



Rapid communication

A rare multi-coordinate tellurite, $\text{NH}_4\text{ATe}_4\text{O}_9 \cdot 2\text{H}_2\text{O}$ ($A = \text{Rb}$ or Cs): The occurrence of TeO_3 , TeO_4 , and TeO_5 Polyhedra in the same material

Jun-Ho Kim, P. Shiv Halasyamani*

Department of Chemistry, University of Houston, 136 Fleming Building, Houston, TX 77204-5003, USA

ARTICLE INFO

Article history:

Received 13 March 2008

Received in revised form

18 April 2008

Accepted 23 April 2008

Available online 7 May 2008

Keywords:

Hydrothermal synthesis

Tellurites

Layered compounds

Stereo-active lone-pair

ABSTRACT

Two new tellurites, $\text{NH}_4\text{RbTe}_4\text{O}_9 \cdot 2\text{H}_2\text{O}$ and $\text{NH}_4\text{CsTe}_4\text{O}_9 \cdot 2\text{H}_2\text{O}$ have been synthesized and characterized. The compounds were synthesized hydrothermally, in near quantitative yields, using the alkali metal halide, TeO_2 , and NH_4OH as reagents. The iso-structural materials exhibit layered, two-dimensional structural topologies consisting of TeO_x ($x = 3, 4$, or 5) polyhedra separated by NH_4^+ , H_2O , Rb^+ or Cs^+ cations. Unique to these materials is the presence of TeO_3 , TeO_4 , and TeO_5 polyhedra. Thermogravimetric and infrared spectroscopic data are also presented. Crystal data: $\text{NH}_4\text{RbTe}_4\text{O}_9 \cdot 2\text{H}_2\text{O}$: Monoclinic $I2/a$ (no. 15), $a = 18.917(3)\text{Å}$, $b = 6.7002(11)\text{Å}$, $c = 21.106(5)\text{Å}$, $\beta = 101.813(2)^\circ$, $V = 2618.5(9)\text{Å}^3$, $Z = 8$; $\text{NH}_4\text{CsTe}_4\text{O}_9 \cdot 2\text{H}_2\text{O}$: Monoclinic $I2/a$ (no. 15), $a = 18.9880(12)\text{Å}$, $b = 6.7633(4)\text{Å}$, $c = 21.476(2)\text{Å}$, $\beta = 102.3460(10)^\circ$, $V = 2694.2(3)\text{Å}^3$, $Z = 8$.

© 2008 Elsevier Inc. All rights reserved.

1. Introduction

The stereo-active lone-pair observed in Se^{4+} , Sn^{2+} , Sb^{3+} , Te^{4+} , etc., cations in oxide coordination, profoundly influences not only their local coordination, but also the macroscopic crystallographic symmetry [1,2]. The stereo-active lone-pair itself has a rich and fascinating history. The original work of Sidgwick and Powell [3] followed by the valence shell electron pair repulsion (VSEPR) theory of Gillespie and Nyholm [4] attempted to rationalize the coordination geometry of the lone-pair cation. It was Orgel [5], however, who explained the structural distortion and polarization through the mixing of the metal cation s and p orbitals. Recently, this traditional view of the metal cation s - p orbital mixing has been shown to be incomplete. Watson and Parker [6,7], Lefebvre et al. [8,9], Spaldin, Seshadri et al. [10,11], Mudring and Rieger [12] and Woodward et al. [13], have shown that the oxide anion plays an important role in the lone-pair formation. Specifically, these researchers argue that the interaction of the s and p orbitals of the metal cation with the oxide anion p states is critical for lone-pair formation. The observed lone-pair, sometimes referred to as a non-bonding electron pair or an inert pair [13], has profound structural implications [1,2,14,15].

The occurrence of a stereo-active lone-pair imparts polarity to the metal oxide polyhedron, that is the AO_xE ($A =$ lone-pair cation and $E =$ stereo-active lone-pair) has a dipole moment. If, in a solid-state structure, the dipole moments are aligned the material

in question will also be crystallographically polar, exhibiting the correct symmetry for technologically important properties such as ferroelectricity, pyroelectricity, and piezoelectricity [16]. If, however, as often the case the lone-pair polyhedra align in an anti-parallel manner, a centrosymmetric structure is observed.

With the lone-pair cations, a variety of oxide coordination environments are observed. For Se^{4+} , SeO_3 polyhedra are always observed, whereas with Sb^{3+} both SbO_3 and SbO_4 groups are found. Interestingly for Te^{4+} , TeO_3 , TeO_4 , and TeO_5 polyhedra occur, all of which are distorted, attributable to the stereo-active lone-pair. Different metal coordination environments for the same cation in the same compound do occasionally occur, but are limited to two different coordination environments, usually three and four. What has not been observed is the same cation in three different coordination environments, specifically TeO_3 , TeO_4 and TeO_5 polyhedra, in the same material. We report here rare examples of tellurites exhibiting three different coordination environments within the same compound. The synthesis, structure, and characterization of $\text{NH}_4\text{ATe}_4\text{O}_9 \cdot 2\text{H}_2\text{O}$ ($A = \text{Rb}$ or Cs) are reported.

2. Experimental

Single crystals of $\text{NH}_4\text{RbTe}_4\text{O}_9 \cdot 2\text{H}_2\text{O}$ and $\text{NH}_4\text{CsTe}_4\text{O}_9 \cdot 2\text{H}_2\text{O}$ were obtained by hydrothermal reactions. RbCl (2.75 mmol, 99%, Aldrich), or CsCl (2.75 mmol, 99%, Aldrich), TeO_2 (1.65 mmol, 99% Aldrich) and 2 mL of NH_4OH (30% EM Science) were loaded in separate 23 mL Teflon-lined autoclaves. The autoclaves were

* Corresponding author. Fax: +1713 743 0796.

E-mail address: psh@uh.edu (P.S. Halasyamani).

closed, gradually heated to 230 °C, held for 2 days, cooled slowly to 100 °C at 6 °C h⁻¹ and cooled to room temperature over 10 h. Colorless square plate-shaped crystals, the only products from the reactions, subsequently shown to be NH₄RbTe₄O₉·2H₂O and NH₄CsTe₄O₉·2H₂O, were obtained after filtration in 80% and 90% yields based on TeO₂, respectively. IR (KBr, cm⁻¹): 3400 (ν_{N-H}), 3170 (ν_{O-H}), 1670 (ν_{O-H}), 770 (ν_{Te-O}), 702 (ν_{Te-O}), 674 (ν_{Te-O}), 639 (ν_{Te-O}), 593 (ν_{Te-O}). Thermogravimetric measurements, on both materials, indicated that the H₂O molecules are lost around 190 °C (Rb phase) and 50 °C (Cs phase). Rapid weight loss events occur above this temperature resulting in the decomposi-

tion of the materials to amorphous phases (see Supporting Information).

2.1. Single crystal X-ray diffraction

For NH₄RbTe₄O₉·2H₂O and NH₄CsTe₄O₉·2H₂O, data were collected using a Siemens SMART diffractometer equipped with a 1 K CCD area detector using graphite monochromated MoK α radiation [17]. A hemisphere of data was collected using a narrow-frame method with scan widths of 0.30°, and an exposure time of

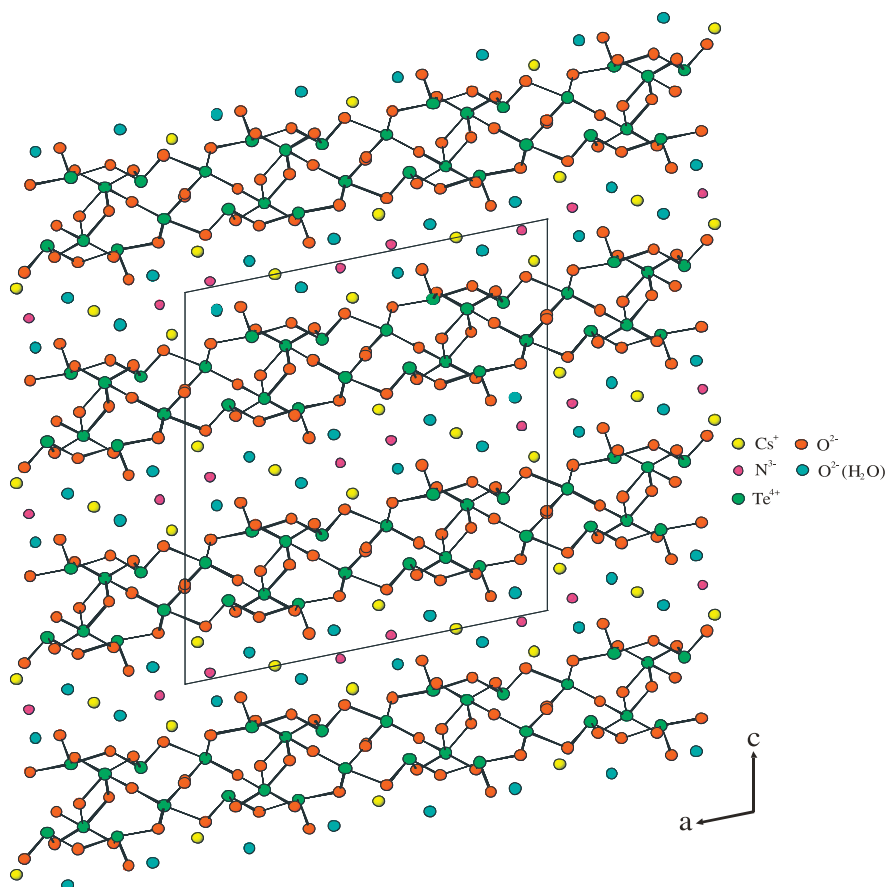


Fig. 1. Ball-and-stick representation of NH₄CsTe₄O₉·2H₂O. Note how the tellurite layers are separated by NH₄⁺ and Cs⁺ cations, as well as H₂O molecules.

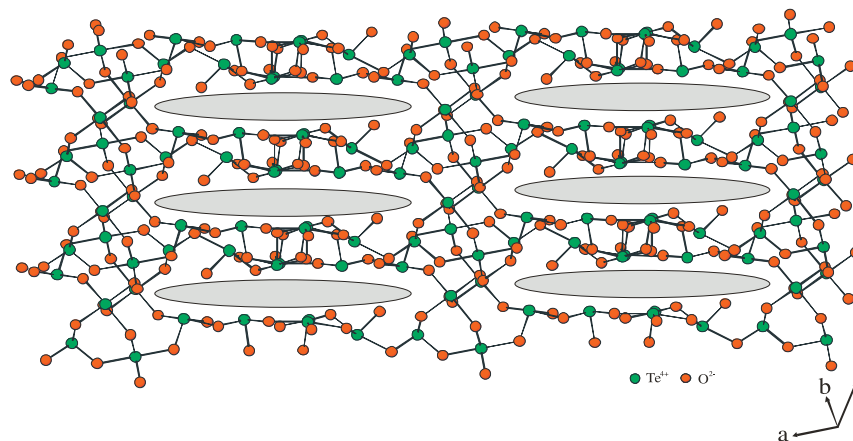


Fig. 2. Ball-and-stick representation of one layer of NH₄CsTe₄O₉·2H₂O. The NH₄⁺ and Cs⁺ cations, and H₂O molecules have been removed for clarity. The gray ovals represent voids in the layer created by the stereo-active lone-pairs on the Te⁴⁺ cations.

25 s per frame. The first 50 frames were remeasured at the end of the data collection to monitor instrument and crystal stability. The maximum correction applied to the intensities was <1%. The data were integrated using the Siemens SAINT program [18], with the intensities corrected for Lorentz, polarization, air absorption, and absorption attributable to the variation in the path length through the detector faceplate. ψ -scans were used for the absorption correction on the hemisphere of data. The data were solved and refined using SHELXS-97 [19] and SHELXL-97 [20], respectively. All of the atoms were refined with anisotropic thermal parameters and converged for $I > 2(I)$. All calculations were performed using the WinGX-98 crystallographic software package [21]. Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de) on quoting the depository nos. CSD-418572 and CSD-418573.

3. Results and discussion

$\text{NH}_4\text{ATe}_4\text{O}_9 \cdot 2\text{H}_2\text{O}$ ($A = \text{Rb}$ or Cs) are iso-structural, with both materials exhibiting layered structures, that consist of linked TeO_3 , TeO_4 , and TeO_5 polyhedra separated by NH_4^+ , Rb^+ or Cs^+ cations (see Fig. 1). A unique feature of these materials is the occurrence of TeO_3 , TeO_4 , and TeO_5 polyhedra within the same material. The three polyhedra form a $[\text{Te}_4\text{O}_9]^{2-}$ layer that can be better formulated in connectivity terms as $[(\text{TeO}_{3/2})^+ \cdot 2(\text{TeO}_{3/2}\text{O}_{1/1})^- \cdot (\text{TeO}_{5/2})^-]^{2-}$ with charge balance maintained by the NH_4^+ and alkali metal. Hydrogen bonding interactions are observed between the $[\text{Te}_4\text{O}_9]^{4-}$ anionic layers and the NH_4^+ cations and H_2O molecules. The layers themselves are quite puckered attributable to the lone-pairs (see Fig. 2). Also, as seen in Fig. 2, voids are observed in the structure. The voids are created by the ‘clustering’ of the lone-pairs. This type of ‘clustering’ has been observed previously [22].

The Te–O bond distances and angles for $\text{NH}_4\text{RbTe}_4\text{O}_9 \cdot 2\text{H}_2\text{O}$ and $\text{NH}_4\text{CsTe}_4\text{O}_9 \cdot 2\text{H}_2\text{O}$ are very similar. The Te–O bond distances for the Rb-phase range from 1.829(9) to 2.330(9) Å, whereas for the Cs-phase the analogous distances are between 1.837(5) and

2.326(5) Å. The bond angle ranges of the TeO_3 , TeO_4 , and TeO_5 polyhedra are, not surprisingly, substantially different, but similar between the Rb- and Cs-phases. For both materials, with the TeO_3 polyhedra the O–Te–O bond angles range from 91.1(4)° to 94.9(4)°, whereas for the TeO_4 polyhedra the O–Te–O bond angles are between 78.5(4)° and 177.2(2)°. Finally for the TeO_5 polyhedra the bond angles range from 74.6(4)° to 177.5(2)°. Bond valence [23,24] calculations on the reported materials result in values between 3.6 and 4.1 for the Te^{4+} cations.

The unique and novel feature of $\text{NH}_4\text{ATe}_4\text{O}_9 \cdot 2\text{H}_2\text{O}$ ($A = \text{Rb}$ and Cs) is the occurrence of all three TeO_3 , TeO_4 , and TeO_5 polyhedra. This is extremely rare with respect to tellurites. In other reported tellurites, the Te^{4+} coordination is limited to one or two coordination environments [25–34]. There has been a report of a tellurium oxy-halide that contains TeO_3 , TeO_4 , and TeO_5 polyhedra [35]. In the reported materials each Te^{4+} cation exhibits a stereo-active lone-pair placing the cation in a locally asymmetric and polar coordination environment. Using a methodology described earlier [36–38], we were able to calculate the magnitude of the local dipole moment of the polyhedra (see Fig. 3 and Table 1, and Supporting Information). We observe a slight decrease in the magnitude of the dipole moment with increasing oxide coordination. The direction of the dipole moment is estimated to be in the opposite direction of the stereo-active lone-pair.

As stated, the occurrence of the stereo-active lone-pair imparts polarity to the tellurite polyhedra. Within each layer, however, the various dipole moments are pointed in an anti-parallel manner. This anti-parallel arrangement results in a centrosymmetric structure (see Fig. 4).

Table 1

Magnitudes of the dipole moment for the TeO_3 , TeO_4 , and TeO_5 polyhedra (D = Debyes)

	$\text{NH}_4\text{RbTe}_4\text{O}_9 \cdot 2\text{H}_2\text{O}$	$\text{NH}_4\text{CsTe}_4\text{O}_9 \cdot 2\text{H}_2\text{O}$
TeO_3	10.41 D	10.25 D
TeO_4	9.66 D	9.89 D
TeO_4	9.26 D	8.85 D
TeO_5	8.98 D	8.84 D

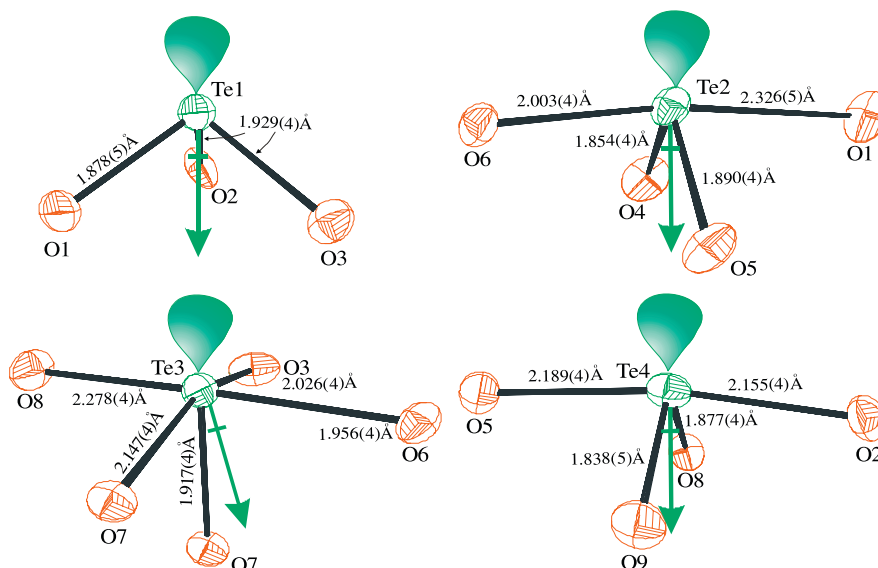


Fig. 3. ORTEP (50% probability ellipsoids) for the TeO_3 , TeO_4 , and TeO_5 polyhedra in $\text{NH}_4\text{CsTe}_4\text{O}_9 \cdot 2\text{H}_2\text{O}$ are shown. The stereo-active lone-pair is depicted schematically, and the approximate direction of the dipole moment is given.

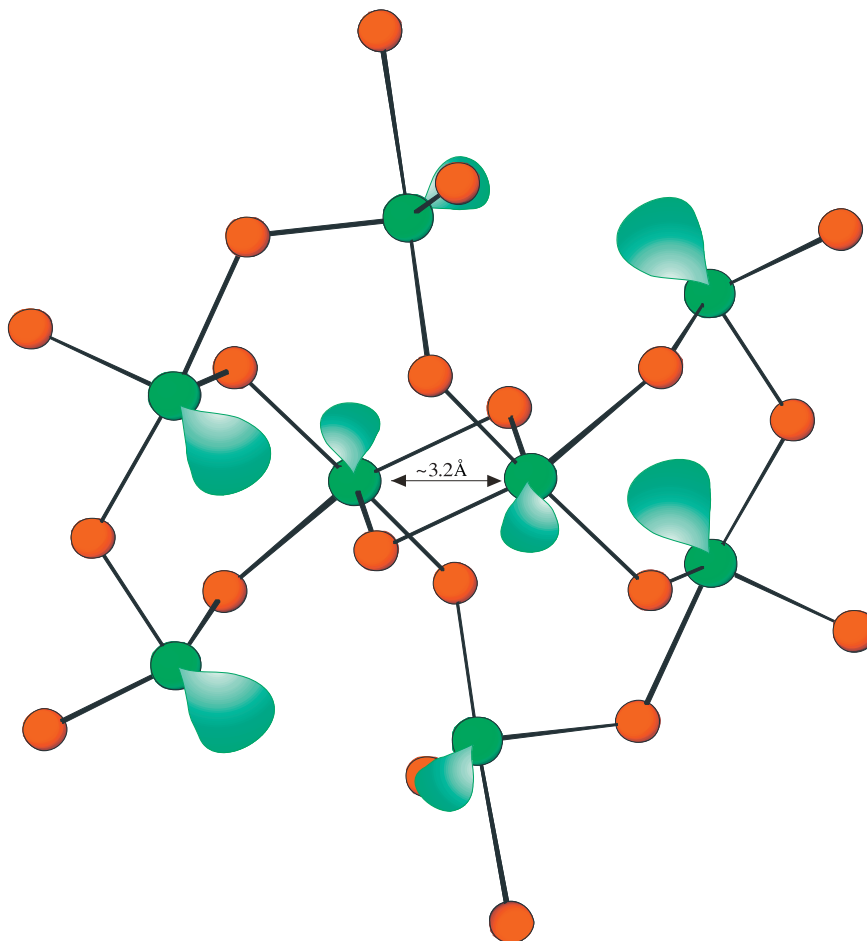


Fig. 4. Ball-and-stick representation of the TeO_3 , TeO_4 , and TeO_5 polyhedra in $\text{NH}_4\text{CsTe}_4\text{O}_9 \cdot 2\text{H}_2\text{O}$. The closest Te-Te contact is 3.2 Å. Note how the stereo-active lone-pairs point in opposite directions.

The question of why the local polarity is not retained in the solid-state structure is relevant. With materials containing a lone-pair cation it is not unusual for the compound to crystallize in a polar space group, that is having the lone-pairs aligned. With $\text{NH}_4\text{ATE}_4\text{O}_9 \cdot 2\text{H}_2\text{O}$ ($A = \text{Rb}$ or Cs) there is a large 'concentration' of lone-pairs in the structure. It is suggested that in order to minimize lone-pair–lone-pair interactions, the lone-pairs point in opposite directions resulting in a centrosymmetric structure.

In conclusion, we have reported the first examples of a tellurite exhibiting TeO_3 , TeO_4 , and TeO_5 polyhedra in the same structure. The materials were synthesized hydrothermally and in high yields. We are in the process of expanding our efforts to determine if additional materials can be synthesized that contain multi-coordinate lone-pair polyhedra.

Acknowledgement

We thank the Robert A. Welch Foundation, the Texas Center for Superconductivity, the ACS PRF 47345-AC10, and the NSF (DMR-0652150) for support.

Appendix A. Supporting material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2008.04.032.

References

- [1] Z. Mayerova, M. Johnsson, S. Lidin, *Angew. Chem. Int. Ed.* 45 (2006) 5602–5606.
- [2] P.S. Halasyamani, *Chem. Mater.* 16 (2004) 3586–3592.
- [3] N.V. Sidgwick, H.M. Powell, *Proc. R. Soc. London Ser. A* 176 (1940) 153–180.
- [4] R.J. Gillespie, R.S.Q. Nyholm, *Rev. Chem. Soc.* 11 (1957) 339–380.
- [5] L.E. Orgel, *J. Chem. Soc.* (1959) 3815–3819.
- [6] G.W. Watson, S.C. Parker, *J. Phys. Chem. B* 103 (1999) 1258–1262.
- [7] G.W. Watson, S.C. Parker, G. Kresse, *Phys. Rev. B* 59 (1999) 8481–8486.
- [8] I. Lefebvre, M. Lannoo, G. Allan, A. Ibanez, J. Fourcade, J.C. Jumas, *Phys. Rev. Lett.* 59 (1987) 2471–2474.
- [9] I. Lefebvre, M.A. Szymanski, J. Olivier-Fourcade, J.C. Jumas, *Phys. Rev. B* 58 (1998) 1896–1906.
- [10] R. Seshadri, N.A. Hill, *Chem. Mater.* 13 (2001) 2892–2899.
- [11] U.V. Waghmare, N.A. Spaldin, H.C. Kandpal, R. Seshadri, *Phys. Rev. B* 67 (2003) 12511–1–12511–10.
- [12] A.-V. Mudring, F. Rieger, *Inorg. Chem.* 44 (2005) 6240–6243.
- [13] M.W. Stoltzfus, P.M. Woodward, R. Seshadri, J.-H. Klepeis, B. Bursten, *Inorg. Chem.* 46 (2007) 3839–3850.
- [14] Z. Mayerova, M. Johnsson, S.J. Lidin, *Solid State Chem.* 178 (2005) 3471–3475.
- [15] Z. Mayerova, M. Johnsson, S. Lidin, *Solid State Sci.* 8 (2006) 849–854.
- [16] J.F. Nye, *Physical Properties of Crystals*, Oxford University Press, Oxford, 1957.
- [17] Crystal data for $\text{NH}_4\text{RbTe}_4\text{O}_9 \cdot 2\text{H}_2\text{O}$: colorless square plate-shaped crystal ($0.03 \times 0.04 \times 0.07 \text{ mm}^3$), $M_r = 793.94$, monoclinic $I2/a$ (no. 15), $a = 18.917(3) \text{ \AA}$, $b = 6.7002(11) \text{ \AA}$, $c = 21.106(5) \text{ \AA}$, $\beta = 101.813(2)^\circ$, $V = 2618.5(9) \text{ \AA}^3$, $Z = 8$, $\rho_{\text{calcd}} = 4.028 \text{ g cm}^{-3}$, $\mu = 125.63 \text{ cm}^{-1}$, $2\theta_{\text{max}} = 56.16^\circ$, 7888 reflections measured, 3107 unique ($R_{\text{int}} = 0.1234$), $R_1 = 0.0524$, $wR_2 = 0.1467$ [for $I > 2\sigma(I)$], GOF = 1.056 for 155 parameters. Crystal data for $\text{NH}_4\text{CsTe}_4\text{O}_9 \cdot 2\text{H}_2\text{O}$: colorless square plate-shaped crystal ($0.02 \times 0.05 \times 0.08 \text{ mm}^3$), $M_r = 841.38$, monoclinic $I2/a$ (no. 15), $a = 18.9880(12) \text{ \AA}$, $b = 6.7633(4) \text{ \AA}$, $c = 21.476(2) \text{ \AA}$, $\beta = 102.3460(10)^\circ$, $V = 2694.2(3) \text{ \AA}^3$, $Z = 8$, $\rho_{\text{calcd}} = 4.149 \text{ g cm}^{-3}$, $\mu = 112.84 \text{ cm}^{-1}$, $2\theta_{\text{max}} = 56.56^\circ$, 8170 reflections measured, 3209 unique ($R_{\text{int}} = 0.0350$), $R_1 = 0.0287$, $wR_2 = 0.0600$ [for $I > 2\sigma(I)$], GOF = 0.956 for 159 parameters. Data collection: Siemens SMART area detector, MoK α radiation ($\lambda = 0.71073 \text{ \AA}$), $T = 293 \text{ K}$.

- [18] SAINT; 4.05 ed., Siemens Analytical X-ray Systems, Inc., Madison, WI, 1995.
- [19] G.M. Sheldrick, SHELXS-97—A program for automatic solution of crystal structures, University of Goettingen, Goettingen, Germany, 1997.
- [20] G.M. Sheldrick, SHELXL-97—A program for crystal structure refinement, University of Goettingen, Goettingen, 1997.
- [21] L.J. Farrugia, *J. Appl. Crystallogr.* 32 (1999) 837.
- [22] M. Johnston, W.T.A. Harrison, *J. Am. Chem. Soc.* 124 (2002) 4576–4577.
- [23] I.D. Brown, D. Altermatt, *Acta Crystallogr. Sec. B* 41 (1985) 244–247.
- [24] N.E. Brese, M. Okeeffe, *Acta Crystallogr. Sec. B* 47 (1991) 192–197.
- [25] V. Balraj, K. Vidyasagar, *Inorg. Chem.* 37 (1998) 4764–4774.
- [26] V. Balraj, K. Vidyasagar, *Inorg. Chem.* 38 (1999) 1394.
- [27] M. Dutreilh, P. Thomas, J.C. Champarnaud-Mesjard, B. Frit, *Solid State Sci.* 3 (2001) 423.
- [28] H.S. Ra, K.M. Ok, P.S. Halasyamani, *J. Am. Chem. Soc.* 125 (2003) 7764–7765.
- [29] E.O. Chi, K.M. Ok, Y. Porter, P.S. Halasyamani, *Chem. Mater.* 18 (2006) 2070–2074.
- [30] Y.-L. Shen, H.-L. Jiang, J. Xu, J.-G. Mao, K.W. Cheah, *Inorg. Chem.* 44 (2005) 9314–9321.
- [31] H.-L. Jiang, M.-L. Feng, J.-G. Mao, *J. Solid State Chem.* 179 (2006) 1911–1917.
- [32] H.-L. Jiang, F. Kong, J.-G. Mao, *J. Solid State Chem.* 180 (2007) 1764–1769.
- [33] H.-L. Jiang, Z. Xie, J.-G. Mao, *Inorg. Chem.* 46 (2007) 6495–6501.
- [34] F. Kong, H.-L. Jiang, J.-G. Mao, *J. Solid State Chem.* 181 (2008) 263–268.
- [35] H.-L. Jiang, J.-G. Mao, *Inorg. Chem.* 45 (2006) 717–721.
- [36] P.A. Maggard, T.S. Nault, C.L. Stern, K.R. Poeppelmeier, *J. Solid State Chem.* 175 (2003) 27–33.
- [37] H.K. Izumi, J.E. Kirsch, C.L. Stern, K.R. Poeppelmeier, *Inorg. Chem.* 44 (2005) 884–895.
- [38] K.M. Ok, P.S. Halasyamani, *Inorg. Chem.* 44 (2005) 3919–3925.