Synthesis and Crystal Structure of $\text{Ti}_2[(\text{S}_{0.6}\text{Se}_{0.4})\text{O}_4]\text{Te}(\text{OH})_6$

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The crystal structure of the thallium sulfate selenate tellurate $\text{Ti}_2[(\text{S}_{0.6}\text{Se}_{0.4})\text{O}_4]\text{Te}(\text{OH})_6$ was determined with single-crystal X-ray diffraction data. The title compound crystallizes in the monoclinic system with the $P2_1/c$ space group. The unit-cell dimensions at 298 K are $a = 12.3580(10)\text{Å}$, $b = 7.2310(10)\text{Å}$, $c = 11.9860(10)\text{Å}$, $\beta = 111.090(10)^\circ$, $V = 999.33(19)\text{Å}^3$, $D_x = 5.029\text{ g/cm}^3$, and $Z = 4$. The R value is 0.047 for 1799 reflections. The anions are disposed in a number of sheets of pure $(\text{S},\text{Se})\text{O}_4$ tetrahedra, alternating with sheets of pure $\text{Te}(\text{OH})_6$ octahedra. All of those planes are intercalated in a bidimensional arrangement by Ti^+ cations.

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Alkali-sulfate and selenate tellurate compounds having the formula $\text{M}_2\text{XO}_4\text{Te}(\text{OH})_6$ with ($\text{M} = \text{K}, \text{NH}_4, \text{Ti}$ and $\text{X} = \text{S}, \text{Se}$) have been crystallographically studied in order to examine the effect and the influence of cationic and/or anionic substitution over the crystalline symmetry and physical properties. The ammonium sulfate tellurate, $(\text{NH}_4)_2\text{SO}_4\text{Te}(\text{OH})_6$, is monoclinic Cc , whereas the $(\text{NH}_4)_2\text{SeO}_4\text{Te}(\text{OH})_6$ material crystallizes in the $P2_1/c$ space group.^{1,2} On the other hand, the thallium sulfate tellurate $\text{Ti}_2\text{SO}_4\text{Te}(\text{OH})_6$ crystallizes in the $P2_1/a$ space group.³

We have been continuing our study of sulfate-selenate solid solutions of tellurate salts, among which we have reported $\text{Rb}_2[(\text{S}_{0.5}\text{Se}_{0.5})\text{O}_4]\text{Te}(\text{OH})_6$ and $\text{Cs}_2[(\text{S}_{0.57}\text{Se}_{0.43})\text{O}_4]\text{Te}(\text{OH})_6$.^{4,5} We have now prepared $\text{Ti}_2[(\text{S}_{0.6}\text{Se}_{0.4})\text{O}_4]\text{Te}(\text{OH})_6$. In this study we clearly show the crystallographic differences and the effect of extensions of the anionic and cationic volume groups, which can help us to understand which, if any, geometrical features can be responsible for the electrical properties.

Crystals of TiSSeTe were prepared at room temperature by the slow evaporation of an aqueous solution of a mixture of telluric acid, H_6TeO_6 (Aldrich, 99%), thallium carbonate Ti_2CO_3

O_3 (Aldrich 99.9%), selenic acid H_2SeO_4 (Aldrich 94%) and thallium sulfate Ti_2SO_4 (Aldrich 99.999%) at room temperature (The stoichiometric ratio is 1:0.5:0.5:0.5).

Schematically the reactions are:

Several recrystallizations were necessary to obtain single crystals suitable for an X-ray diffraction study. The composition

Fig. 1 Chemical diagram of the title compound.

of the obtained crystals was determined by chemical analysis, and confirmed by a crystal-structure refinement. A schematic diagram of the compound is shown in Fig. 1.

The unit-cell dimensions were measured and refined using indexation of diffraction markings collected with a Bruker-Nonius X8-APEX2 CCD area-detector diffractometer using the APEX2 program. The structure of $\text{Ti}_2[(\text{S}_{0.6}\text{Se}_{0.4})\text{O}_4]\text{Te}(\text{OH})_6$ was analyzed with the crystallographic CRYSTALS program. Density was measured, at room temperature, using the pycnometric method, by flotation in CCl_4 . The chemical crystal data, the parameters used for the X-ray diffraction data collection and the strategy used for the crystal structure determination and their results are listed in Table 1. The final positions and equivalent isotropic thermal parameters are given in Table 2. Hydrogen atoms were not determined.

Table 1 Crystal and experimental data

Empirical Formula	$\text{Ti}_2[(\text{S}_{0.6}\text{Se}_{0.4})\text{O}_4]\text{Te}(\text{OH})_6$
Formula weight	756.62
Crystal system	monoclinic
Space group	$P2_1/c$
a	$12.358(10)\text{Å}$
b	$7.231(10)\text{Å}$
c	$11.986(10)\text{Å}$
β	$111.09(10)^\circ$
Z	4
D_x	5.029 g/cm^3
No. of reflexions used	1799
R_{int}	0.09
$2\theta_{\text{max}}$	50.78 with Mo K_α
R	0.047
R_1 for all	0.0472, wR_2 for all = 0.0566 $R_1(I > 3\sigma)$ and $wR_2(I > 3\sigma)$
S	0.90
$(\Delta\rho)_{\text{max}}$	3.96 eÅ^{-3}
$(\Delta\rho)_{\text{min}}$	-3.86 eÅ^{-3}
Measurement	Bruker-Nonius X8-APEX2 CCD
Structure determination	ShelxS 97
Refinement	full-matrix ShelxL
ICSD number	419174

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Table 2 Atomic coordinates and equivalent thermal parameters of non-hydrogen atoms

Atom	x	y	z	U(eq)	Occ
Te1	0.5000	0.0000	0.5000	0.0124	1
Te2	0.0000	0.0000	0.0000	0.0126	1
Tl1	0.35340(6)	0.03537(10)	0.10541(7)	0.0178	1
Tl2	0.84569(6)	0.49837(9)	0.14433(6)	0.0183	1
(S,Se)1	0.75005(16)	-0.00994(16)	0.24434(16)	0.0247	0.60(4),0.40(4)
O1	0.3748(10)	0.0665(16)	0.5498(11)	0.0187	1
O2	0.3886(10)	-0.0778(17)	0.3495(10)	0.0163	1
O3	0.4928(12)	0.2431(16)	0.4341(11)	0.0191	1
O4	0.1401(10)	-0.1172(16)	0.1046(11)	0.0163	1
O5	-0.0962(12)	-0.2075(17)	0.0069(13)	0.0241	1
O6	-0.0163(12)	0.1060(19)	0.1384(12)	0.0242	1
O7	0.8561(12)	0.0092(15)	0.3593(12)	0.0228	1
O8	0.7732(10)	0.0797(18)	0.1379(12)	0.0197	1
O9	0.6431(11)	0.0876(17)	0.2537(12)	0.0212	1
O10	0.7198(12)	-0.2171(17)	0.2199(14)	0.0229	1

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

The $\text{Ti}_2[(\text{S}_{0.6}\text{Se}_{0.4})\text{O}_4]\text{Te}(\text{OH})_6$ solid solution crystallizes in the monoclinic structure. The proper space group is $P2_1/c$. The atomic arrangement of the structure is depicted in Fig. 2. Projection on to the (0 1 0) plane shows that this structure is probably built by planes of pure (S,Se) O_4 tetrahedra and pure TeO_6 octahedra. Planes containing $\text{Te}(\text{OH})_6$ octahedral, are parallel to (1 0 0) at $x/a = 0$ and $x/a = 1/2$, to (0 0 1) at $z/c = 0$ and $z/c = 1/2$, whereas planes of pure (S,Se) O_4 tetrahedra are at $x/a = 1/4$ and $x/a = 3/4$ for the first type and at $z/c = 1/4$ and $z/c = 3/4$ for the second one. The Ti^+ cation is intercalated between the two kinds of planes.

The Te atom in the $\text{Ti}_2[(\text{S}_{0.6}\text{Se}_{0.4})\text{O}_4]\text{Te}(\text{OH})_6$ structure occupies two special positions. As a consequence, the structure shows two kinds of octahedral, Te_1O_6 and Te_2O_6 , with Te-O values of between 1.903(13) and 1.934(12) Å. The O-Te-O angles range from 87.0(5)° to 93.0(5)°. In the mother compound $\text{Ti}_2\text{SO}_4\text{Te}(\text{OH})_6$,³ the Te-O distances vary from 1.885(9) Å to 1.941(6) Å. Consequently, the TeO_6 octahedra are more regular in a mixed solid solution than in sulfate. In the studied structure, the S and Se atoms occupy the same crystallographic sites. The (S,Se)-O distances vary from 1.528(14) Å to 1.546(12) Å. However, the S-O distances in the sulfate are between 1.436(7) Å and 1.467(8) Å, and the Se-O bond lengths range from 1.904(4) Å to 1.918(3) Å in the studied alkali selenate tellurate.² As a consequence, the (S,Se)-O bond lengths have intermediate values between the S-O and Se-O distances. The O-(S,Se)-O

Fig. 2 Projection of $\text{Ti}_2[(\text{S}_{0.6}\text{Se}_{0.4})\text{O}_4]\text{Te}(\text{OH})_6$ crystal structure on the (0 1 0) plane.

angles range from 106.7(6)° to 111.9(7)°. However, the O-S-O angles are between 107.4(5) and 109.6(5)° in the sulfate. These values confirm that the tetrahedral groups are more deformed in a mixed solid solution. This behavior can be related to the difference between the S and Se atomic radius. The coordination environments around the Ti^+ cations are slightly different, with Tl1 having eight neighbors and Tl2 having nine neighbors.

In contrast, the first Ti^+ cations in $\text{Ti}_2\text{SO}_4\text{Te}(\text{OH})_6$ material is coordinated by eight oxygen atoms, and the second one is coordinated by seven oxygen atoms.³ The Ti-O distances in the studied solid solution varied from 2.808(14) to 3.465(14) Å.

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