Short Communication

Crystal Structure of Sodium Ditellurite, Na$_4$Te$_4$O$_{10}$

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We are interested in determining the structure of tellurite glasses modified with alkali oxide, $(M_2O)_x(TeO_2)_{1-x}$ (where M = Li, Na, K, Rb). The addition of sodium oxide leads to a particularly interesting glass-forming system[1–4] which has been studied by many methods including NMR,[5] IR,[1] Raman[6] and Mösssbauer[7] spectroscopies. Structures of the crystalline phases are useful guides in the interpretation of glass studies and supplement what is known about the architecture of tellurium oxide networks. Crystalline phases in the $(Na_2O)_x(TeO_2)_{1-x}$ system exist at $x=0.0$ (TeO$_2$), $x=0.20$ (Na$_2$Te$_4$O$_9$), $x=0.33$ (Na$_4$Te$_4$O$_{10}$) and $x=0.50$ (Na$_2$TeO$_3$).[8] Prior to our study of this system, only the structures of TeO$_2$[9,10] and Na$_2$TeO$_3$[11] had been determined. In an earlier paper, we described crystalline Na$_2$Te$_4$O$_9$,[12] and we report here the structure of sodium ditellurite Na$_4$Te$_4$O$_{10}$ as determined by X-ray crystallography.

Experimental

Sample preparation. Na$_4$Te$_4$O$_{10}$ was prepared from stoichiometric amounts of tellurium(IV) oxide (TeO$_2$, 99.995%, Aldrich) and sodium carbonate (99.995+%, Aldrich). The mixture was placed in a silica glass tube, heated at 750 °C for ca. 8 min, and then poured onto a stainless steel plate. Pieces of the resulting colorless glass were melted in a silica glass boat at 575 °C for 90 min and cooled at about 1 °C min^{-1} to 460 °C. The sample was kept at this temperature for 4 days and then cooled to 400 °C in 5 or 10 °C increments (ca. 1 °C min^{-1}) during the next 2 days. Finally, the sample was slowly cooled to room temperature.

X-Ray structure determination of Na$_4$Te$_4$O$_{10}$. Colorless crystals were obtained from the melt as described above. Several samples were removed from the boat and cleaved

to small fragments, but all exhibited splitting or twinning to some degree. Eventually, a small crystal (dimensions 0.08 × 0.10 × 0.12 mm) was cleaved from a larger sample which was twinned only to a minor degree (ca. 10%). The selected sample was transferred to the goniostat where it was cooled to −170 °C for characterization and data collection. A systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima corresponding to a monoclinic space group, either $C\,2/c$ or Cc. Subsequent solution and refinement confirmed the centrosymmetric $C\,2/c$ choice (Table 1).

Data were collected using a continuous θ, 2θ scan with fixed background counts at each extreme of the scan. Intensities were corrected for Lorentz and polariza-

Table 1. Crystallographic data.

Crystal data	
Molar mass (Na$_4$Te$_4$O$_{10}$)	762.36
Crystal system	Monoclinic
a/Å	23.465(6)
b/Å	4.877(1)
c/Å	9.691(2)
V/Å^3	1081.38
Space group	$C\,2/c$
	(No. 15)[13]
β/°	102.81(1)
ρ_{calc}/g cm^{-3}	4.682
Z (molecules/cell)	4
Linear abs. coeff./cm^{-1}	54.565
Data collection	
T/°C	−170
2θ min, max/°	6, 60
Mo $K\alpha$ λ/Å	0.71069
Obsd. data, $I>2.33\sigma(I)$	1132
Refinement	
No. of parameters	81
$\Delta\rho$(max)/e Å^{-3}	1.9
R_w	0.0459
Goodness of fit	1.682
R	0.0446
R_{merge}	0.092

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tion effects and equivalent data were averaged. The structure was readily solved by direct methods (MULTAN78) and standard Fourier techniques. A final difference Fourier was essentially featureless, the largest peaks being in the vicinity of the tellurium atoms. Data regarding the thermal parameters for $Na_4Te_4O_{10}$ (1 p.) and the observed and calculated structure factors for $Na_4Te_4O_{10}$ (3 pp.) are available from the authors upon request.

Results and discussion

Experimental details of the crystallography are given in Table 1. Fractional coordinates of $Na_4Te_4O_{10}$ are given in Table 2, and selected bond lengths and angles in Tables 3 and 4. The unit cell of $Na_4Te_4O_{10}$ is pictured in Fig. 1, and an ORTEP diagram of two asymmetric units is shown in Fig. 2.

Table 2. Fractional coordinates and equivalent isotropic thermal parameters B_{iso} for $Na_4Te_4O_{10}$.[a]

Atom	X	Y	Z	$B_{iso}/Å^2$
Te(1)	0.31025(4)	0.0886(2)	0.0473(1)	0.48(2)
Te(2)	0.43945(3)	0.0050(2)	0.3217(1)	0.40(2)
Na(3)	0.4487(2)	0.4836(12)	0.0884(6)	0.63(11)
Na(4)	0.3289(2)	0.5043(12)	0.2949(6)	0.87(9)
O(5)	0.3524(4)	0.4008(21)	0.0390(10)	0.68(18)
O(6)	0.4469(4)	0.3815(21)	0.3452(10)	0.61(20)
O(7)	0.4532(4)	−0.0271(20)	0.1377(10)	0.76(20)
O(8)	0.3536(4)	0.0037(22)	0.2534(10)	0.74(18)
O(9)	0.2527(4)	0.2483(23)	0.1349(10)	0.89(22)

[a] $B_{iso} = (8\pi^2/3) \Sigma_i U_{ii}$, where the U_{ii} are the diagonal elements of the anisotropic thermal parameters.[14]

Table 3. Selected bond lengths in $Na_4Te_4O_{10}$.

Bond	Distance (Å)	Bond	Distance (Å)
Te(1)–Te(1)[c]	3.1881(18)	Na(3)–O(7)	2.432(12)
Te(2)–Te(2)[b]	3.4285(18)	Na(3)–O(6)[g]	2.438(11)
Te(1)–Te(2)	3.5849(15)	Na(3)–O(6)[b]	2.444(10)
Te(1)–O(5)	1.827(10)	Na(3)–O(7)[a]	2.534(12)
Te(1)–O(9)	1.912(9)	Na(3)–O(6)	2.548(11)
Te(1)–O(8)[b]	2.073(9)	Na(3)–O(8)[b]	3.820(11)
Te(1)–O(9)[c]	2.186(9)	Na(4)–O(5)[e]	2.353(11)
Te(1)–O(8)[j]	3.261(9)	Na(4)–O(9)	2.435(11)
Te(2)–O(6)	1.854(10)	Na(4)–O(9)[f]	2.476(11)
Te(2)–O(7)[a]	1.887(9)	Na(4)–O(8)[h]	2.556(12)
Te(2)–O(8)[b]	1.975(9)	Na(4)–O(8)[b]	2.562(12)
Te(2)–O(7)[d]	2.467(9)	Na(4)–O(5)	2.704(11)
Te(2)–O(7)[e]	3.010(10)	Na(4)–O(6)	2.767(10)
Na(3)–Na(3)[k]	3.255(10)	Na(4)–O(9)[i]	4.187(12)
Na(3)–Na(3)[b]	3.503(10)	O(5)–O(9)[c]	2.759(13)
Na(4)–Na(4)[f]	4.358(9)	O(6)–O(8)[b]	2.847(13)
Na(3)–Na(4)[g]	3.527(8)	O(7)–O(7)[b]	2.728(19)
Na(3)–Na(4)	3.795(7)	O(8)–O(9)[b]	2.673(13)
Na(3)–O(5)	2.240(10)	O(9)–O(9)[c]	2.589(19)

[a] $x, y−1, z.$ [b] $\bar{x}+1, y, \bar{z}+1/2.$ [c] $\bar{x}+1/2, \bar{y}+1/2, \bar{z}.$ [d] $\bar{x}+1, y−1, \bar{z}+1/2.$ [e] $x, \bar{y}+1, z+1/2.$ [f] $\bar{x}+1/2, y+1/2, \bar{z}+1/2.$ [g] $x, \bar{y}+1, z−1/2.$ [h] $\bar{x}+1, y+1, \bar{z}+1/2.$ [i] $x, y+1, z.$ [j] $\bar{x}+1, \bar{y}, \bar{z}.$ [k] $\bar{x}+1, \bar{y}+1, \bar{z}.$
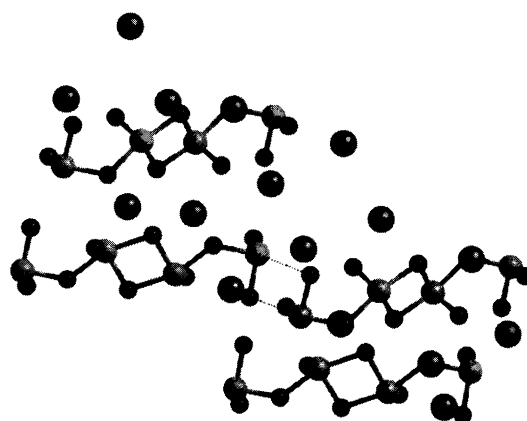

Fig. 1. Unit cell of $Na_4Te_4O_{10}$ showing the $Te_4O_{10}^{4-}$ fragments surrounded by sodium cations. The dashed lines indicate secondary interactions. Light shaded circles (tellurium) connected to darker circles (oxygen) represent the tellurium–oxygen network. The sodium cations are shaded circles shown with no directed bonds.
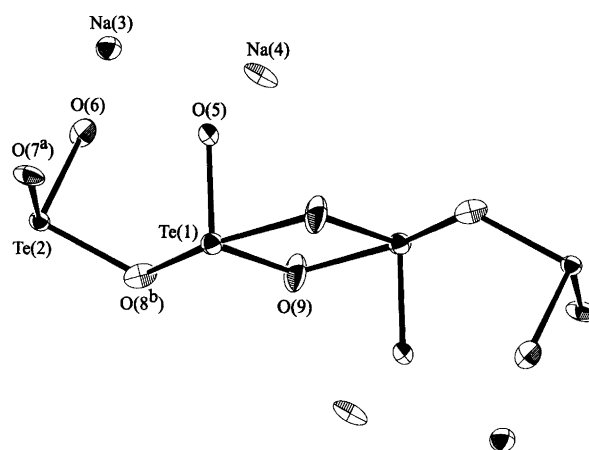

Fig. 2. ORTEP diagram of $Na_4Te_4O_{10}$, showing numbering scheme and thermal ellipsoids (90% probability surfaces). Symmetry operations for superscripted numbers are as follows: [a] $x, y−1, z.$ [b] $\bar{x}+1, y, \bar{z}+1/2.$

Sodium tetratellurite, $Na_2Te_4O_9$, and sodium ditellurite, $Na_4Te_4O_{10}$, are the two crystalline compositions between pure tellurium(IV) dioxide, TeO_2, and sodium tellurite, Na_2TeO_3. Tellurium dioxide can be found in two modifications: paratellurite (α-TeO_2) and tellurite (β-TeO_2). Both contain one tellurium atom coordinated to four oxygen atoms in a distorted trigonal bipyramid conformation (including the lone pair of electrons in an equatorial position). Paratellurite is a three-dimensional network of these TeO_4 units linked together by oxygen atoms shared in an equatorial position to one TeO_4 unit and in the axial position of the next TeO_4 unit. Tellurite consists of pairs of TeO_4 groups connected by a common edge to form Te_2O_6 units in infinite two-dimensional sheets. As in paratellurite, the oxygen are shared in a

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Table 4. Selected bond angles in $Na_4Te_4O_{10}$.

Bond	Angle (°)	Bond	Angle (°)
O(5)–Te(1)–O(9)	97.0(4)	O(7)–Na(3)–O(7)^a	158.3(5)
O(5)–Te(1)–O(8)^b	93.1(4)	O(6)^g–Na(3)–O(6)^b	96.4(3)
O(5)–Te(1)–O(9)^c	86.4(4)	O(6)^g–Na(3)–O(7)^a	116.0(4)
O(9)–Te(1)–O(8)^b	84.2(4)	O(6)^b–Na(3)–O(7)^a	75.7(3)
O(9)–Te(1)–O(9)^c	78.1(4)	O(5)^e–Na(4)–O(9)	135.7(4)
O(8)^b–Te(1)–O(9)^c	162.0(4)	O(5)^e–Na(4)–O(9)^f	69.6(3)
O(6)–Te(2)–O(7)^a	99.6(4)	O(5)^e–Na(4)–O(8)^h	87.7(4)
O(6)–Te(2)–O(8)^b	96.0(4)	O(5)^e–Na(4)–O(8)^b	109.5(4)
O(6)–Te(2)–O(7)^d	88.8(4)	O(9)–Na(4)–O(9)^f	85.28(28)
O(7)^a–Te(2)–O(8)^b	93.4(4)	O(9)–Na(4)–O(8)^h	123.3(4)
O(7)^a–Te(2)–O(7)^d	76.3(4)	O(9)–Na(4)–O(8)^h	64.6(3)
O(8)^b–Te(2)–O(7)^d	169.2(3)	O(9)^f–Na(4)–O(8)^h	78.6(4)
O(5)–Na(3)–O(7)	102.5(4)	O(9)^f–Na(4)–O(8)^h	135.8(4)
O(5)–Na(3)–O(6)^g	92.4(4)	O(8)^h–Na(4)–O(8)^h	144.7(4)
O(5)–Na(3)–O(6)^b	157.7(4)	Te(2)^i–O(7)–Te(2)^h	103.1(4)
O(5)–Na(3)–O(7)^a	82.0(4)	Te(2)^b–O(8)–Te(1)^h	124.6(4)
O(7)–Na(3)–O(6)^g	85.2(4)	Te(1)–O(9)–Te(1)^c	101.9(4)
O(7)–Na(3)–O(6)^b	98.7(4)		

^{a} $x, y-1, z.$ ^{b} $\bar{x}+1, y, \bar{z}+1/2.$ ^{c} $\bar{x}+1/2, \bar{y}+1/2, \bar{z}.$ ^{d} $\bar{x}+1, y-1, \bar{z}+1/2.$ ^{e} $x, \bar{y}+1, z+1/2.$ ^{f} $\bar{x}+1/2, y+1/2, \bar{z}+1/2.$ ^{g} $x, \bar{y}+1, z-1/2.$ ^{h} $\bar{x}+1, y+1, \bar{z}+1/2.$ ^{i} $x, y+1, z.$

Te–$_{eq}$O$_{ax}$–Te fashion. The tellurium–oxygen network of sodium tellurite, made from TeO_2 modified by 50 mol% sodium oxide, is completely depolymerized into TeO_3^{2-} trigonal pyramids. The two crystallographically distinct sodium cations are octahedrally coordinated to the non-bridging oxygen of the TeO_3^{2-} units.

The structures of the intermediate compositions, $Na_4Te_4O_{10}$ and $Na_2Te_4O_9$, have characteristics common to both TeO_2 and Na_2TeO_3, specifically a combination of bridging and nonbridging oxygen atoms. In the case of crystalline $Na_2Te_4O_9$, the extended TeO_2 network is fractured into infinite $Te_4O_9^{2-}$ sheets separated by alternating layers of sodium cations, whereas the structure of $Na_4Te_4O_{10}$ consists of $Te_4O_{10}^{4-}$ fragments surrounded by sodium cations (Fig. 1). Each $Te_4O_{10}^{4-}$ unit contains an edge-sharing group made up of two Te(1) atoms connected through two O(9) atoms (Fig. 2). The Te_2O_6 edge-sharing group bond lengths and bond angles are similar to those found in two other crystals in this system, β-TeO_2 and $Na_2Te_4O_9$. In sodium ditellurite, both tellurium Te(1) atoms in the Te_2O_6 unit are covalently bonded to one nonbridging oxygen and three bridging oxygen atoms in a trigonal bipyramid conformation.

The remainder of the $Te_4O_{10}^{4-}$ fragment consists of two Te(2) atoms each with two nonbridging oxygen and a third bridging oxygen O(8), which connects Te(2) to the edge-sharing group (Fig. 2). The short intermolecular distance between Te(2) and O(7)^d, 2.467 Å, indicates secondary bonding between $Te_4O_{10}^{4-}$ fragments and is represented by a dashed line in Fig. 1. The short Te(2)–Te(2)^b intermolecular contact distance of 3.4285 Å is further evidence of secondary bonding. This Te(2)–Te(2)^b distance is shorter than the 3.5849 Å distance between Te(1) and Te(2), which are joined through O(8)^b. In addition, the short Te(2)–Te(2)^b distance is

intermediate between the tellurium atom contact distances typically found in corner-sharing (3.7 Å) and edge-sharing (3.2 Å) configurations. The resulting trigonal bipyramid configuration surrounding Te(2) consists of O(7)^d and O(8)^b in the axial positions, O(6) and O(7)^a in two of the equatorial sites, and the lone pair of electrons in the remaining equatorial position. By including the secondary bonding, the $Te_4O_{10}^{4-}$ groups are linked together in extended two-dimensional chains.

The sodium cations occupy the spaces between the $(Te_4O_{10}^{4-})_\infty$ chains. Na(3) is coordinated by six nonbridging oxygen atoms, and Na(4) has seven oxygen contacts, the closest and two farthest of which are nonbridging oxygen. We are continuing our study of sodium tellurite glasses with neutron scattering experiments, combined with the crystal data as an aid in the interpretation of the glass results.

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