



High-pressure single-crystal X-ray diffraction of Tl_2SeO_4

Andrzej Grzechnik*, Tomasz Breczewski, Karen Friese

Departamento de Física de la Materia Condensada, Universidad del País Vasco, E-48080 Bilbao, Spain

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ABSTRACT

The effect of pressure on the crystal structure of thallium selenate (Tl_2SeO_4) ($Pm\bar{c}n$, $Z = 4$), containing the Tl^+ cations with electron lone pairs, has been studied with single-crystal X-ray diffraction in a diamond anvil cell up to 3.64 GPa at room temperature. No phase transition has been observed. The compressibility data are fitted by a Murnaghan equation of state with the zero-pressure bulk modulus $B_0 = 29(1)$ GPa and the unit-cell volume at ambient pressure $V_0 = 529.6(8) \text{ \AA}^3$ ($B' = 4.00$). Tl_2SeO_4 is the least compressible in the c direction, while the pressure-induced changes of the a and b lattice parameters are quite similar. These observations can be explained by different pressure effects on the nine- and 11-fold coordination polyhedra around the two non-equivalent Tl atoms. The SeO_4^{2-} tetrahedra are not rigid units and become more distorted. Their contribution to the compressibility is small. The effect of pressure on the isotypical oxide materials A_2TO_4 with the β - K_2SO_4 structure is discussed. It appears that the presence of electron lone pairs on the Tl^+ cation does not seem to influence the compressibility of Tl_2SeO_4 .

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1. Introduction

The crystal structure of thallium selenate (Tl_2SeO_4) at room temperature is isotypical to β - K_2SO_4 ($Pm\bar{c}n$, $Z = 4$) and consists of isolated tetrahedra SeO_4^{2-} and of two non-equivalent Tl^+ cations surrounded by nine and 11 oxygen atoms (Fig. 1) [1–5]. Tl_2SeO_4 undergoes a ferroelastic phase transition at 661 K and ambient pressure [1–3]. In the paraelectric phase above 661 K, the structure is isotypical to α - K_2SO_4 ($P6_3/mmc$, $Z = 2$) with a pronounced disorder of both selenate anions and Tl^+ cations. The α - K_2SO_4 structure is the aristotype for the whole family of the A_2TX_4 compounds ($T = \text{Cr, Mo, W, S, Se, Zn, Co, Cd, Hg, etc.}; X = \text{O, F, Cl, Br, I, etc.}$) [1–9].

The low-temperature behaviour of Tl_2SeO_4 is distinctly different from that of other compounds with the β - K_2SO_4 structure, which commonly transform first to an incommensurately modulated phase with a wave vector of $(1/3+\delta)c^*$ and then into an acentric lock-in phase with a triplicated c -axis ($P2_1cn$, $Z = 12$) [5,7]. No incommensurate phase was reported for Tl_2SeO_4 . Instead, Tl_2SeO_4 undergoes a first-order phase transition to a polymorph with symmetry $P2_12_12_1$ ($Z = 4$) at 72 K [5,10–12]. This transformation is associated with a discontinuous increase of the unit-cell volume [11]. In this new phase, the coordination numbers of the Tl^+ cations are reduced to 8 and 10, respectively [5].

The high-pressure behaviour of the A_2TX_4 compounds with the β - K_2SO_4 structure was systematically studied by Serghiou et al. [13]. Whether they amorphize or undergo *crystal-to-crystal* phase transitions seems to depend predominantly on the ratio of the size of the tetrahedral group to the size of the A^+ cation. For the small ratios, new polymorphs are observed, while amorphous solids form when the ratios are high. Similar geometrical considerations were also applied to discuss the ambient-pressure incommensurate lattice instabilities in the materials with large TX_4 groups [7,14,15]. It was pointed out that the A_2TX_4 compounds that amorphize upon compression also have incommensurate modulations at low temperatures and ambient pressure [13]. Disorder of the TX_4 tetrahedra [16] or of the anionic X sub-lattice [17] was proposed to explain the amorphization. Machon et al. [18–20] demonstrated that the high-pressure behaviour of the A_2TX_4 compounds could also be extremely sensitive to deviations from ideal hydrostaticity during the measurements. The pressure-induced transformations in fact depend on the character of compression, i.e., hydrostatic versus non-hydrostatic, with the latter favouring the amorphization. Nevertheless, it was found that in Cs_2HgBr_4 the appearance of the amorphous phase is preceded by the occurrence of undetermined pressure-induced incommensurate and lock-in phases [20].

The presence of non-bonded electron lone pairs on the Tl^+ cations in Tl_2SeO_4 [4–6] could be considered as a feature of covalent bonding [21]. Hence, the argument based on the ratio of the TX_4/A ionic sizes to rationalize the pressure-induced structural instabilities in the A_2TX_4 compounds [13] might be not necessarily applicable to the materials in which the A^+ cation

* Corresponding author. Fax: +34 94 601 35 00.

E-mail address: andrzej.grzechnik@ehu.es (A. Grzechnik).

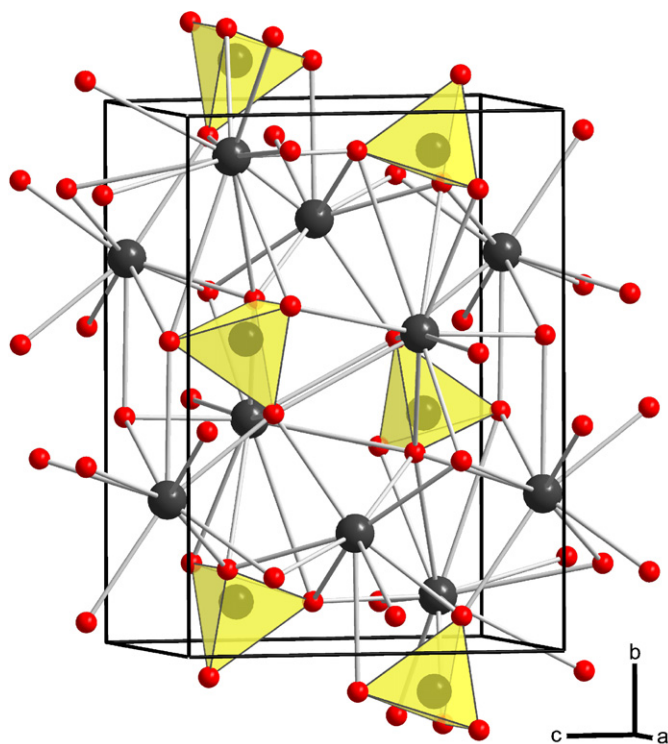


Fig. 1. Crystal structure of Tl_2SeO_4 at ambient pressure and room temperature ($Pm\bar{c}n$, $Z = 4$). Drawn are the tetrahedra around the Se atoms.

possesses the electron lone pair like Tl^+ . The general effect of pressure on inorganic solids is to suppress the electron lone pairs so that it is only at high pressures that the crystal structures mainly depend on the ionic radii [21]. In this study, we investigate the high-pressure behaviour of Tl_2SeO_4 with the $\beta\text{-K}_2\text{SO}_4$ structure ($Pm\bar{c}n$, $Z = 4$) using single-crystal X-ray diffraction in a diamond anvil cell at room temperature. We want to know whether the compressibility of the compounds with the $\beta\text{-K}_2\text{SO}_4$ structure is dependent on the ratio of the TX_4/A ionic sizes and whether the compressibility of the thallium bearing compounds is influenced by the existence of the Tl^+ electron lone pair.

2. Experimental

The crystals came from the same batch as the ones studied previously [5]. Single-crystal intensities were measured at room temperature using a Stoe diffractometer IPDS-2T with the $\text{MoK}\alpha$ radiation. The intensities at ambient pressure were measured from a crystal mounted on a glass pin. High-pressure data were collected in two separate runs on two other crystals (crystal no. 1: 0.63, 2.01, and 3.14 GPa; crystal no. 2: 1.29, 2.62, and 3.64 GPa) in the Ahsbahs-type diamond anvil cell [22]. In total, 250 μm holes were drilled into stainless steel gaskets preindented to a thickness of about 120 μm . The intensities were indexed, integrated, and corrected for absorption using the STOE software [23]. Shaded areas of the images by the diamond anvil cell were masked prior to integration. The intensities were integrated simultaneously with three orientation matrices, corresponding to the crystal of Tl_2SeO_4 and to the two diamonds of the cell. Owing to their hemispherical shape, no absorption correction was necessary for the diamond anvils. The ruby luminescence method [24] was used for pressure calibration and isopropanol, which is hydrostatic to 4.20 GPa [25] and does not react with Tl_2SeO_4 , was used as a pressure medium (other pressure media that are hydrostatic to higher pressures, e.g., various mixtures of methanol, ethanol, and

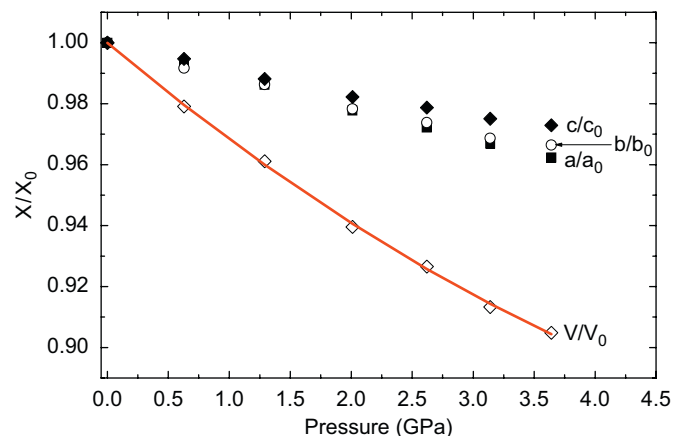


Fig. 2. Pressure dependence of normalized lattice parameters and unit-cell volumes. The solid line is the Murnaghan equation of state.

water, dissolve our sample). The data were refined using the programme JANA2006 [26].¹

3. Results and discussion

Indexing and analysis of the single-crystal X-ray diffraction data indicated that the crystal structure of Tl_2SeO_4 ($Pm\bar{c}n$, $Z = 4$) is stable upon compression to 3.64 GPa at room temperature. The lattice parameters and the unit-cell volume at ambient conditions are $a = 6.084(1) \text{ \AA}$, $b = 10.965(3) \text{ \AA}$, $c = 7.938(2) \text{ \AA}$, and $529.6(4) \text{ \AA}^3$, respectively [4,5]. The pressure dependence of the normalized lattice parameters and unit-cell volumes is presented in Fig. 2. Tl_2SeO_4 is the least compressible along the c -axis. The pressure-induced changes of the a and b lattice parameters are not much different from each other. The P - V data could be fitted by a Murnaghan equation of state with the zero-pressure bulk modulus $B_0 = 29(1) \text{ GPa}$ and the unit-cell volume at ambient pressure $V_0 = 529.6(8) \text{ \AA}^3$ (for the fixed first pressure derivative of the bulk modulus $B' = 4.00$).

Surprisingly, the bulk moduli of K_2CrO_4 [16] and Tl_2SeO_4 are essentially the same. Also, the relative changes of the lattice parameters in both compounds on compression are qualitatively equivalent. These observations clearly suggest a common compressibility mechanism in the oxide materials with the $\beta\text{-K}_2\text{SO}_4$ structure. It would mean that the compressibility of the thallium bearing compounds is not substantially influenced by the existence of the Tl^+ electron lone pair.

The phase transition in Tl_2SeO_4 to the phase with symmetry $P2_12_12_1$ ($Z = 4$) [5,10–12] is not expected on compression because it is associated with a discontinuous unit-cell volume increase [11]. According to our equation of state and to the thermal contraction data of reference 11, the unit-cell volume $V = 517.86(6) \text{ \AA}^3$ at 85 K and atmospheric pressure, slightly above the transition at 72 K, would be equivalent to compressing the material to 0.68 GPa at room temperature. To make sure that the symmetry is not reduced to $P2_12_12_1$ at high pressures, we carefully examined the reconstructed reciprocal spaces at 2.62 and 3.64 GPa, but did not find any reflections violating the extinction rules for the c and n glide planes.

The details of our structural refinements of the single-crystal X-ray diffraction data are presented in Tables 1 and 2.¹ At each

¹ Further details of the crystallographic investigations can be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository numbers CSD 419775–419777.

Table 1
Experimental data for the single-crystal measurements at different pressures (*Pmcn*, *Z* = 4)

	0.0001 GPa	2.62 GPa	3.64 GPa
Crystal data			
<i>a</i> (Å)	6.084(1)	5.915(1)	5.855(1)
<i>b</i> (Å)	10.965(3)	10.678(2)	10.597(2)
<i>c</i> (Å)	7.938(2)	7.769(1)	7.724(1)
<i>V</i> (Å ³)	529.6(4)	490.7(2)	479.2(2)
ρ (g/cm ³)	6.9177	7.4658	7.6442
μ (mm ⁻¹)	67.557	72.909	74.652
<i>G</i> _{iso}	0.059(4)	0.013(2)	0.012(2)
Data collection			
No. measured refl.	1992	1561	1531
Range of <i>hkl</i>	−6 ≤ <i>h</i> ≤ 6 −10 ≤ <i>k</i> ≤ 10 −8 ≤ <i>l</i> ≤ 8	−7 ≤ <i>h</i> ≤ 7 −5 ≤ <i>k</i> ≤ 5 −10 ≤ <i>l</i> ≤ 10	−7 ≤ <i>h</i> ≤ 7 −4 ≤ <i>k</i> ≤ 5 −10 ≤ <i>l</i> ≤ 10
No. unique refl.	316	271	258
No. observed refl. ^a	255	138	136
<i>R</i> (int) _{obs/all} ^b	8.32/8.49	6.08/7.53	6.39/7.71
sin(θ)/ λ	0.5044	0.6654	0.6681
Refinement^b			
<i>R</i> _{obs}	4.49	5.25	4.90
<i>wR</i> _{obs}	4.90	4.13	3.91
<i>R</i> _{all}	5.44	13.97	11.36
<i>wR</i> _{all}	4.95	5.05	4.76
<i>GoF</i> _{all}	3.10	1.81	1.76
<i>GoF</i> _{obs}	2.78	1.49	1.47
No. parameters	27	27	27

^a Criterion for observed reflections is $|F_{\text{obs}}| > 3\sigma$.^b All agreement factors are given in %, weighting scheme $1/[\sigma^2(F_{\text{obs}}) + (0.01F_{\text{obs}})^2]$.**Table 2**
Positional and isotropic thermal displacement parameters (Å²) at different pressures (*Pmcn*, *Z* = 4)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
0.0001 GPa				
Tl1	0.25	0.7162(2)	−0.0014(2)	0.0421(7)
Tl2	0.25	0.0836(2)	0.1720(2)	0.429(8)
Se	0.25	0.4218(4)	0.2104(5)	0.028(1)
O1	0.25	0.423(5)	0.008(6)	0.09(1)
O2	0.25	0.562(4)	0.281(5)	0.07(1)
O3	0.031(5)	0.356(3)	0.280(3)	0.068(8)
2.62 GPa				
Tl1	0.25	0.7149(6)	−0.0045(3)	0.053(4)
Tl2	0.25	0.0878(6)	0.1648(3)	0.049(3)
Se	0.25	0.422(2)	0.2142(6)	0.029(2)
O1	0.25	0.378(15)	0.014(7)	0.11(2)
O2	0.25	0.574(12)	0.283(5)	0.05(1)
O3	0.024(5)	0.362(7)	0.286(3)	0.05(1)
3.64 GPa				
Tl1	0.25	0.7133(6)	−0.0065(3)	0.047(4)
Tl2	0.25	0.0890(6)	0.1625(3)	0.040(3)
Se	0.25	0.420(2)	0.2150(7)	0.031(2)
O1	0.25	0.392(11)	0.005(5)	0.06(2)
O2	0.25	0.578(12)	0.275(5)	0.05(1)
O3	0.022(5)	0.358(5)	0.285(3)	0.031(8)

pressure, the starting positional parameters for the Tl and Se atoms (*Pmcn*, *Z* = 4) were taken from Ref. [5]. The positions of the O atoms were determined from the difference $F_{\text{obs}} - F_{\text{calc}}$ Fourier synthesis. The thermal displacement parameters for Tl were refined anisotropically, while the Se and O atoms were treated isotropically. We also included an isotropic Gaussian extinction

Table 3
Selected distances, angles, and bond valence sums of the cations at different pressures (*Pmcn*, *Z* = 4)

	0.0001 GPa	2.62 GPa	3.64 GPa
Distances (Å)			
Tl1–O2	2.81(4)	2.69(8)	2.60(8)
O3 (2x)	2.89(3)	2.82(3)	2.78(3)
O3 (2x)	2.91(3)	2.84(3)	2.80(4)
O2	2.99(5)	2.79(11)	2.78(10)
O1	3.22(5)	3.60(16)	3.40(12)
O1 (2x)	3.40(2)	3.12(5)	3.13(4)
<Tl1–O>	3.05	2.96	2.91
Tl2–O1	2.67(5)	2.74(6)	2.65(4)
O3 (2x)	3.05(3)	2.93(6)	2.95(5)
O2 (2x)	3.074(6)	2.988(8)	2.970(8)
O3 (2x)	3.38(3)	3.28(3)	3.25(2)
O3 (2x)	3.45(3)	3.35(7)	3.29(5)
O2	3.49(4)	2.988(8)	2.970(8)
O1	3.94(5)	3.31(16)	3.44(11)
<Tl2–O>	3.27	3.10	3.09
Se–O3 (2x)	1.61(3)	1.59(4)	1.58(3)
O1	1.61(5)	1.62(7)	1.65(5)
O2	1.63(5)	1.71(13)	1.73(12)
<Se–O>	1.62	1.63	1.64
Angles (deg)			
O3–Se–O3	111.3(15)	115(3)	115(2)
O3–Se–O1	110.3(13)	103(3)	105(2)
O3–Se–O2	107.6(13)	106(3)	108(2)
O1–Se–O2	110(2)	115(6)	116(4)
Polyhedral volume (Å³)			
SeO ₄ ^{2−}	2.2(1)	2.1(2)	2.1(2)
Bond valence sums			
Tl1	0.86(3)	1.13(8)	1.26(8)
Tl2	0.70(3)	0.84(5)	0.90(4)
Se	6.4(3)	6.2(6)	6.1(5)

correction (*G*_{iso}) in the refinements. The relevant distances, angles, and bond valence sums are listed in Table 3.

The average <Se–O> distances and polyhedral volumes [27] of the SeO₄^{2−} tetrahedra (Fig. 1) are essentially independent of pressure (Table 3). However, the tetrahedra become more distorted on compression at room temperature. The same behaviour was already observed while lowering temperature at atmospheric conditions [5]. The most striking observation is that the bond valence sum² of the Se⁶⁺ cation practically does not change in this highly compressible material.

As pointed out earlier, the cations in the 11-fold coordination in all the compounds with the β -K₂SO₄ structure are underbonded with their bond valence sums lower than the ideal value of one [7]. This pronounced underbonding was related to the low-temperature structural instabilities. In addition, in all the Tl₂TO₄ materials, the Tl⁺ cations in the nine-fold coordination are also underbonded [5–9]. In Tl₂SeO₄, the <Tl1–O> and <Tl2–O> average distances decrease on compression and their relative change between 0.0001 and 3.64 GPa is 5% and 6%, respectively (Table 3). In the same pressure range, however, the difference between the shortest and longest Tl1–O distances increases, while the difference in the Tl2–O distances decreases. The bond valence sums for the thallium atoms at the Tl1 site increase much more than that at the Tl2 site on compression, with the latter still being lower than 1 at 3.64 GPa (Table 3). This clearly demonstrates that the coordination sphere of the Tl1 atom is more sensitive to pressure. Such distinct behaviours of the coordination polyhedra

² The bond valences are calculated assuming Brown's parameters implemented in the JANA2006 programme [26].

around the two non-equivalent TI^+ cations could be assigned to the fact that the stereochemical activity, although very weak, is higher at the TI1 site [6]. The activity should be additionally suppressed at high pressures [21].

The shortest TI2-O distance, which is nearly parallel to the c -axis (Fig. 1), hardly changes within estimated standard deviations (Table 3) with increasing pressure, explaining why the linear compressibility along this crystallographic direction is relatively low (Fig. 2). This observation agrees very well with the fact that the least-affected lattice parameter during the phase transition to the $P2_12_12_1$ polymorph at 72 K and atmospheric conditions is also the c -axis [4,5,11]. For both cases (i.e., at high pressures and at low temperatures, respectively), the relatively small change of the c lattice parameter can thus be attributed to the most stable bonding pattern TI2-O1-Se between the TI^+ cations and the selenate anions along this axis.

4. Conclusions

A comparison of our P - V data for TI_2SeO_4 , containing the TI^+ cations with electron lone pairs, with those for K_2CrO_4 [16] suggests that the A_2TO_4 oxides with the β - K_2SO_4 type structure ($Pm\bar{c}n$, $Z = 4$) are in general highly compressible, irrespective of the size TO_4/A ratio. The effect of pressure is to change the unit-cell dimensions along the a and b directions more than that along the c -axis. This results from the same compressibility mechanism for the A_2TO_4 compounds, regardless whether the A^+ cations possess electron lone pairs or not. The most affected structural units seem to be the nine- and 11-fold coordination polyhedra around the two non-equivalent A^+ cations.

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