (P₀² + 2F₀²)/3
(Δ/σ)ₑₘᵩᵩ = 0.001
Δρₑₘᵩᵩ = 1.27 e Å⁻³
Δρₑₘᵩᵪ = −0.85 e Å⁻³
Extinction correction: SHELXL-2017/1 (Sheldrick 2015), Fc = kFc[1+0.001xFc²λ²/sin(2θ)]⁻¹/₄
Extinction coefficient: 0.00046 (3)
**Special details**

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

**Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)**

|          | x   | y   | z   | Uiso* / Ueq |
|----------|-----|-----|-----|-------------|
| Sn1      | 0.000000 | 0.000000 | 0.000000 | 0.00501 (4) |
| Te1      | 0.20584 (2) | 0.000000 | 0.250000 | 0.00804 (4) |
| O1       | 0.43242 (10) | 0.13738 (10) | 0.39972 (11) | 0.0129 (2) |
| O2       | 0.16789 (10) | 0.16789 (10) | 0.16789 (10) | 0.0078 (3) |

**Atomic displacement parameters (Å²)**

|          | U11 | U22 | U33 | U12 | U13 | U23 |
|----------|-----|-----|-----|-----|-----|-----|
| Sn1      | 0.00501 (4) | 0.00501 (4) | 0.00501 (4) | −0.00031 (3) | 0.000000 | 0.000000 |
| Te1      | 0.00518 (5) | 0.01273 (6) | 0.00620 (5) | 0.000000 | 0.000000 | −0.00229 (4) |
| O1       | 0.0095 (4) | 0.0117 (4) | 0.0174 (5) | 0.0019 (3) | 0.0018 (4) | 0.0094 (4) |
| O2       | 0.0078 (3) | 0.0078 (3) | 0.0078 (3) | 0.0020 (3) | 0.0020 (3) | 0.0020 (3) |

**Geometric parameters (Å, °)**

|                | Sn1—O1       | Sn1—O1       | Te1—O1       | O1—Sn1—O1   |
|----------------|--------------|--------------|--------------|--------------|
| Sn1—O1i        | 2.0421 (11)  | 2.0421 (11)  | 1.8800 (11)  | O1—Sn1—O1   |
| Sn1—O1ii       | 2.0421 (11)  | 2.0421 (11)  | 1.8800 (11)  | O1—Sn1—O1   |
| Sn1—O1iii      | 2.0421 (11)  | 2.0421 (11)  | 1.8800 (11)  | O1—Sn1—O1   |
| Sn1—O1iv       | 2.0421 (11)  | 2.0421 (11)  | 1.8800 (11)  | O1—Sn1—O1   |
| Sn1—O1v        | 2.0421 (11)  | 2.0421 (11)  | 2.1278 (3)   | O1—Sn1—O1   |
| O1—Sn1—O1v     | 86.09 (4)    | 86.09 (4)    | 86.09 (4)    | O1—Sn1—O1   |
| O1—Sn1—O1v     | 93.91 (4)    | 93.91 (4)    | 93.91 (4)    | O1—Sn1—O1   |
| O1—Sn1—O1v     | 93.91 (4)    | 93.91 (4)    | 93.91 (4)    | O1—Sn1—O1   |
| O1—Sn1—O1v     | 86.09 (4)    | 86.09 (4)    | 86.09 (4)    | O1—Sn1—O1   |
| O1—Sn1—O1v     | 86.09 (4)    | 86.09 (4)    | 86.09 (4)    | O1—Sn1—O1   |
| O1—Sn1—O1v     | 86.09 (4)    | 86.09 (4)    | 86.09 (4)    | O1—Sn1—O1   |
| O1—Sn1—O1v     | 86.09 (4)    | 86.09 (4)    | 86.09 (4)    | O1—Sn1—O1   |
| O1—Sn1—O1v     | 86.09 (4)    | 86.09 (4)    | 86.09 (4)    | O1—Sn1—O1   |
| O1—Sn1—O1v     | 86.09 (4)    | 86.09 (4)    | 86.09 (4)    | O1—Sn1—O1   |

Symmetry codes: (i) y, −z+1/2, x−1/2; (ii) −x+1/2, −y, z−1/2; (iii) x−1/2, y, −z+1/2; (iv) z−1/2, −x+1/2, −y; (v) −z+1/2, x−1/2, y; (vi) −y, −z−1/2, −x+1/2; (vii) −z+1/2, −x+1/2, −y+1/2; (viii) x, −y, z+1/2; (ix) −y+1/2, −z+1/2, −x+1/2; (x) −x+1/2, −y, z+1/2; (xi) z, x, y; (xii) y, z, x.