Synthesis, Calorimetric and X ray diffraction studies in the solid solution \( \text{Tl}_2(\text{SO}_4)_{1-x}(\text{SeO}_4)_x\text{Te(OH)}_6 \)  \( 0 \leq X \leq 1 \)

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Abstract

The crystal structures of the thallium tellurate solid solutions \( \text{Tl}_2(\text{SO}_4)_{1-x}(\text{SeO}_4)_x\text{Te(OH)}_6 \) were determined by X-ray diffraction method. The \( \text{Tl}_2\text{SeO}_4\text{Te(OH)}_6 \) (TlSeTe) and \( \text{Tl}_2(\text{SO}_4)_{0.6}(\text{SeO}_4)_{0.4}\text{Te(OH)}_6 \) (TlSSeTe) compounds crystallize in the monoclinic system with \( \text{P2}_1/c \) space group. Whereas the \( \text{Tl}_2\text{SO}_4\text{Te(OH)}_6 \) (TlSTe) compound crystallizes in the \( \text{P2}_1/a \) one. The following parameters of TlSeTe structure are: \( a = 12.358(3)\angs \); \( b = 7.231(1)\angs \); \( c = 11.986(2)\angs \); \( \beta = 111.092(2)^\circ \); \( Z = 4 \).

The TlSeTe structure can be regarded as being built of isolated \( \text{TeO}_6 \) octahedra and \( \text{SeO}_4 \) tetrahedra. The \( \text{Tl}^+ \) cations are intercalated between these kinds of polyhedra. The main feature of this structure is the coexistence of two different and independent anions (\( \text{SeO}_4 \) and \( \text{TeO}_6 \)) in the same unit cell. The structure is stable thanks to O-H...O hydrogen bonds which link tetrahedral and octahedral groups.

Crystals of \( \text{Tl}_2\text{SeO}_4\text{Te(OH)}_6 \) undergo two endothermal peaks at 373K and 437K. These transitions detected by DSC and analysed by dielectric measurements. However, the evolution of the conductivity versus temperature showed the presence of a protonic conduction phase transition at 437 K. The phase transition at 373K can be related to structural phase transition.

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PACS: Type pacs here, separated by semicolons ;

Keywords: Structure, Calorimetry, Sulfate selenate tellurate.

1. Introduction

Alkali metal sulphate, selenate and phosphate tellurate compounds having the formula \( \text{M}_2\text{XO}_4\text{Te(OH)}_6 \) (\( \text{M} = \text{Na}^+, \text{K}^+, \text{NH}_4^+, \text{Tl}^+, \text{Rb}^+ \) and \( \text{Cs}^+ \), \( X = \text{S}, \text{Se} \) and \( \text{P} \)) form broad families with interesting properties, such as superprotonic conduction and ferroelectricity [1-5].

The coexistence of different anions in the same unit cell connected by hydrogen bonds and the structural arrangement of all the polyhedra are the origin of structural phase transition accompanied by important physical properties. Both \( \text{K}_2\text{SeO}_4\text{Te(OH)}_6 \) and \( (\text{NH}_4)_2\text{SeO}_4\text{Te(OH)}_6 \) have a ferro-paraelectric phase transition at 433K and an ionic-protonic conduction one at 480 and 443K respectively [6, 7]. In order to examine the effect and the

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doi:10.1016/j.phpro.2009.11.018
influence of anionic and/or cationic substitution over crystalline symmetry in the selenate tellurate compounds and to confirm the presence and the importance of these physical properties, we have extended our research to the addition thallium selenate tellurate Tl₂SeO₄·Te(OH)₆ (TlSeTe) compound. In the present work, the synthesis, X-Ray and calorimetric studies of mixed crystal Tl₂(SO₄)ₓ(SeO₄)₁₋ₓ·Te(OH)₆ were carried out in order to determine the effect of this substitution.

2. Experimental details

Transparent, colourless single crystals of the title compounds were synthesized by slow evaporation, at room temperature, from aqueous solution of a mixture of carbonate thallium, sulphate thallium, selenic acid and telluric acid in according to the following reaction:

\[ \text{H}_2\text{TeO}_6 + (1-x)(\text{Tl}_2\text{CO}_3 + \text{H}_2\text{SeO}_4 ) + x\text{Tl}_2\text{SO}_4 \rightarrow \text{Tl}_2(\text{SO}_4)_{x}(\text{SeO}_4)_{1-x} \cdot \text{Te(OH)}_6 + \text{CO}_2 + \text{H}_2\text{O} \]

The formula of Tl₂(SO₄)ₓ(SeO₄)₁₋ₓ·Te(OH)₆ materials were determined by chemical analysis and confirmed by structural refinement. The unit cell dimensions were measured and refined using indexation of diffraction markings collected with a Kappa–CCD diffractometer with graphite monochromated Mo Kα radiation [8]. The unit cell parameters were identified and refined using a Denzo and collect programs [9]. The integrated intensities were corrected for Lorentz and polarization effects [10]. All subsequent computations were carried out using the computer program SHELX [11, 12]. The structure was solved by conventional Patterson and difference-Fourier techniques and refined by the full matrix least squares procedure. The structural graphics were created by the DIAMOND program [13]. The chemical crystal data, the parameters used for the X-ray diffraction data collection, the strategy used for the crystal structure determinations and their results are listed in Table 1. The final positions are presented in Table 2 for the Tl₂SeO₄·Te(OH)₆ compound. Differential scanning calorimetric measurements were realized on DSC SETARAM 92 between 300 and 750K.

Table 1. Main crystallographic feature, X-ray diffraction data parameters, and final results for Tl₂SeO₄·Te(OH)₆

| Crystal data          | Tl₂SeO₄·Te(OH)₆ |
|-----------------------|-----------------|
| Formula               | Tl₂SeO₄·Te(OH)₆ |
| Crystal system        | Monoclinic      |
| Space group           | P₂₁/c           |
| a (Å)                 | 12.358(3)       |
| b (Å)                 | 7.231(1)        |
| c (Å)                 | 11.986(2)       |
| β (°)                 | 111.092(2)      |
| V (Å³)                | 999.6(4)        |
| Z                      | 4               |
| Formula weight (g mol⁻¹) | 394.57        |
| ρcal (g.cm⁻³)         | 2.53            |
| Experimental details  |                 |
| Temperature (K)       | 293(2)          |
| Wavelength (Mo Kα) (Å) | 0.071           |
| Diffractometer        | Enraf Kappa CCD area detector |
| Monochromator         | Graphite        |
| Maximum Bragg angle (°) | 25.67         |
| h, k, l               | -16→16, -8→0, 0→14 |
| Measured reflections  | 4285            |
| Independent reflections | 1963            |
| Reflections used      | 1409            |
| WR(F²)u               | 0.035           |
| R                      | 0.030           |
| _μmax (e Å⁻³)         | 0.83            |
| _μmin (e Å⁻³)         | -0.47           |
Table 2: Fractional atomic coordinates and temperature factors for Tl$_2$SeO$_4$·Te(OH)$_6$.

| Atoms | X      | Y      | Z      | $U_{eq}$ | Occupation |
|-------|--------|--------|--------|----------|------------|
| Tl$_1$ | 0.15412 (8) | 0.49829 (12) | 0.35541 (9) | 0.0142 (6) | 1          |
| Tl$_2$ | 0.35341 (8) | 0.53561 (15) | 0.10536 (9) | 0.0138 (6) | 1          |
| Te$_1$ | 0.5000 | 0.5000 | 0.5000 | 0.0078 (8) | 0.5        |
| Te$_2$ | 0.0000 | 0.5000 | 0.0000 | 0.0084 (8) | 0.5        |
| O$_1$  | 0.6120 (12) | 0.582(2) | 0.6495 (13) | 0.016 (4) | 1          |
| H$_1$  | 0.6076 | 0.6945 | 0.6548 | 0.025 | 1          |
| O$_2$  | 0.3727 (11) | 0.566(2) | 0.5470 (12) | 0.013 (4) | 1          |
| H$_2$  | 0.3958 | 0.6336 | 0.6058 | 0.020 | 1          |
| O$_3$  | 0.4962 (10) | 0.7437 (19) | 0.4351 (11) | 0.010 (3) | 1          |
| H$_3$  | 0.4309 | 0.7650 | 0.3868 | 0.015 | 1          |
| O$_4$  | 0.0957 (12) | 0.704 (2) | -0.0073 (15) | 0.031 (4) | 1          |
| H$_4$  | 0.0950 | 0.7146 | -0.0757 | 0.046 | 1          |
| O$_5$  | -0.1400 (11) | 0.621 (2) | -0.1038 (12) | 0.014 (3) | 1          |
| H$_5$  | -0.1369 | 0.7312 | -0.0878 | 0.021 | 1          |
| O$_6$  | -0.0167 (13) | 0.608 (2) | 0.1366 (14) | 0.026 (4) | 1          |
| H$_6$  | -0.0743 | 0.5656 | 0.1460 | 0.040 | 1          |
| Se$_1$ | 0.2496 (3) | 0.5097 (5) | -0.2448 (4) | 0.0429 (12) | 1          |
| O$_7$  | 0.3570 (12) | 0.411 (2) | -0.2558 (13) | 0.015 (3) | 1          |
| O$_8$  | 0.2775 (11) | 0.716 (2) | -0.2218 (11) | 0.016 (4) | 1          |
| O$_9$  | 0.1446 (15) | 0.490 (2) | -0.3590 (16) | 0.019 (4) | 1          |
| O$_{10}$ | 0.2264 (10) | 0.417 (2) | -0.1387 (12) | 0.011 (3) | 1          |

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

3. Results and discussion

3.1 Structure description:

Sulphate and/or selenate tellurate compounds exhibit simple structural arrangements and interesting physical properties. The main feature of the atomic arrangement in these compounds is the coexistence of two different types of anions (TeO$_6^{2-}$, SO$_4^{2-}$ and/or SeO$_4^{2-}$ groups) in the unit cell, connected by O-H…O hydrogen bonds. At room temperature Tl$_2$SeO$_4$·Te(OH)$_6$ is monoclinic. The space group is P2$_1$/c. The unit cell parameters are: $a= 12.358(3)$Å; $b= 7.231(1)$Å; $c= 11.986(2)$Å; $\beta= 111.092(2)^\circ$ and $Z= 4$. Cited parameters are similar to those of thallium sulphate selenate tellurate solid solution Tl$_2$(SO$_4$)$_{0.6}$(SeO$_4$)$_{0.4}$·Te(OH)$_6$ [19]. The TlSeTe structure can be regarded as being built by planes of pure octahedra Te(OH)$_6$ (at $x= 0$ and $x= a/2$), alternating with planes of pure tetrahedra SeO$_4^{2-}$ (at $x= a/4$ and $x= 3a/4$). The Tl$^+$ cation is intercalated, in bidimensional arrangement, between the two kinds of planes. Figure 1 shows a projection on the ac plane of NaNST structure and confirm our last description and the figure 2 shows the structural arrangement of TlSSeTe solid solution [19].
The Te atom, in the Tl₂SeO₄·Te(OH)₆ structure, occupies two special positions. In consequence, the structure shows two kinds of octahedral, Te(1)O₆ and Te(2)O₆. In fact, the Te₁-O distances, in Te₁O₆ groups, are between 1.912(3) and 1.921(5) Å and the O-Te₁-O angle values vary from 87.6(6)° and 92.4(6)°. Whereas these distances, in Te₂O₆ groups, vary from 1.892(6) and 1.937(3) Å with O-Te₂-O angle values between 87.3(3) and 92.7(7)°. In the Tl₂SeO₄·Te(OH)₆ structure, the Te-O distances are between 1.910(11) and 1.918(12) Å for the first octahedral type and between 1.903(13) and 1.934(12) Å for the second type [19]. In the selenate tellurate compounds, the TeO₆ octahedra are less regular in the KSeTe compound (the Te-O distances are between 1.867 and 1.946 Å and O-Te-O angles values vary from 88 to 92.8°) than in TlSeTe material. On the other hand, the distances Te-O observed in the
Cs$_2$SeO$_4$.Te(OH)$_6$ compound are definitely lower than that of Tl$_2$SeO$_4$.Te(OH)$_6$ compound. Indeed, this is due to the difference of the cations radii intercalated in these structures. The tetrahedral coordination of the Se atom is built with four oxygen atoms. The Se–O distances in the Tl$_2$SeO$_4$.Te(OH)$_6$ structure, vary between 1.516(1) and 1.555(3) Å with O–Se–O angles ranging between 106.7(7)$^\circ$ and 111.6(8)$^\circ$ (Table 3). In the TlSSeTe mixed solid solution the S/Se-O distances vary from 1.528(14)Å to 1.546(12)Å. Whereas The S-O distances in the TlSTe structure range from 1.460 et 1.484Å [19]. From the values, listed in table 4, we show an important deformation of these groups by comparison with other structures such as, TlSSeTe, Cs$_2$SeO$_4$.Te(OH)$_6$ and Rb$_2$SeO$_4$.Te(OH)$_6$ [14, 17-18].

Table 3. Atomic distances (Å) and angles (°) in Tl$_2$SeO$_4$.Te(OH)$_6$

|                  | Te$_{10}$O$_6$                        | Te$_{12}$O$_6$                        |
|------------------|---------------------------------------|---------------------------------------|
|                  | O$_2$–Te$_1$–O$_3$(a) = 89.3 (6)       | O$_8$(a) – Te$_2$–O$_4$(a) = 89.0 (7)  |
|                  | O$_1$–Te$_1$–O$_2$(a) = 90.7 (6)       | O$_4$–Te$_2$–O$_6$(a) = 91.0 (7)      |
|                  | O$_2$–Te$_1$–O$_1$(a) = 92.4 (6)       | O$_8$(a)–Te$_2$–O$_3$(a) = 91.1 (6)   |
|                  | O$_3$(a)–Te$_1$–O$_3$(a) = 90.0 (6)    | O$_4$(a) – Te$_2$–O$_5$(a) = 88.6 (9) |
|                  | 1.921 (5)                             | 1.912 (5)                             |
|                  | Te$_1$–O$_1$(a) = 1.921 (5)           | Te$_2$–O$_4$(a) = 1.912 (5)           |
|                  | Te$_1$–O$_2$(a) = 1.912 (3)           | Te$_2$–O$_5$(a) = 1.937 (3)           |
|                  | Te$_1$–O$_3$(a) = 1.920(4)            | Te$_2$–O$_6$(a) = 1.892 (6)           |
|                  | Te$_1$–O$_3$ = 1.920 (4)              | Te$_2$–O$_6$ = 1.892 (6)              |
|                  |                                           |                                      |
|                  | Se–O$_7$ = 1.555 (2)                   | O$_8$–Se–O$_8$ = 108.5(8)            |
|                  | Se–O$_8$ = 1.535 (2)                   | O$_8$–Se–O$_10$ = 110.5 (8)          |
|                  | Se–O$_9$ = 1.516 (2)                   | O$_8$–Se–O$_7$ = 111.6 (8)           |
|                  | Se–O$_{10}$ = 1.551 (2)               | O$_8$–Se–O$_7$ = 111.0 (9)           |
|                  |                                       | O$_8$–Se–O$_{10}$ = 105.8 (8)        |
|                  |                                       | O$_{10}$–Se–O$_7$ = 106.7 (7)        |
|                  | Tl$_1$–O$_1$(b) = 2.971(4)            | Tl$_1$–O$_1$(d) = 2.925(4)            |
|                  | Tl$_1$–O$_2$(c) = 2.906 (3)           | Tl$_1$–O$_2$(c) = 2.994(4)            |
|                  | Tl$_1$–O$_3$(b) = 2.946 (6)           | Tl$_1$–O$_3$(f) = 2.981 (2)           |
|                  | Tl$_1$–O$_4$(d) = 3.083 (3)           | Tl$_1$–O$_5$(c) = 3.225 (5)           |
|                  | Tl$_1$–O$_5$(c) = 2.812 (4)           | Tl$_1$–O$_6$(d) = 2.846 (2)           |
|                  | Tl$_1$–O$_6$(b) = 2.812 (4)           | Tl$_1$–O$_7$(e) = 3.391 (4)           |
|                  | Tl$_1$–O$_7$(b) = 2.887 (8)           | Tl$_1$–O$_8$(b) = 3.122 (3)           |
|                  | Tl$_1$–O$_8$(c) = 3.473 (5)           | Tl$_2$–O$_8$(c) = 2.898 (3)           |
|                  |                                           |                                      |
| Symmetry codes : | a : -x, -y, -z ; b: x, -3/2y,1/2z ; c: x, y, z ; d: -x, -y, -z ; e: x, -3/2y, -1/2z ; f: -x, -1/2y, -1/2 |

Differently to TISTe and TISSeTe structures where the two cations don’t have the same number of coordination, in the Tl$_2$SeO$_4$.Te(OH)$_6$ structure, the environment of the thallium cations is made from eight oxygen atoms [18-19]. In consequence, the environment of Tl$^1$(1) is made up of two oxygen atoms belonging to Te$_2$O$_8$ (O$_1$; O$_2$), four oxygens: (O$_5$, O$_6$, O$_8$, and O$_9$) of second octahedral Te$_2$O$_6$. The two other oxygen atoms O$_4$ and O$_5$ belong to the SeO$_4$ tetrahedrons. In the other hand, the environment of Tl$^1$(2) is made up of three atoms belonging to SeO$_4$ tetrahedra, three oxygen atoms belonging to Te$_2$O$_8$ (O$_1$, O$_2$ and O$_3$) and two oxygen atoms belonging to Te$_2$O$_6$ octahedron. The Tl-O distances range from 2.812 (4) to 3.473 (5) Å.
Table 4. Distances and hydrogen bond angles in Tl$_2$SeO$_4$.Te(OH)$_6$.

| Distances O…O(Å) | Distances O…H(Å) | Angles O…H — O(°) |
|------------------|------------------|------------------|
| O$_1$ ... O$_7$(M) = 2.661(3) | O$_7$...H$_1$(M) = 1.931 (3) | O$_4$..H$_1$(M)  —  O$_7$ = 147.81(3) |
| O$_3$...O$_8$(N)  = 2.695 (4)  | O$_8$...H$_3$(N)  = 1.880 (5) | O$_5$..H$_2$(Q)  —  O$_8$ = 173.07 (3) |
| O$_5$ ... O$_9$(Q) = 2.705(5)  | O$_9$...H$_5$(Q)  = 1.967(3) | O$_5$..H$_2$(Q)  —  O$_9$ = 149.22 (4) |
| O$_6$ ... O$_{10}$(P) = 2.608(2) | O$_{10}$...H$_6$(P) =1.854 (4) | O$_6$..H$_6$(P)  —  O$_{10}$ = 152.17 (3) |

Symmetry codes: M : -x+1, y+1/2, -z+1/2 ; N : x,-y+3/2 z+1/2 ; Q : -x, y+1/2, -z-1/2 ; P : -x, -Y+1, -z.

In Tl$_2$SeO$_4$.Te(OH)$_6$ structure, the selenate tetrahedrons are connected with tellurate octahedrons by O-H...O hydrogen bonds assured by protons belonging to hydroxide groups. In the selenate groups, all the oxygen atoms participate in the establishment of the hydrogen bonds. The figure 3 shows clearly all hydrogen bonds. The O...O distances are between 2.608(2) and 2.705(3)Å and the O-H...O angles vary from 147.81(3) to 173.07(3)°. Differently to all the other alkali selenate tellurate materials studied, the O...O distances, in Tl$_2$SeO$_4$.Te(OH)$_6$ structure, are less than 2.7Å (Table 4). So these hydrogen bonds are considered strong. In consequence, the presence of the thallium cations increases the anionic interaction between anionic and cationic groups. In TlSeTe structure, O...H and O-H...O values can favour the appearance of high protonic conductivity at high temperature which is the origin of the super-protonic phase transition characterized by the breaking of hydrogen bonds which link anionic groups.

![Fig. 3. Hydrogen bonds in Tl$_2$SeO$_4$.Te(OH)$_6$](image)

3.2/ Calorimetric study:

A typical result of the calorimetric study of the Tl$_2$SeO$_4$.Te(OH)$_6$ is presented in figure 4. The DSC thermogram shows three endothermic peaks at 373K, 395K and 437K. The transition enthalpy are, respectively, $\Delta H_1 = 20.69$ Jg$^{-1}$ for the first transition, and $\Delta H_2 = 66.77$ Jg$^{-1}$ whereas $\Delta H_3 = 242.5$ Jg$^{-1}$ for the third anomaly observed toward 437K. By comparison with similar compound, the first anomaly is attributed to a structural phase transition [6,15-17]. The high-temperature phase transition at about 437K in the TlSeTe compound can be interpreted as a ionic-protonic one. This phase transition can be due to the breaking of the (O-H...O) hydrogen bonds in TlSeTe compound which link all the polyhedra. In consequence, the proton H$^+$ becomes free between the potential holes TeO$_6^{6-}$ and SeO$_4^{2-}$ [6, 20].
4. Conclusion

The Tl$_2$SeO$_4$Te(OH)$_6$ new compound crystallizes in the monoclinic space group P2$_1$/c with four formula units in the unit cell. The structure is built by TeO$_6^{6-}$ and SeO$_4^{2-}$ anions and Tl$^+$ cations. The main feature of the type of the alkaline selenate tellurate structures is the presence of two different and independent anions TeO$_6^{6-}$ and SeO$_4^{2-}$ in the same unit cell which can be in the origin of interesting physical properties, as the ferroelectricity and the protonic conduction. Tl$_2$SeO$_4$Te(OH)$_6$ material exhibits three endothermic peaks at 373K, 395K and 437K detected by calorimetric measurements. The first phase transition at 373K can be attributed to a structural phase transition. By comparison with similar compounds, the second phase transition can be due to a ferroelectric phase transition. The third peak detected at 437K is of ionic protonic conduction type.

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