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# Antimony(III) tellurium(IV) chloride trioxide $SbTeO_3Cl$: synthesis and *ab initio* structure determination from X-ray and neutron powder diffraction data

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The mixed chloride oxide $SbTeO_3Cl$ has been prepared in polycrystalline form by solvolysis reaction from $SbCl_3$ and $TeCl_4$. The X-ray and neutron powder diffraction patterns were indexed in an orthorhombic unit cell; the structure was partially solved in the space group *Pnma* from the X-ray data, and completed and refined from neutron data. The crystal consists of strongly covalent $[SbTeO_3]^+$ layers, perpendicular to the *a* axis, corrugated as a consequence of the electrostatic repulsion of the lone pairs of $Sb^{III}$ and $Te^{IV}$. Both semimetals are three-fold co-ordinated to oxygens in pyramidal configuration. The layers are held together by discrete $Cl^-$ anions. This is one of the few examples of a positively charged two-dimensional network, very uncommon in the crystal chemistry of inorganic oxo compounds.

Antimony and tellurium are typical examples of semimetallic elements for which the isoelectronic character in the oxidation states $Sb^{III}$ and $Te^{IV}$, similarities of ionic radii and co-ordination features (determined by the presence of an electron lone pair) allow one to expect the formation of mixed oxo compounds of both elements, adopting closely related environments in the crystal structure. In a previous work[1] the preparation and structure of the first example of a mixed chloride oxide of both semimetallic elements, $Sb_3TeO_6Cl$, obtained in single-crystal form, were described. In the layered network of composition $(Sb_3TeO_6^+)_n$ the positions of antimony(III) and tellurium(IV) cations were indistinguishable by X-ray diffraction, hence they were assumed to be distributed at random over the semimetal positions.

Later, I reported on the existence of three new halide oxides of Sb and Te, of compositions $SbTeO_3Cl$, $Sb_3Te_2O_7Cl_3$ and $SbTeO_3Br$, for which the X-ray diffraction patterns, IR spectra and thermal behaviour were described.[2] Attempts to grow single crystals failed, but, recently, I optimized the preparation procedure of $SbTeO_3Cl$, obtaining a well crystallized polycrystalline material. The development of X-ray (XRD) and neutron powder diffraction (NPD) techniques for *ab initio* crystal structure determination encouraged me to investigate the structure of $SbTeO_3Cl$ from powder diffraction data. This paper reports on the results of this study.

## Results and Discussion

The compound $SbTeO_3Cl$ was prepared as a white microcrystalline powder by solvolysis from $SbCl_3$ and $TeCl_4$ at 70 °C (see Experimental section), according to equation (1). After an ageing period of 3 d, powder $SbTeO_3Cl$ samples exhibited an excellent crystallinity despite the relatively low reaction temperature, as seen from the X-ray powder diagrams (see Fig. 1).

$$SbCl_3 + TeCl_4 + 3H_2O \xrightarrow{70\,^{\circ}C} SbTeO_3Cl + 6HCl \quad (1)$$

Since the X-ray diffraction (XRD) scattering factors of Sb and Te are considerably higher than that of chlorine and, particularly, oxygen, neutron diffraction techniques were necessary to complement the XRD data. The first 20 peaks of the XRD diagram of $SbTeO_3Cl$ were unambiguously indexed in an orthorhombic unit cell (de Wolff figure of merit $M_{20} = 20$). Given the observed density, the unit cell contains four formula units. The observed reflection conditions suggested the space groups $Pna2_1$ (no. 33) or *Pnma* (no. 62). The latter, centric, was considered to solve the structure. For this crystal symmetry the matching of the observed and calculated XRD profiles without including a structural model led to excellent residuals. The unit-cell parameters after the pattern matching of the XRD data were $a = 11.1935(2)$, $b = 5.4281(1)$, $c = 7.2401(1)$ Å. The matching allowed the precise integration of the diffraction peaks. A set of structure factors in the range 2θ 10 to 60° was used to solve the structure.

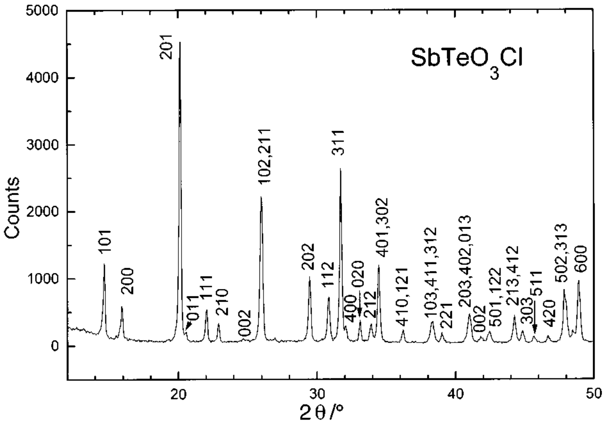

Fig. 1 The XRD diagram for $SbTeO_3Cl$, indexed according to an orthorhombic unit cell

A Patterson map followed by Fourier synthesis allowed the localization of Sb, Te, Cl and O(1) atoms from the XRD data. A first Rietveld refinement of the neutron data at this stage led to discrepancy factors of $R_I = 0.207$. Atom O(2) was located from Fourier synthesis on the NPD data. After the refinement of the anisotropic thermal factors for Cl the $R_I$ factor dropped to 0.064. Given the relatively poor resolution of the neutron diffractometer at high angles, a further fully anisotropic refinement was not considered reliable. The agreement between the observed and calculated NPD profiles is shown in Fig. 2. In order to check the consistency of the neutron-derived structure with the X-ray data, a subsequent refinement of the XRD pattern was performed. A significant preferred orientation effect was observed, which could be minimized in the

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**Table 1** Physical and crystallographic data and parameters for neutron powder data collection and refinement

| | |
|---|---|
| Formula | $ClO_3SbTe$ |
| $M$, $D_c$/g cm$^{-3}$ | 332.8, 5.02 |
| Space group, $Z$ | *Pnma* (no. 62), 2 |
| Crystal symmetry | Orthorhombic |
| $a$/Å | 11.197(2) |
| $b$/Å | 5.427(1) |
| $c$/Å | 7.239(1) |
| $U$/Å$^3$ | 439.93(1) |
| 2θ Range, step/° | 10.0–89.9, 0.01 |
| Collection time/h, sample weight/g | 4, 4 |
| No. reflections | 302 |
| Refined positional parameters | 11 |
| $R_{wp}$, $R_p$, $R_{exp}$, $R_I$ | 0.031, 0.024, 0.020, 0.064 |

| Atom | Site | $x$ | $y$ | $z$ | $B_{eq}$/Å$^2$ |
|---|---|---|---|---|---|
| Sb[a] | 4c | 0.2485(6) | 0.25 | 0.5718(14) | 1.3(2) |
| Te[a] | 4c | 0.0718(7) | 0.25 | 0.1820(10) | 0.8(2) |
| O(1) | 8d | 0.3729(4) | 0.9985(10) | 0.5113(7) | 0.9(1) |
| O(2) | 4c | 0.7187(7) | 0.25 | 0.1918(12) | 0.9(2) |
| Cl | 4c | 0.9226(5) | 0.25 | 0.5950(7) | 3.0(2)[b] |

[a] Better labelled as Sb-rich sites and Te-rich sites, given the possibility of partial mixed occupancy between antimony(III) and tellurium(IV) cations. [b] Anisotropic thermal factors for Cl, $U_{ij}$ (Å$^2$, $\times 10^3$): $U_{11} = 44(3)$, $U_{22} = 49(3)$, $U_{33} = 22(3)$, $U_{12} = U_{23} = 0$, $U_{13} = 13(1)$.

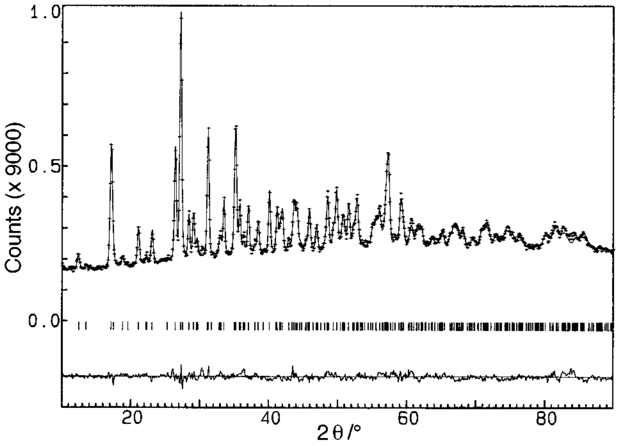

**Fig. 2** Observed (crosses), calculated (full line) and difference (below) neutron powder diffraction profiles for $SbTeO_3Cl$ at 295 K. The short vertical lines indicate the allowed Bragg positions

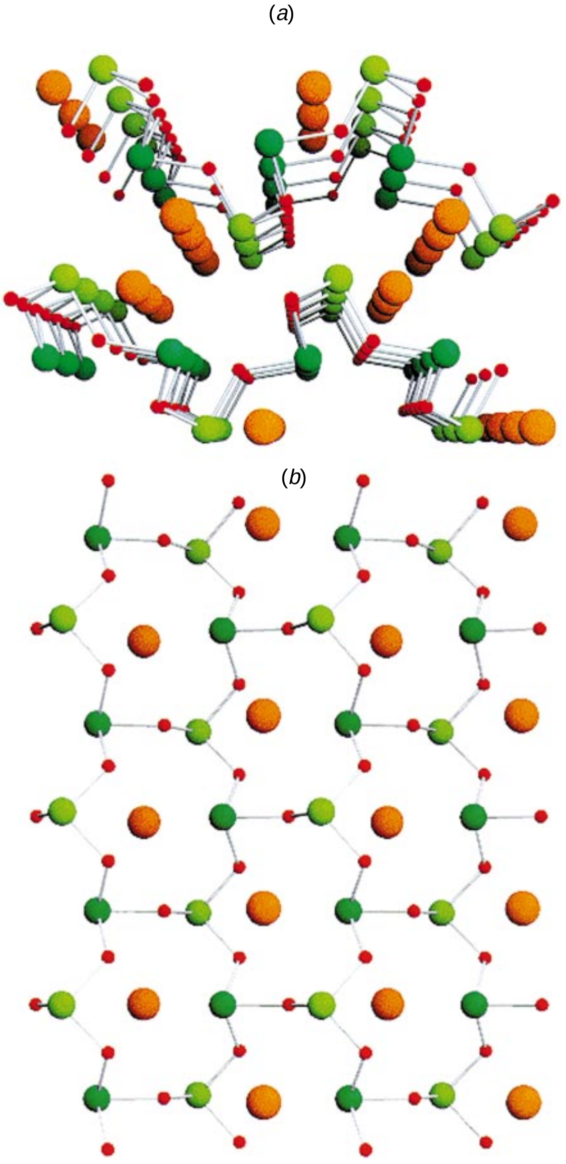

**Fig. 3** Two representations of the $SbTeO_3Cl$ structure: (*a*) along [0 1 0], showing the puckered $[SbTeO_3]^+$ layers perpendicular to the *a* axis; (*b*) view of one single layer, along the [1 0 0] direction. Key: Sb and Te, dark and light green spheres, respectively; O and Cl, red and orange balls, respectively. The *c* axis is oriented from left to right

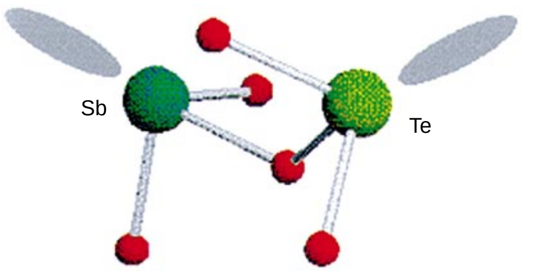

**Fig. 4** Oxygen co-ordination polyhedra about Sb and Te: the electron lone pair physically *occupies* vacant sites in the structure, in the neighbourhood of each (Sb,Te) atom, as suggested

refinement by considering platey-habit crystallites normal to the [0 1 0] direction, leading to acceptable discrepancy factors ($R_p = 0.131$, $R_{wp} = 0.170$, $\chi^2 = 5.21$, $R_I = 0.0954$). However, no improvement in the atomic coordinates (as far as standard deviations are concerned) was observed after the XRD refinement; therefore the final description of the crystal structure refers only to the neutron-derived coordinates.

Table 1 includes the final atomic coordinates and thermal factors obtained from NPD data, and Table 2 lists the main interatomic distances and angles. Two views of the crystal structure are shown in Fig. 3. It is constituted by $SbO_3$ and $TeO_3$ trigonal pyramids (see Fig. 4), the apices of which are occupied by the semimetal atoms. Bonding distances are in the range 1.94–2.00 Å for Sb–O and 1.88–1.93 Å for Te–O. Both kinds of polyhedra are linked together *via* common oxygens, giving rise to corrugated layers of composition $[SbTeO_3]^+$, parallel to the *bc* plane. The strongly covalent two-dimensional networks are positively charged. These layers are held together by $Cl^-$ anions, which are located between the layers at relatively long distances from metal atoms: 3.10 Å for Sb–Cl bonds, 3.16 Å for Te–Cl bonds.

The very irregular oxygen environment around $Sb^{III}$ and $Te^{IV}$ shown in Fig. 4 is due to the electrical repulsion of the electron lone pair, which is thought physically to *occupy* a volume similar to that of an oxygen anion.[3] Considering the lone pair as a sterically significant sphere, the average volume per anion in $SbTeO_3ClE_2$ (E = electron lone pair of both $Sb^{III}$ and $Te^{IV}$) is 18.3 Å$^3$, which compares with the corresponding values of other oxides and chloride oxides of Sb and Te: 16.5 Å$^3$ for $Sb_2Te_2O_9$,[4] 22.8 Å$^3$ for $Sb_3TeO_6Cl$,[1] 19.5 Å$^3$ for $Sb_4O_5Cl_2$[5] and 16.2 Å$^3$ for $Te_6O_{11}Cl_2$.[6]

**Table 2** Main interatomic distances (Å) and angles (°)

| | | | |
|---|---|---|---|
| Sb–O(1) | 1.998(7) ×2 | O(1)–Sb–O(1) | 86.1(4) |
| Sb–O(2) | 1.937(13) | O(1)–Sb–O(2) | 84.5(5) ×2 |
| Sb–Cl | 3.101(10) | | |
| Te–O(1) | 1.932(8) ×2 | O(1)–Te–O(1) | 81.6(4) |
| Te–O(2) | 1.881(11) | O(1)–Te–O(2) | 91.8(6) ×2 |
| Te–Cl | 3.158(5) | | |

**Table 3** Bond valences* ($s_i$) for (Sb,Te)–(O,Cl) bonds, multiplicity of the bonds [$m$] and valences ($\Sigma s_i$) for antimony and tellurium cations within the respective co-ordination polyhedra in the $SbTeO_3Cl$ structure

| | $s_i$ [$m$] | | | |
|---|---|---|---|---|
| Atom | O(1) | O(2) | Cl | $\Sigma s_i$ |
| Sb | 0.93 [2] | 1.10 [1] | 0.13 [1] | 3.09 |
| Te | 1.13 [2] | 1.30 [1] | 0.12 [1] | 3.68 |

* Bond valences are calculated as $s_i = \exp[(r_0 - r_i)/B]$; $B = 0.37$; $r_0(Sb^{III}–O) = 1.973$, $r_0(Sb^{III}–Cl) = 2.35$, $r_0(Te^{IV}–O) = 1.977$, $r_0(Te^{IV}–Cl) = 2.37$ Å (from ref. 7). Individual distances ($r_i$) are taken from Table 2.

Distinction between the positions of $Sb^{III}$ and $Te^{IV}$ in the crystal is possible, in spite of the isoelectronic character of both elements and their similar fermi lengths (see Experimental section), given the significantly shorter observed Te–O than Sb–O bond lengths. In relation to this, the calculation of the bond valences[7] for the antimony and tellurium co-ordination polyhedra is enlightening. As shown in Table 3, bond valence sums for the co-ordination polyhedra of Sb and Te are close to the expected valences of 3 and 4, respectively. However, a partial mixed occupancy of the antimony and tellurium sites should not be discarded, given the size of the thermal motion. It is possible that each site is significantly contaminated with the other ion, leading to the observed valences, slightly higher than 3+ for Sb and lower than 4+ for Te. An average mixed occupancy of about 20% can be estimated from the valence deviations. The contribution of the bonds to chlorine to the total valence of the semimetals is very small, suggesting that the (Sb,Te)–Cl interactions are weak and predominantly ionic.

Examples of positively charged networks are relatively rare in the crystal chemistry of inorganic oxo compounds, considering the large number of known examples of negatively charged networks. With the isolated exception of some crystal structures, like that of $[Te_2O_4H]^+[NO_3]^-$,[8] in most of the complex compounds of the heavier p elements of the Groups 5–7, which have been proposed to be formed by positively charged one- or two-dimensional networks, either[8] a discrete anion does not exist or the anion forms covalent bonds which complete the primary co-ordination polyhedra of the semimetal atoms in the network. In two-dimensional $SbTeO_3Cl$, puckered layers of $[SbTeO_3]^+$ are stacked in a direction perpendicular to the *a* axis, with discrete $Cl^-$ anions localized between the layers. Thus, $SbTeO_3Cl$ is one of the few oxo compounds exhibiting a positively charged two-dimensional network structure.

## Experimental

The compound $SbTeO_3Cl$ was prepared from an equimolar mixture of $SbCl_3$ and $TeCl_4$ (total weight of 5 g) which was hydrolysed by addition of a 2 M HCl aqueous solution (100 $cm^3$). The initially amorphous precipitate was digested in the reaction media at 70 °C, with stirring, for 3 d. This procedure led to a microcrystalline material which was thoroughly washed with water and dried at 120 °C in air.

The chemical analysis of $SbTeO_3Cl$ was performed as follows: 0.1 g was dissolved in concentrated HCl, then diluted to a HCl concentration of about 3 M. The antimony content (quantitatively present as $Sb^{III}$) was determined by titration with $KBrO_3$. In the resulting solution the tellurium content was determined gravimetrically, by reduction to Te metal with an excess of $Na_2SO_3$ and $NH_2NH_2 \cdot 2HCl$. The chlorine content was obtained gravimetrically as AgCl: a new portion of $SbTeO_3Cl$ (0.1 g) was dissolved in an aqueous 3 M solution of KOH, *then* $HNO_3$ was added until neutral pH, and the $Cl^-$ anions from the chloride oxide were precipitated with $AgNO_3$ [Found: Cl, 11.0; O (by difference), 13.7; Sb, 37.1; Te, 38.2. $SbTeO_3Cl$ requires Cl, 10.66; O, 14.42; Sb, 36.58; Te, 38.34%]. The density was determined by immersion in $CCl_4$, $D_{obs} = 5.01(5)$ g $cm^{-3}$.

The XRD patterns were collected with Cu-Kα radiation in a Siemens D-501 goniometer controlled by a DACO-MP computer, by step-scanning from 2θ 10 to 100°, in increments of 0.05°, and a counting time of 4 s each step. The NPD diagram of $SbTeO_3Cl$ was collected at room temperature in the multidetector DN5 diffractometer at the Siloé reactor of the Centre d'Etudes Nucléaires, Grenoble (λ = 1.344 Å). The conditions of the data collection are summarized in Table 1.

The XRD pattern was indexed with the TREOR 4 program.[9] The structure was solved from a Patterson map from XRD data (SHELXS 86 program[10]) and subsequently completed and refined from NPD data. The profile refinements (pattern matching for XRD data and structural refinement for neutron data) were performed with the FULLPROF program.[11] A pseudo-Voigt function was chosen to generate the line shape of the diffraction peaks. The coherent neutron scattering lengths for Sb, Te, O and Cl were, respectively, 5.57, 5.80, 5.803 and 9.577 fm. In the final run the following parameters were refined: background coefficients, zeropoint, half-width, pseudo-Voigt and asymmetry parameters for the peak shape; scale factor, positional and thermal isotropic factors (anisotropic for Cl) and unit-cell parameters. The maximum shift for atomic coordinates in the final refinement cycle of the neutron data was lower than $10^{-4}$.

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