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Twinned crystal structure and compressibility of $TlTeVO_5$

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ABSTRACT

The high-pressure behavior of $TlTeVO_5$ has been investigated *in situ* using single-crystal X-ray diffraction in a diamond anvil cell. This material is structurally stable at least to 7.11 GPa, the highest pressure reached in this study. $TlTeVO_5$ is twinned both at ambient and high pressures ($Pna2_1$, $Z = 4$). The twinning law relating the two individuals is equivalent to a rotation of approximately 3° around the $[1\bar{2}0]$ direction. Within errors, no changes in the orientation of the two individuals are observed as a function of pressure. The refined twin volume fractions do not change within estimated standard deviations, either.

The material is the most and the least compressible along the *c* and *a* axes, respectively. The *P–V* data could be fitted by a Murnaghan equation of state with $B_0 = 32(1)$ GPa, $V_0 = 504.4(4)$ Å^3, and $B' = 7.97(43)$. The most important effect of pressure is the increase of the coordination numbers for the Tl and Te atoms. The Tl–O distance nearly parallel to the [001] direction is the most sensitive structural feature to pressure, resulting in the anisotropic compressibility. The long Te–O distances decrease, while the short ones are constant or even become slightly longer. Such a pressure-induced change of the coordination is interpreted as due to increasing uniformity of the oxygen atoms surrounding the cations and to decreasing activity of the electron lone pairs. The change is accompanied by an increase of the pseudosymmetry of the structure with respect to the centrosymmetric space group *Pnna*.

1. Introduction

The polar and second-harmonic generating oxide $TlTeVO_5$ ($Pna2_1$, $Z = 4$) has a three-dimensional structure in which chains of corner-shared distorted VO_6 octahedra are connected by irregular TeO_4 and TlO_8 polyhedra [1]. The asymmetric environments of the Te^{4+} and Tl^{1+} cations are attributable to their electron lone (E) pairs. In a related material $TlSeVO_5$ ($Pna2_1$, $Z = 4$), the Se^{4+} cations are three-fold coordinated to the oxygen atoms. From the crystallographic analysis of the compounds containing the S^{4+}, Se^{4+}, or Te^{4+} cations, Marukhnov et al. [2] have inferred that the activity of the E pair decreases along the sequence $S^{4+} \rightarrow Se^{4+} \rightarrow Te^{4+}$. They have noticed that the volume and the activity of the E pair diminish when the number of oxygen atoms bonded to the cation increases ([2,3] and references therein).

The effect of pressure, associated with the increase of coordination numbers and with the coordination polyhedra becoming more regular, is similar and the stereochemistry of the electron lone pairs is suppressed on compression [4]. An example could be the paratellurite form of TeO_2 (α-TeO_2, $P4_12_12$, $Z = 4$) that is three-dimensional with the Te atoms in a disphenoidal coordination [5]. When the Te lone electron pair or the next-nearest oxygen atoms are taken into account, the coordination unit around the the Te atoms is a distorted TeO_4E bipyramid or a very deformed TeO_6 octahedron, respectively. α-TeO_2 undergoes a reversible second-order phase transition to an orthorhombic phase ($P2_12_12_1$, $Z = 4$) at 0.9 GPa and room temperature [5–7]. The high-pressure phase is a slight distortion of the paratellurite structure. Raman scattering data [8] seem to indicate a sequence of pressure-induced phases closely related to the $P2_12_12_1$ one occurring at about 4.5 and 11.0 GPa, while another phase crystallizing at 22.0 GPa is supposed to be of the $PbCl_2$ type ($Pnam$, $Z = 4$). A recent study using synchrotron X-ray powder diffraction [9] has confirmed the reversible sluggish formation of the $PbCl_2$-type phase of TeO_2 in the pressure range 20–30 GPa (however, no full-pattern Rietveld refinement of the data has been presented). The coordination number of Te in this new structure would be 9 (the Te–O distances are 2.17–2.56 Å at 30 GPa, assuming the ambient-pressure coordinates for $PbCl_2$), implying the suppression of the stereochemical effect of the lone electron pair on the tellurium atoms.

At atmospheric pressure, the coordination numbers in TlO_n polyhedra range from $n = 3$ to 12. In Tl_2CO_3 ($C2/m$, $Z = 4$) with the relatively low coordination number for the Tl atoms, the

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compression mainly takes place in the region of the structure where the Tl^{1+} lone pairs are located [10]. On the other hand, the presence of the lone pairs does not influence the high-pressure behavior of the materials in which the Tl^{1+} cations have high coordination numbers. For instance, the effect of pressure on the crystal structure of Tl_2SeO_4 ($Pmcn, Z = 4$) with two non-equivalent Tl^{1+} cations surrounded by nine and eleven oxygen atoms results in the compressibility mechanism already observed in other compounds with the β-K_2SO_4 type structure [11].

In this study, which is a continuation of our earlier investigations on Tl-containing compounds [10,11], we are interested in the high-pressure behavior of the twinned crystal structure of $TlTeVO_5$ examined with single-crystal X-ray diffraction in a diamond anvil cell.

2. Experimental

The crystals of $TlTeVO_5$ were synthesized hydrothermally according to Ref. [1].

Single-crystal intensities were measured at room temperature using a STOE diffractometer IPDS-2T with Mo–$K\alpha$ radiation. The intensities at ambient pressure were measured from a crystal mounted on a glass pin. High-pressure data to 7.11 GPa were collected in a diamond anvil cell of the Boehler-Almax type [12]. A 250 μm hole was drilled into a stainless steel gasket preindented to a thickness of about 100 μm. The intensities were indexed and integrated using the STOE software [13]. Shaded areas of the images by the diamond anvil cell were masked prior to integration. The corrections for the effect of absorption by the diamond anvils and the crystal were made using the program Absorb [14] and the STOE software [13], respectively. The ruby luminescence method [15] was used for pressure calibration and a mixture of pentane and isopentane, which is hydrostatic to 7.4 GPa [16] and does not react with $TlTeVO_5$, was used as pressure medium. The error in pressure determination is estimated to be 0.02 GPa. All the data were refined using the program Jana2006 [17].[1]

3. Results and discussion

Several crystals of $TlTeVO_5$ were mounted on glass pins and tested at ambient conditions. Each crystal was affected by twinning, which seems to be intrinsic to this compound. Eventually, one of them was selected for the structure determination. To index all the reflections, two orientation matrices, corresponding to two identical (within errors) orthorhombic lattices with space group symmetry $Pna2_1$ ($Z = 4$) [1], were necessary. The lattice parameters and the unit-cell volume at ambient conditions are $a = 7.313(2)$ Å, $b = 8.747(2)$ Å, $c = 7.887(2)$ Å, and 504.5(4) Å^3, respectively. The matrix relating the two individuals

$$\begin{pmatrix} 0.999 & -0.032 & -0.048 \\ 0.023 & 1.0 & 0.0 \\ 0.042 & 0.0 & 0.999 \end{pmatrix}$$

is equivalent to a rotation of approximately 3° around the $[1\bar{2}0]$ direction. Fig. 1 shows a section of the reciprocal space were the twinning can well be observed. Note the difference in intensities of the reflections corresponding to the two twin individuals.

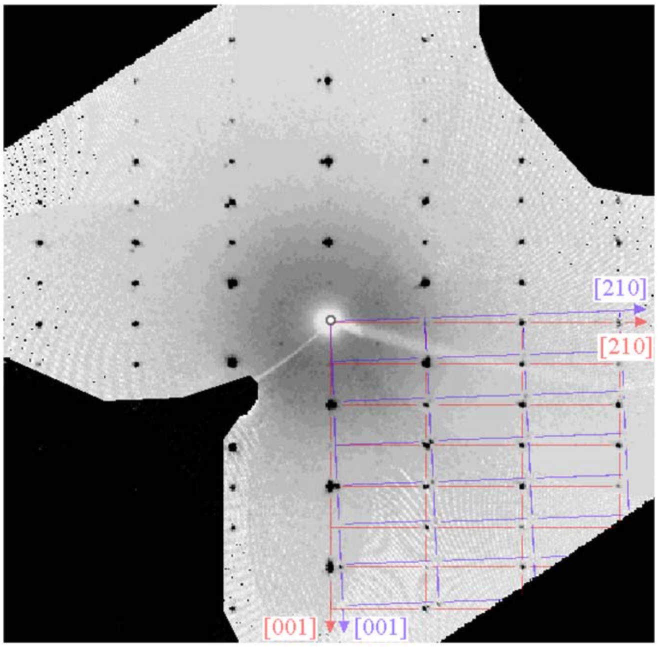

Fig. 1. Section of a reciprocal space of $TlTeVO_5$ at ambient conditions as reconstructed from the measured frames. The splitting of reflections is well observed. The lattices of the two twin individuals are indicated in the lower right corner.

From the fact that all crystals investigated by us show the same twin relationship, we conclude that the twinning is present in the structure of $TlTeVO_5$ rather than coincidental intergrowth of two individuals. As the twinning law corresponds only to a very small rotation of the two lattices with respect to each other, one might assume a small monoclinic distortion of an underlying pseudo-orthorhombic structure being responsible for the observed twinning. However, when indexing the data with two individuals, we never found any significant deviation from the 90° angles and trial refinements assuming twin models with monoclinic symmetry for the two individuals did not result in better overall agreement factors than the orthorhombic model.

The final structural refinement with the program Jana2006 [17] was performed with space group symmetry $Pna2_1$ ($Z = 4$) (Tables 1–3) using the starting model from Ref. [1]. Attributable to the twinning, some of the reflections are fully or partially overlapped. These were included in the refinement process and the overlap was treated in the calculations using the corresponding options in Jana2006 (allowing for a maximum angular difference of 0.5° for overlapped reflections). An isotropic Gaussian extinction correction (G_{iso}) was also included in the refinements. Thermal displacement parameters of all the atoms were refined anisotropically. The obtained volume fractions of the two individuals were 91.4(5) and 8.6(5)%. Attributable to the high f' value for the Tl atom (9.669) at the wavelength used (Mo–$K\alpha$), the correct polar structure could be easily identified.[2]

Considering the structural details in Tables 2 and 3, the twinned structure of $TlTeVO_5$ obtained in this study is in principle equivalent to that of Ref. [1], although our structure corresponds to the *inversion-related form*. It is characterized by chains of corner-shared distorted VO_6 octahedra connected via irregular TeO_4 and TlO_8 polyhedra to form a three-dimensional structure. The V^{5+} cations are displaced from the centers of their octahedra. The asymmetric environments of the Te^{4+} and Tl^{1+} cations are due

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[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 420592 and 420593.

[2] We also tested a model with additional inversion twinning. However the volume fractions corresponding to the other *inversion-related form* refined to 0%.

Table 1
Experimental data for the measurements at different pressures ($Pna2_1$, $Z = 4$).

	Ambient pressure	7.11 GPa
Crystal data		
a (Å)	7.313(2)	7.100(2)
b (Å)	8.747(2)	8.427(2)
c (Å)	7.887(2)	7.414(2)
V (Å^3)	504.5(4)	443.6(3)
ρ (g/cm^3)	6.0926	6.9293
μ (mm^{-1})	39.343	44.746
G_{iso}	0.078(8)	0.022(8)
Data collection		
No. measured refl.	5889	2208
Range of hkl	$0 \leqslant h \leqslant 10$	$0 \leqslant h \leqslant 7$
	$0 \leqslant k \leqslant 12$	$0 \leqslant k \leqslant 9$
	$-11 \leqslant l \leqslant 11$	$-9 \leqslant l \leqslant 9$
No. unique refl.	1689	461
No. observed refl^a	1124	156
$R(\text{int})_{\text{obs/all}}$^{b}	8.87/9.75	9.94/13.09
$\text{Sin}(\theta)/\lambda$	0.7435	0.6669
Refinement^b		
R_{obs}	4.21	4.99
wR_{obs}	3.93	4.13
R_{all}	6.39	12.12
wR_{all}	4.07	4.90
GoF_{all}	1.75	1.46
GoF_{obs}	1.47	0.93
No. parameters	74	35

[a] Criterion for observed reflections is $|F_{obs}| > 3\sigma$·

[b] All agreement factors are given in %, weighting scheme $1/[\sigma^2(F_{obs})+(0.01F_{obs})^2]$.

Table 2
Positional and isotropic thermal displacement parameters (in Å^2) at different pressures.

Atom	X	y	Z	U_{iso}
Ambient pressure				
Tl	0.0227(1)	0.1099(1)	0.099	0.0251(2)
Te	−0.0256(2)	0.4679(1)	0.4014(1)	0.0110(2)
V	−0.2220(4)	0.2599(4)	0.7136(3)	0.0109(7)
O1	−0.225(2)	0.182(2)	0.521(2)	0.019(4)
O2	0.128(2)	0.635(1)	0.450(1)	0.013(3)
O3	−0.434(2)	0.324(1)	0.739(2)	0.017(4)
O4	−0.102(2)	0.450(1)	0.638(1)	0.013(3)
O5	−0.255(2)	0.077(1)	0.851(1)	0.018(3)
7.11 GPa				
Tl	0.0193(5)	0.1146(3)	−0.0892	0.025(1)
Te	−0.010(1)	0.4532(4)	−0.3711(5)	0.019(1)
V	−0.224(3)	0.261(2)	−0.693(1)	0.025(3)
O1	−0.220(6)	0.175(6)	−0.490(6)	0.030(6)
O2	0.133(7)	−0.360(6)	−0.436(5)	0.030(6)
O3	−0.423(8)	0.335(7)	−0.721(6)	0.030(6)
O4	−0.093(6)	0.447(6)	−0.614(6)	0.030(6)
O5	−0.234(9)	0.056(5)	−0.826(6)	0.030(6)

Table 3
Selected distances (Å) at different pressures.

	Ambient pressure	7.11 Gpa
V–O(1)	1.66(1)	1.67(5)
V–O(2)	2.18(1)	2.09(4)
V–O(3)	1.66(1)	1.56(6)
V–O(3)	2.24(1)	2.30(6)
V–O(4)	1.98(1)	1.91(5)
V–O(5)	1.94(1)	1.99(5)
Te–O(1)	–	2.48(5)
Te–O(2)	1.84(9)	1.93(5)
Te–O(4)	1.93(8)	1.90(5)
Te–O(4)	2.30(8)	2.21(5)
Te–O(5)	1.91(1)	2.05(6)
Tl–O(1)	–	3.47(5)
Tl–O(1)	3.01(1)	2.92(5)
Tl–O(2)	2.60(9)	2.59(5)
Tl–O(2)	2.16(9)	2.73(5)
Tl–O(3)	2.92(1)	2.79(4)
Tl–O(3)	2.80(1)	2.64(6)
Tl–O(4)	3.39(1)	3.35(5)
Tl–O(5)	2.83(1)	2.70(5)
Tl–O(5)	3.10(1)	2.74(5)

to their electron lone pairs. The E pairs produce “gaps” or “tunnels” which run parallel to the crystallographic *a* axis.

Indexing and analysis of the single-crystal X-ray diffraction data on compression indicated that the crystal structure of $TlTeVO_5$ ($Pna2_1$, $Z = 4$) is stable at least to 7.11 GPa at room temperature. The same twin relationship of the two individuals is observed in all the high-pressure data. Within errors, we do not notice any changes in the orientation of the two individuals as a function of pressure. Also, their refined volume fractions do not change within estimated standard deviations.

The results of our structural refinement of the data measured at 7.11 GPa using the coordinates from our ambient-pressure model are given in Tables 1–3. The thermal displacement parameters for the Tl atom were treated anisotropically while those for the other atoms were refined isotropically. The parameters for all the O atoms were restricted to be equal.

The pressure dependence of the normalized lattice parameters and unit-cell volumes is presented in Fig. 2. $TlTeVO_5$ is the most and the least compressible along the *c* and *a* axes, respectively. The *P–V* data could be fitted by a Murnaghan equation of state with the zero-pressure bulk modulus $B_0 = 32(1)$ GPa and the unit-cell volume at ambient pressure $V_0 = 504.4(4)$ Å^3 for the first pressure derivative of the bulk modulus $B' = 7.97(43)$.

The major contribution to the bulk compressibility arises from the changes in the polyhedra around the Tl atoms as can be deduced from the comparison of relative changes of average $\langle$Tl–O$\rangle$, $\langle$Te–O$\rangle$, and $\langle$V–O$\rangle$ distances (Table 3). The latter seems to be hardly pressure dependent. The most striking effect of pressure is the apparent increase of the coordination numbers for the Tl and Te atoms (Table 3 and Fig. 3). Assuming a limiting Te–O distance of 2.5 Å and a Tl–O distance of 3.5 Å for the first coordination spheres, the coordination number for the Te atoms is increased from 4 at ambient pressure to 5 at 7.11 GPa, while the coordination number is increased from 8 to 9 for the Tl atoms. The Tl–O(1) distance nearly parallel to the [001] direction across the quasi-tunnel is the most sensitive structural feature to pressure, resulting in the anisotropic compressibility (Fig. 2). It decreases to 3.47 Å at 7.11 GPa, i.e., to the value not much larger than the longest Tl–O(4) distance at ambient pressure. Similarly, the Te–O(1) distance across the tunnel shortened to 2.48 Å at 7.11 GPa is comparable to the longest Te–O(4) distance at ambient pressure. The long Te–O distances decrease, while the short ones are constant or even become slightly longer. Overall, such a pressure-induced change of the coordination numbers and closure of the empty “tunnel” along the *a* axis are signs of increasing uniformity of the oxygen atoms surrounding the Te^{4+} and Tl^{1+} cations and of decreasing activity of their E pairs ([2–10] and references therein).

As $TlTeVO_5$ is polar, found in the polar crystal class *mm*2, it is also worthwhile to elucidate the effect of pressure on its symmetry (or pseudosymmetry). It is especially interesting to know whether the structure evolves towards centrosymmetric symmetry (as might be intuitively assumed owing to the suppression of the stereoactivity of the electron lone pair) or whether—on the contrary—the distortions from a hypothetical

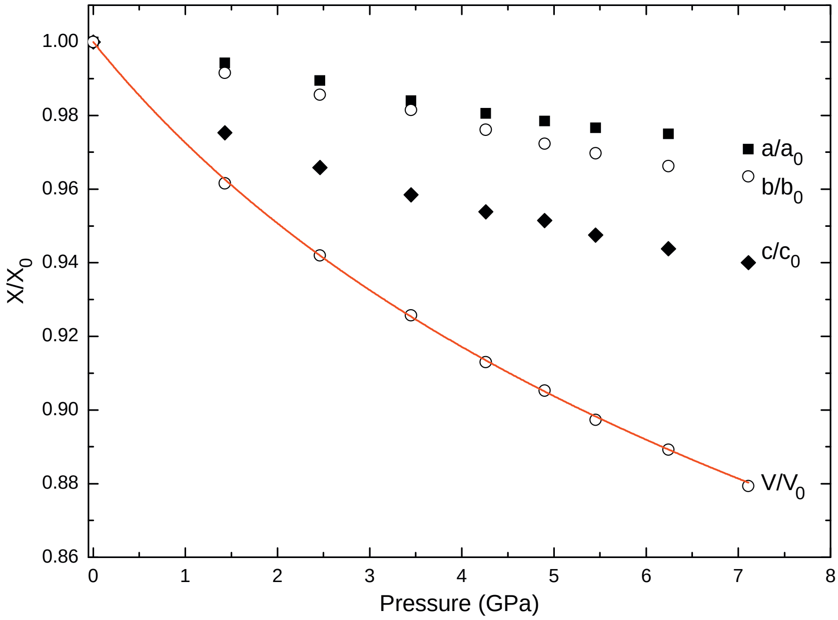

Fig. 2. Pressure dependence of normalized lattice parameters and unit-cell volumes. The solid line is the Murnaghan equation of state.

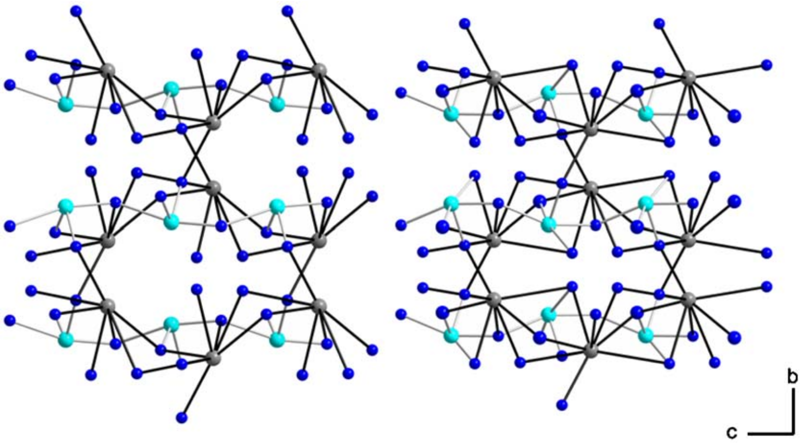

Fig. 3. Coordination spheres of the Tl and Te atoms at ambient pressure (left) and at 7.11 GPa (right). The gray, cyan, and blue symbols represent the Tl, Te, and O atoms, respectively. The Tl–O and Te–O distances below 3.5 and 2.5 Å are drawn, respectively.

centrosymmetric structure become larger. We thus analyzed the pseudosymmetry of the structure both at ambient and at high pressures using the program PSEUDO [18], available on the Bilbao Crystallographic Server.[3] The analysis shows that the structure of $TlTeVO_5$ at ambient pressure and at 7.11 GPa ($Pna2_1$, $Z = 4$) exhibits strong pseudosymmetry with respect to a centrosymmetric structure with space group *Pnna*—a minimal supergroup of $Pna2_1$. The maximal displacements of individual atoms necessary to obtain such a hypothetical centrosymmetric structure are 0.669 Å at ambient pressure and 0.618 Å at 7.11 GPa. This confirms that the effect of pressure is to increase the pseudosymmetry of the structure, i.e., the atoms are moved towards the position they would occupy in a hypothetical centrosymmetric *Pnna* structure.

4. Conclusions

The stereochemical activity of electron lone pairs on the Tl^{1+} and Te^{4+} cations in twinned $TlTeVO_5$ ($Pna2_1$, $Z = 4$) decreases upon compression resulting in the increase of the pseudosymmetry of the structure towards a non-polar structure. The increase of the coordination numbers around both cations is not associated with any pressure-induced phase transition. We are now investigating other lone-pair materials under high pressure, and will be reporting on the results in the near future.

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