

A high-pressure single-crystal synchrotron diffraction study of $\text{NH}_4\text{RbTe}_4\text{O}_9 \cdot 2\text{H}_2\text{O}$: stability of three different TeO_x coordination polyhedra

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The crystal structure of ammonium rubidium nona-oxotetra-tellurate(IV) dihydrate has been studied as a function of pressure up to 7.40 GPa. The ambient-pressure structure is characterized by the co-existence of three different Te–O polyhedra (TeO_3 , TeO_4 and TeO_5), which are connected to form layers. NH_4^+ , H_2O and Rb^+ are incorporated between the layers. Both the Rb1 position, which is located on a twofold axis, and the Rb2 position are partially occupied. The three different types of coordination polyhedra around Te^{4+} are stable up to at least 5.05 GPa. No phase transition is observed. The fit of the unit-cell volume as a function of pressure gives a zero-pressure bulk modulus of 34 (1) GPa with a zero-pressure volume of $V_0 = 2620$ (4) Å³ [$B' = 1.4$ (2)].

Comment

The high-pressure behaviour of compounds with elements containing lone-pair electrons is far from uniform (Grzechnik, 2007). While in some compounds the application of pressure leads to phase transitions in which the coordination number around the lone-pair cation is increased, *e.g.* in $\text{Bi}_2\text{Ga}_4\text{O}_9$ (Friedrich *et al.*, 2010), BiB_3O_6 (Dinnebier *et al.*, 2009) or PbS (Grzechnik & Friese, 2010*a*), in others first-order phase transitions with breaking of bonds are observed, *e.g.* lillianite ($\text{Pb}_3\text{Bi}_2\text{S}_6$; Olsen *et al.*, 2008) and heyrovskyite ($\text{Pb}_6\text{Bi}_2\text{S}_9$; Olsen *et al.*, 2011). Pressure-induced amorphization is also observed in compounds containing lone-electron pairs, *e.g.* in $\text{Bi}_4\text{M}_3\text{O}_{12}$ compounds with $M = \text{Si}$, Ge or Ti (Arora *et al.*, 2004; Meng *et al.*, 1998; Grzechnik, 2009), in Tl_2CO_3 (Grzechnik & Friese, 2008, 2010*b*) or in Tl_2MoO_4 (Machon *et al.*, 2010).

At atmospheric pressure, the coordination number (CN) of Te^{4+} cations in oxides ranges from 3 to 7 (Marukhnov *et al.*,

2007). The higher the CN the more the stereoactivity of the lone pair is suppressed. To the best of our knowledge, only two compounds containing Te^{4+} have been studied under high pressure, *viz.* TlTeVO_5 (Grzechnik *et al.*, 2009) and $(\text{NH}_4)_2\text{WTe}_2\text{O}_8$ (Grzechnik *et al.*, 2010). With increasing pressure, the CN of Te^{4+} in TlTeVO_5 is increased from 4 at ambient pressure to 5 at higher pressures, and thus follows the trend observed for many other compounds with lone-electron pairs. For $(\text{NH}_4)_2\text{WTe}_2\text{O}_8$, on the other hand, the behaviour with increasing pressure is rather unusual. In the ambient-pressure structure, two distinct Te^{4+} sites are present, both of them being fourfold coordinated by oxygen (Kim *et al.*, 2007). Surprisingly, at high pressure (5.09 GPa), the CN of one of the Te^{4+} sites is reduced from 4 to 3, resulting in two different coordination polyhedra for the two symmetrically independent Te^{4+} sites (Grzechnik *et al.*, 2010). This seems to be the only known case where the CN around a lone-pair element decreases with increasing pressure, indicating an increase in the stereoactivity of the lone pair at higher pressures.

The compound studied here, $\text{NH}_4\text{RbTe}_4\text{O}_9 \cdot 2\text{H}_2\text{O}$, is exceptional, as three different coordination polyhedra around Te^{4+} , namely TeO_3 , TeO_4 and TeO_5 (Fig. 1), exist simultaneously at ambient pressure. The three polyhedra are connected to form $[\text{Te}_4\text{O}_9]^{2-}$ layers in the *ab* plane (Fig. 2). NH_4^+ and Rb^+ cations are incorporated between the layers and provide the necessary charge balance and, in addition, water molecules are located between the layers (Kim & Halasyamani, 2008). Given the unusual behaviour of $(\text{NH}_4)_2\text{WTe}_2\text{O}_8$ under pressure and the unique structure of $\text{NH}_4\text{RbTe}_4\text{O}_9 \cdot 2\text{H}_2\text{O}$ characterized by the co-existence of three different coordination polyhedra around Te^{4+} , we thought it would be worthwhile to carry out a high-pressure study of this compound.

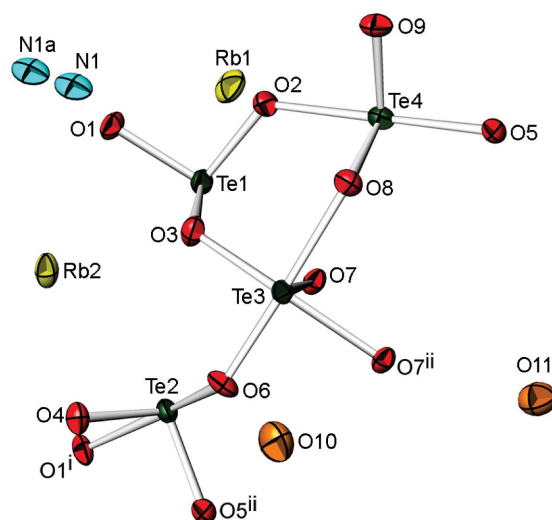


Figure 1

A view of the structure of $\text{NH}_4\text{RbTe}_4\text{O}_9 \cdot 2\text{H}_2\text{O}$ at ambient pressure, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $-x, y - \frac{1}{2}, -z + \frac{1}{2}$; (ii) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z + \frac{1}{2}$]

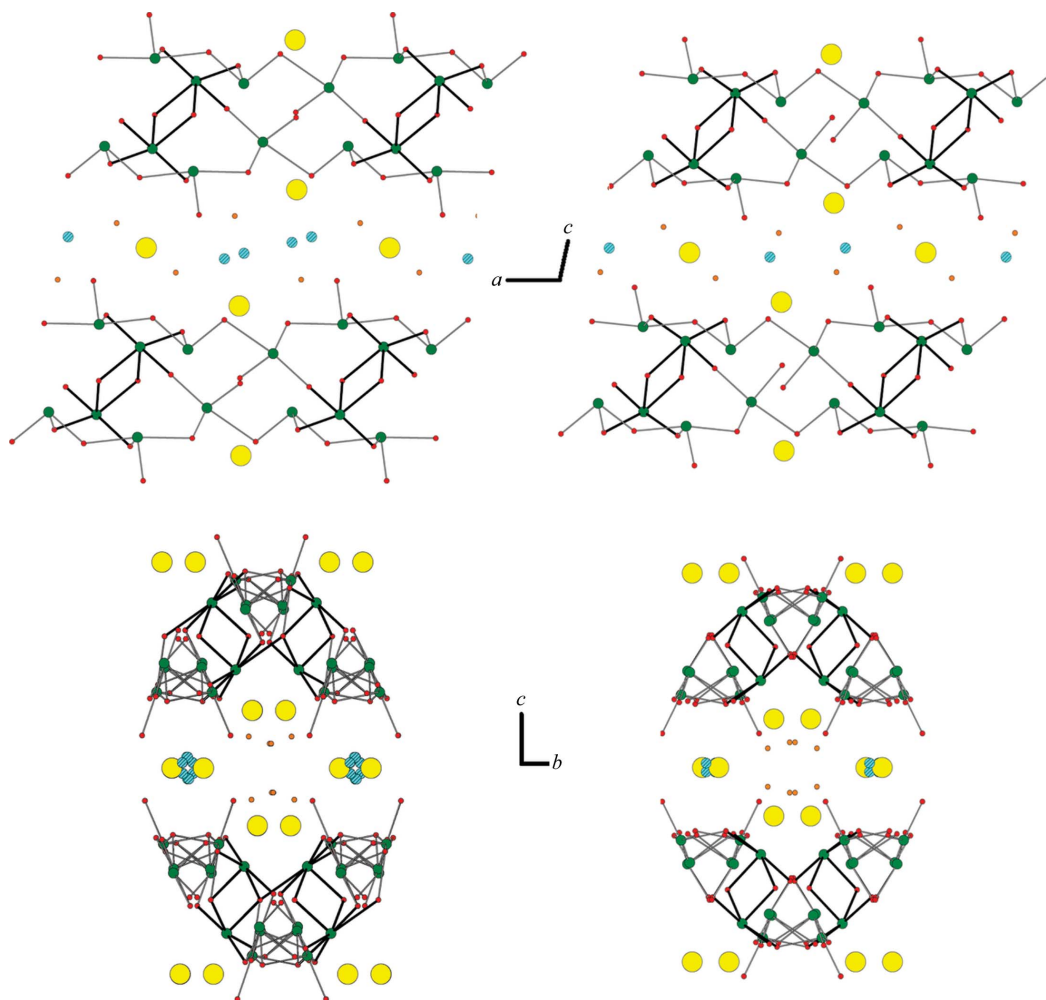


Figure 2

Partial views along [010] (top) and [100] (bottom) of the structure of $\text{NH}_4\text{RbTe}_4\text{O}_9 \cdot 2\text{H}_2\text{O}$ at ambient pressure (left) and 5.05 GPa (right). Te–O bonds are indicated. Rb^+ cations are shown as large circles (yellow in the electronic version of the paper), Te^{4+} cations as mid-sized circles (green), O atoms as small circles (red) and N atoms as mid-sized hatched hatched circles (turquoise). The relative scaling for the figures is based on the lengths of the c axes of both phases.

Measurements at ambient pressure using laboratory equipment on crystals from the same batch as those investigated earlier by Kim & Halasyamani (2008) confirm the results of the previous structure determination (see Fig. 1). However, in the earlier structure determination the Rb1 position, located on a twofold axis, is fully occupied and the Rb2 position, located on a general position, is only half occupied, whereas our refinement of the occupancy factors indicates that both Rb positions are partially occupied. In addition, in the earlier publication the N-atom position could be approximated by a single position, while our data are best approximated by assuming two atomic positions, both with an occupancy of 0.5. Refinement of the data at higher pressures does not lead to significantly different occupancy factors for Rb^+ and NH_4^+ . Only at the highest pressure at which structure refinement was carried out (5.05 GPa) is the N-atom position better approximated by a single position.

Our studies, based on synchrotron data, show that the compound is stable up to at least 5.05 GPa, and there are no indications of a structural phase transition (Fig. 3). At 7.40 GPa, only the lattice parameters could be extracted from

the experiment, but nevertheless there was no evidence for the presence of a phase transition. The unit-cell volume could be fitted with a Birch–Murnaghan equation of state (Angel, 2000) with a zero-pressure bulk modulus $B_0 = 34$ (1) GPa and a zero-pressure volume $V_0 = 2620$ (4) \AA^3 [$B' = 1.4$ (2)]. The bulk compressibility can be mainly attributed to changes in the thickness of the $[\text{Te}_4\text{O}_9]^{2-}$ layers (ambient: 7.969 \AA ; 5.05 GPa: 7.055 \AA). A comparison with other compounds containing elements with lone-pair electrons shows that the high compressibility of the title compound is comparable with that of TlTeVO_5 [32 (1) GPa; Grzechnik *et al.*, 2009], which contains both Tl^+ and Te^{4+} cations, or with the compressibilities of Tl^+ -containing compounds, *e.g.* Tl_2MoO_4 ($B_0 = 24.6$; Machon *et al.*, 2010) or Tl_2SeO_4 [$B_0 = 29$ (1); Grzechnik *et al.*, 2008].

At ambient pressure, atom Te1 is coordinated by three O atoms, atoms Te2 and Te4 by four O atoms, and atom Te3 by five O atoms (Table 1). The shapes of the coordination polyhedra around the three symmetrically independent Te^{4+} cations, as well as the average Te–O distances, do not change substantially with increasing pressure (Fig. 2 and Table 1),

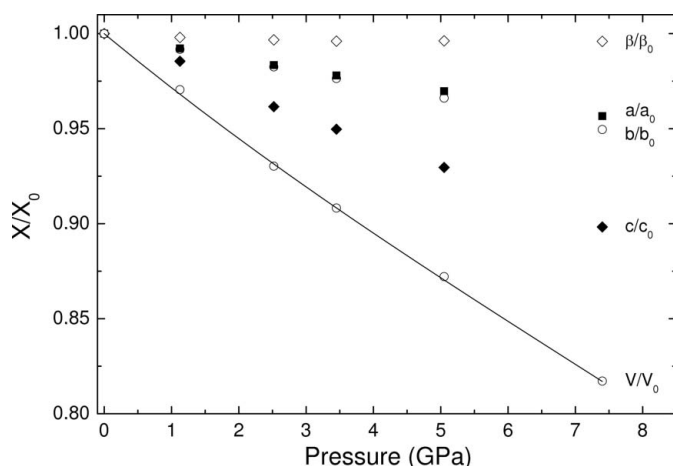


Figure 3
Relative lattice parameters and unit-cell volumes of $\text{NH}_4\text{RbTe}_4\text{O}_9 \cdot 2\text{H}_2\text{O}$ as a function of pressure. The solid line is the fit of the Birch–Murnaghan equation of state to the compressibility data.

although a detailed comparison is difficult as the s.u. values on the Te–O distances are very large for the high-pressure data. This is a consequence of the limited availability of data, due to the restricted access to reciprocal space in the diamond anvil cell experiment, which in combination with the relatively large unit cell and the low symmetry of the compound leads to a low data-to-parameter ratio. All these observations suggest that the application of pressure has no pronounced influence on the stereochemical activity of the lone pair of electrons in $\text{NH}_4\text{RbTe}_4\text{O}_9 \cdot 2\text{H}_2\text{O}$.

Experimental

Crystals of the title compound were synthesized according to the method described by Kim & Halasyamani (2008). Ambient-pressure data were measured on a crystal mounted on a glass pin on a Stoe IPDS 2T diffractometer and integrated using the *X-AREA* program (Stoe & Cie, 2006). A series of other crystals were tested on the same diffractometer and the best one was chosen for the high-pressure experiments. High-pressure data were collected at 1.13, 2.52, 3.45, 5.05 and 7.40 GPa in an Almax-type diamond anvil cell (Boehler, 2006) at room temperature on beamline D3 of the DORIS III storage ring at DESY at a wavelength of 0.3978 Å. A 0.250 mm hole was drilled into a stainless steel gasket preindented to a thickness of about 0.120 mm. A 1:1 mixture of pentane and isopentane was used as the pressure medium. The ruby luminescence method (Mao *et al.*, 1986) was used for pressure calibration. For the high-pressure measurements up to 5.05 GPa, the intensities were indexed and integrated using the program *XDS* (Kabsch, 2010). Further data treatment was carried out according to the procedures described by Posse *et al.* (2011). Reflections affected by overlap with diamond reflections or strong gasket rings were identified according to the criteria described by Friese *et al.* (2009). The faces of the crystals were optimized using the program *X-SHAPE* (Stoe & Cie, 2005) and a numerical absorption correction was applied with the program *JANA2006* (Petříček *et al.*, 2006). The data at 7.40 GPa were not of sufficient quality for structure refinement, although lattice parameters could still be extracted.

$\text{NH}_4\text{RbTe}_4\text{O}_9 \cdot 2\text{H}_2\text{O}$ at ambient pressure

Crystal data

$\text{NH}_4\text{RbTe}_4\text{O}_9 \cdot 2\text{H}_2\text{O}$
 $M_r = 793.9$
Monoclinic, $I2/a$
 $a = 18.999$ (1) Å
 $b = 6.7318$ (4) Å
 $c = 21.1835$ (11) Å
 $\beta = 101.887$ (4)°

$V = 2651.2$ (3) Å³
 $Z = 8$
Mo $K\alpha$ radiation
 $\mu = 12.41$ mm⁻¹
 $T = 293$ K
 $0.18 \times 0.12 \times 0.06$ mm

Data collection

Stoe IPDS 2T diffractometer
Absorption correction: numerical
(*JANA2006*; Petříček *et al.*, 2006)
 $T_{\min} = 0.055$, $T_{\max} = 0.226$

22317 measured reflections
4518 independent reflections
2836 reflections with $I > 3\sigma(I)$
 $R_{\text{int}} = 0.060$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.043$
 $S = 1.50$
4518 reflections

163 parameters
H-atom parameters not defined
 $\Delta\rho_{\text{max}} = 3.11$ e Å⁻³
 $\Delta\rho_{\text{min}} = -2.15$ e Å⁻³

$\text{NH}_4\text{RbTe}_4\text{O}_9 \cdot 2\text{H}_2\text{O}$ at 1.13 GPa

Crystal data

$\text{NH}_4\text{RbTe}_4\text{O}_9 \cdot 2\text{H}_2\text{O}$
 $M_r = 793.9$
Monoclinic, $I2/a$
 $a = 18.770$ (4) Å
 $b = 6.645$ (4) Å
 $c = 20.800$ (7) Å
 $\beta = 101.61$ (18)°

$V = 2541$ (3) Å³
 $Z = 8$
Synchrotron radiation
 $\lambda = 0.3978$ Å
 $\mu = 2.22$ mm⁻¹
 $T = 293$ K
 $0.22 \times 0.12 \times 0.03$ mm

Data collection

Huber four-circle diffractometer
with Marresearch MarCCD165
area detector
Absorption correction: numerical
(*JANA2006*; Petříček *et al.*, 2006)
 $T_{\min} = 0.532$, $T_{\max} = 0.786$

2941 measured reflections
987 independent reflections
987 reflections with $I > 3\sigma(I)$
 $R_{\text{int}} = 0.189$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.125$
 $wR(F^2) = 0.115$
 $S = 3.38$
987 reflections

85 parameters
H-atom parameters not defined
 $\Delta\rho_{\text{max}} = 4.36$ e Å⁻³
 $\Delta\rho_{\text{min}} = -3.28$ e Å⁻³

$\text{NH}_4\text{RbTe}_4\text{O}_9 \cdot 2\text{H}_2\text{O}$ at 2.52 GPa

Crystal data

$\text{NH}_4\text{RbTe}_4\text{O}_9 \cdot 2\text{H}_2\text{O}$
 $M_r = 793.9$
Monoclinic, $I2/a$
 $a = 18.604$ (4) Å
 $b = 6.583$ (2) Å
 $c = 20.295$ (11) Å
 $\beta = 101.5$ (2)°

$V = 2436$ (2) Å³
 $Z = 8$
Synchrotron radiation
 $\lambda = 0.3978$ Å
 $\mu = 2.22$ mm⁻¹
 $T = 293$ K
 $0.22 \times 0.12 \times 0.03$ mm

Data collection

Huber four-circle diffractometer
with Marresearch MarCCD165
area detector
Absorption correction: numerical
(*JANA2006*; Petříček *et al.*, 2006)
 $T_{\min} = 0.553$, $T_{\max} = 0.824$

3724 measured reflections
1119 independent reflections
1119 reflections with $I > 3\sigma(I)$
 $R_{\text{int}} = 0.139$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.108$
 $wR(F^2) = 0.092$
 $S = 2.97$
 1119 reflections

85 parameters
 H-atom parameters not defined
 $\Delta\rho_{\max} = 3.99 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -3.83 \text{ e } \text{\AA}^{-3}$

NH₄RbTe₄O₉·2H₂O at 3.45 GPa

Crystal data

NH₄RbTe₄O₉·2H₂O
 $M_r = 793.9$
 Monoclinic, $I2/a$
 $a = 18.501 \text{ (3) } \text{\AA}$
 $b = 6.542 \text{ (1) } \text{\AA}$
 $c = 20.045 \text{ (7) } \text{\AA}$
 $\beta = 101.41 \text{ (10)}^\circ$

$V = 2378.2 \text{ (13) } \text{\AA}^3$
 $Z = 8$
 Synchrotron radiation
 $\lambda = 0.3978 \text{ \AA}$
 $\mu = 2.22 \text{ mm}^{-1}$
 $T = 293 \text{ K}$
 $0.22 \times 0.12 \times 0.03 \text{ mm}$

Data collection

Huber four-circle diffractometer
 with Marresearch MarCCD165
 area detector
 Absorption correction: numerical
 (JANA2006; Petříček *et al.*, 2006)
 $T_{\min} = 0.554, T_{\max} = 0.824$

3087 measured reflections
 1036 independent reflections
 1036 reflections with $I > 3\sigma(I)$
 $R_{\text{int}} = 0.133$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.098$
 $wR(F^2) = 0.085$
 $S = 2.70$
 1036 reflections

85 parameters
 H-atom parameters not defined
 $\Delta\rho_{\max} = 3.43 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -2.90 \text{ e } \text{\AA}^{-3}$

NH₄RbTe₄O₉·2H₂O at 5.05 GPa

Crystal data

NH₄RbTe₄O₉·2H₂O
 $M_r = 793.9$
 Monoclinic, $I2/a$
 $a = 18.344 \text{ (4) } \text{\AA}$
 $b = 6.473 \text{ (3) } \text{\AA}$
 $c = 19.62 \text{ (1) } \text{\AA}$
 $\beta = 101.4 \text{ (2)}^\circ$

$V = 2283 \text{ (2) } \text{\AA}^3$
 $Z = 8$
 Synchrotron radiation
 $\lambda = 0.3978 \text{ \AA}$
 $\mu = 2.49 \text{ mm}^{-1}$
 $T = 293 \text{ K}$
 $0.22 \times 0.12 \times 0.03 \text{ mm}$

Data collection

Huber four-circle diffractometer
 with Marresearch MarCCD165
 area detector
 Absorption correction: numerical
 (JANA2006; Petříček *et al.*, 2006)
 $T_{\min} = 0.498, T_{\max} = 0.783$

2411 measured reflections
 645 independent reflections
 644 reflections with $I > 3\sigma(I)$
 $R_{\text{int}} = 0.229$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.119$
 $wR(F^2) = 0.096$
 $S = 3.13$
 645 reflections
 82 parameters

1 restraint
 H-atom parameters not defined
 $\Delta\rho_{\max} = 3.87 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -3.50 \text{ e } \text{\AA}^{-3}$

Coordinates from Kim & Halasyamani (2008) were used as a starting model. Correction factors for resonant scattering were taken from the DABAX library (<http://www.esrf.eu/UsersAndScience/Experiments/TBS/SciSoft/xop2.3/Main>). For the refinement at ambient pressure, all atoms were treated anisotropically. Occupancies for the Rb positions were refined, but restrained to give a full occupancy per formula unit. For N, the assumption of one single

Table 1

Te—O distances (Å) below 2.4 Å as a function of pressure (GPa).

| | Ambient | 1.13 | 2.52 | 3.45 | 5.05 |
|----------------------|-----------|----------|----------|----------|----------|
| Te1—O1 | 1.879 (7) | 1.87 (7) | 1.86 (5) | 1.89 (5) | 1.91 (8) |
| Te1—O2 | 1.949 (6) | 1.84 (5) | 1.94 (4) | 1.95 (4) | 1.86 (6) |
| Te1—O3 | 1.924 (6) | 1.87 (4) | 1.91 (3) | 2.01 (3) | 2.07 (6) |
| Te2—O1 ⁱ | 2.343 (6) | 2.17 (5) | 2.21 (3) | 2.16 (3) | 2.19 (5) |
| Te2—O4 | 1.849 (7) | 1.92 (7) | 1.87 (5) | 1.90 (5) | 2.05 (9) |
| Te2—O5 ⁱⁱ | 1.893 (7) | 1.85 (6) | 1.88 (4) | 1.88 (4) | 1.94 (7) |
| Te2—O6 | 2.012 (6) | 2.09 (5) | 1.99 (4) | 2.00 (4) | 2.09 (6) |
| Te3—O3 | 2.033 (7) | 2.05 (5) | 1.99 (3) | 2.00 (4) | 2.03 (7) |
| Te3—O6 | 1.968 (6) | 1.90 (5) | 2.00 (3) | 2.02 (4) | 1.95 (6) |
| Te3—O7 | 1.925 (6) | 1.99 (7) | 1.95 (5) | 2.01 (5) | 1.92 (8) |
| Te3—O7 ⁱⁱ | 2.161 (7) | 2.14 (7) | 2.13 (5) | 2.08 (5) | 2.08 (8) |
| Te3—O8 | 2.275 (6) | 2.21 (5) | 2.23 (3) | 2.25 (3) | 2.13 (5) |
| Te4—O2 | 2.127 (7) | 2.09 (4) | 2.05 (3) | 2.07 (3) | 2.04 (5) |
| Te4—O5 | 2.202 (7) | 2.22 (4) | 2.22 (3) | 2.15 (3) | 2.09 (4) |
| Te4—O8 | 1.882 (6) | 1.87 (4) | 1.90 (3) | 1.87 (3) | 1.85 (4) |
| Te4—O9 | 1.839 (7) | 1.71 (8) | 1.83 (5) | 1.84 (5) | 1.74 (9) |

Symmetry codes: (i) $-x, y - \frac{1}{2}, -z + \frac{1}{2}$; (ii) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z + \frac{1}{2}$.

position as in Kim & Halasyamani (2008) led to very large displacement parameters. Therefore, split atom positions were introduced. Refinement of occupancy factors led to an equal occupancy for both positions and these were fixed to 0.5 in the final refinement cycles. As only some of the H atoms could be located in the difference Fourier maps, H atoms were not included in the model.

For the high-pressure data, measured at the synchrotron, Te atoms were refined anisotropically, and Rb, O and N atoms were refined isotropically. Occupancy factors for Rb and N atoms were fixed at the ambient-pressure values for all pressures, as trial refinements showed no significant deviations. The displacement parameters of the O atoms forming the coordination polyhedra of Te were restrained to be equal, as were those of the two water O atoms (O10 and O11).

The relatively large positive and negative residual densities for the high-pressure data can be explained by the experimental set up, as not all parts of reciprocal space were accessible. The high-pressure data are also affected by larger experimental errors than the ambient-pressure data. This might lead to artefacts in the electron density. The respective difference density maxima/minima distances from the closest atom sites are: 0.403 Å from Rb1 and 1.544 Å from Te1 at ambient pressure; 0.481 Å from Rb1 and 1.480 Å from Te1 at 1.13 GPa; 0.552 Å from Rb1 and 1.420 Å from Te1 at 2.52 GPa; 0.700 Å from Rb2 and 1.64 Å from O2 at 3.45 GPa; 1.48 Å from O11 and 1.60 Å from O11 at 5.05 GPa.

Data collection: *X-AREA* (Stoe & Cie, 2006) at ambient pressure; *Automar* (Marresearch, 2009) at 1.13, 2.52, 3.45 and 5.05 GPa. Cell refinement: *X-AREA* at ambient pressure; *XDS* (Kabsch, 2010) at 1.13, 2.52, 3.45 and 5.05 GPa. Data reduction: *X-AREA* and *JANA2006* (Petříček *et al.*, 2006) at ambient pressure; *XDS* and *JANA2006* at 1.13, 2.52, 3.45 and 5.05 GPa. At all pressures, method used to solve structure: coordinates from Kim & Halasyamani (2008); program(s) used to refine structure: *JANA2006*; molecular graphics: *ATOMS* (Dowty, 1999); software used to prepare material for publication: *JANA2006*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LG3063). Services for accessing these data are described at the back of the journal.

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