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$KVTeO_5$ and a redetermination of the Na homologue

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A single crystal of $KVTeO_5$, potassium vanadium tellurite, has been grown. The present structure determination has been conducted together with the refinement of the $NaVTeO_5$ homologue, sodium vanadium tellurite, for the sake of precise comparison. The network consists of $[VTeO_5]_n$ ribbons built up by VO_4 tetrahedra linking centrosymmetric Te_2O_6 groups and stacked along the [010] direction; the alkali cations are intercalated in between. The Te^{IV} atom exhibits a typical one-sided coordination number (CN) of 4, completed by a lone pair, which forms a distorted triangular bipyramid with the four O atoms.

Comment

The study of TeO_2–V_2O_5–M_2O systems, with M = Li, Na, K, Rb, Cs or Ag, has revealed some interesting new compounds with original crystal structures, such as $Te_2V_2O_9$ and the $MVTeO_5$ family (Chase & Philips, 1964; Darriet *et al.*, 1969, 1972; Darriet & Galy, 1973; Darriet, 1973; Alves Weill, 2000). These compounds can also be obtained in glassy forms which exhibit interesting electronic properties, varying from purely electronic conductivity ($Te_2V_2O_9$) to ionic conductivity as the M_2O proportion increases (Dhawan *et al.*, 1982; Lebrun *et al.*, 1989; Jayasinghe *et al.*, 1997; Montani *et al.*, 2000). The structural relationship between the crystalline and amorphous states of these compounds, together with the solid-state chemistry involved, calls for further investigation to relate such basic aspects with the electronic behaviour.

The series with M = Na, K and Ag was chosen in order to appreciate the role of the size (M = K) or atomic number (M = Ag) of the cation on the structural features, compared with the M = Na compound, and to act as good probes to mark the radial distribution functions (RDF) obtained *via* wide-angle X-ray scattering (WAXS) analysis on glassy samples. In order to understand better the RDF of the glassy structures, we report the structure of $KVTeO_5$, and, for the isostructural $NaVTeO_5$, a redetermination which provides a more accurate description of its geometry than that supplied by Darriet *et al.* (1972).

The projection of the $MVTeO_5$ structure onto the (100) plane (Fig. 1) shows that the Te^{IV} atom exhibits a typical one-sided coordination (coordination number of 4), completed by a lone pair (E), to form a distorted triangular bipyramid. Two of these polyhedra share the O5–O5^{ii} centrosymmetric edge [symmetry code: (ii) $2 - x$, $1 - y$, $1 - z$], building Te_2O_6 groups which are connected to each other by VO_4 tetrahedra to form $[VTeO_5]_n$ ribbons developed along the [101] direction and stacked along [010]. The M atoms are bonded to eight O atoms, building bicapped triangular prisms which share O2/O3/O5 faces to make an infinite zigzag string along [001]. These strings share corners, with VO_4 and Te_2O_6 groups strengthening the atomic network.

While the $KVTeO_5$ crystal structure is clearly analogous to the Na homologue, the bigger size of K compared with Na induces an increase of the a and b cell parameters, while c remains almost unchanged. This reflects the relatively rigid nature of the ribbons, meaning that all the expansion occurs in the space between the ribbons.

A bond-valence analysis shows that, while the bond-valence sum around Na is satisfactory (0.94), that around K is large (1.35), indicating that the space available for the cation is too small for K, even allowing for the expansion of the cell. The global instability index (Salinas-Sanchez *et al.*, 1992) is consequently larger for K (0.17) than for Na (0.15), indicating that the K crystals are approaching the stability limit (0.20).

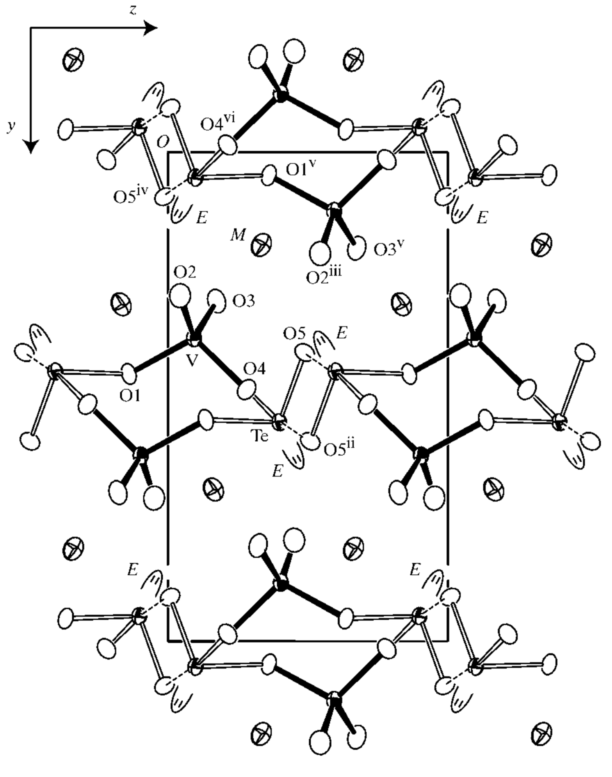

Figure 1
The projection of the $MVTeO_5$ crystal structure on to the (100) plane. Displacement ellipsoids are drawn at the 50% probability level and E indicates the lone pairs. Symmetry codes are as in Tables 1 and 2.

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In both structures, while the O atoms can be separated into different categories according to their chemical equivalence (nature and number of bonded elements), the lengths of the bonds are different in each group and the differences also depend on the nature of the *M* element. For example, despite O1 and O4 being equivalent (one bond to Te, V and *M* cations), the V—O1 bond is longer than V—O4. In this case, the main reason can be traced to the trigonal–bipyramidal bonding around Te, which causes the axial bond to O4 to be longer than the equatorial bond to O1. This difference is more pronounced in the Na than in the K crystal, but in both cases, the difference in V—O bond lengths is not fully compensated, since O1 appears overbonded and, at least in the case of the K crystal, O4 appears underbonded.

Such facts clearly show that increasing the size of the *M* cation leads to a separation of the ribbons up to a limit, reached in the case of the K crystal, above which a slight distortion is necessary to compensate. The pressure effect induced by the large K size might then be responsible for the shortening of the V—O bonds, therefore decreasing the difference between chemically equivalent O atoms but increasing the distortion of the Te_2O_6 groups. Such facts are of paramount importance in elaborating the model necessary for the simulation of the medium-range order of the glassy forms.

Experimental

MVTeO$_5$ compounds with M = K or Na were obtained by direct synthesis in air at 723 and 773 K, respectively, from carefully mixed and ground stoichiometric mixtures, according to the reaction

$$M\mathrm{VO}_3 + \mathrm{TeO}_2 \rightarrow M\mathrm{VTeO}_5.$$

The MVO$_3$ metavanadates were synthesized by reaction of the corresponding carbonates with vanadic oxide, V_2O_5, at 773 K according to the reaction

$$M_2\mathrm{CO}_3 + \mathrm{V}_2\mathrm{O}_5 \rightarrow 2M\mathrm{VO}_3 + \mathrm{CO}_2.$$

The alkali carbonates and vanadium and tellurium oxides were purchased from Aldrich at 99.9% purity. To obtain single crystals, $KVTeO_5$ was melted at 773 K and cooled to 723 K at a rate of 5 K h^{-1}, while a melting temperature of 823 K was needed for the Na compound. The densities of the crystals were determined by helium pycnometry using an Accupyc 1330 Micromeritics pycnometer.

$KVTeO_5$

Crystal data

$KVTeO_5$
M_r = 297.64
Monoclinic, $P2_1/c$
a = 6.3870 (3) Å
b = 11.6150 (8) Å
c = 6.8840 (3) Å
β = 105.100 (3)°
V = 493.06 (5) Å^3
Z = 4
D_x = 4.010 Mg m^{-3}
D_m = 4.00 (1) Mg m^{-3}
D_m measured by helium pycnometry
Mo $K\alpha$ radiation
Cell parameters from 3558 reflections
θ = 1.0–35.0°
μ = 8.58 mm^{-1}
T = 293 (2) K
Block, colourless
0.06 × 0.06 × 0.05 mm

Data collection

Nonius KappaCCD area-detector diffractometer
ψ and ω scans
3494 measured reflections
2137 independent reflections
1726 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.036
$\theta_{\max}$ = 35°
$h = -10 \rightarrow 10$
$k = -18 \rightarrow 16$
$l = -10 \rightarrow 11$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.063
S = 1.08
2137 reflections
74 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0163P)^2 + 0.1396P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = 0.001
$\Delta\rho_{\max}$ = 1.97 e Å^{-3}
$\Delta\rho_{\min}$ = −1.78 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0199 (8)

Table 1
Selected geometric parameters (Å, °) for $KVTeO_5$.

Te—O5	1.866 (2)	K—O2	2.671 (2)
Te—O1$^{\rm i}$	1.920 (2)	K—O2$^{\rm iii}$	2.712 (3)
Te—O4	2.010 (2)	K—O5$^{\rm iv}$	2.748 (2)
Te—O5$^{\rm ii}$	2.291 (2)	K—O5	2.756 (3)
V—O2	1.627 (3)	K—O3$^{\rm v}$	2.756 (2)
V—O3	1.640 (2)	K—O1$^{\rm v}$	2.844 (3)
V—O4	1.803 (2)	K—O4$^{\rm vi}$	2.963 (3)
V—O1	1.847 (2)	K—O3$^{\rm vii}$	2.990 (2)

O5—Te—O1$^{\rm i}$	97.36 (10)	O2—V—O3	109.06 (13)
O5—Te—O4	93.27 (10)	O2—V—O4	112.01 (12)
O1$^{\rm i}$—Te—O4	89.70 (10)	O3—V—O4	109.02 (12)
O5—Te—O5$^{\rm ii}$	76.46 (11)	O2—V—O1	109.68 (12)
O1$^{\rm i}$—Te—O5$^{\rm ii}$	84.77 (9)	O3—V—O1	107.17 (11)
O4—Te—O5$^{\rm ii}$	167.57 (10)	O4—V—O1	109.77 (11)

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

$NaVTeO_5$

Crystal data

$NaVTeO_5$
M_r = 281.53
Monoclinic, $P2_1/c$
a = 5.8840 (2) Å
b = 11.3760 (3) Å
c = 6.8190 (2) Å
β = 103.0680 (17)°
V = 444.62 (2) Å^3
Z = 4
D_x = 4.206 Mg m^{-3}
D_m = 4.20 (1) Mg m^{-3}
D_m measured by helium pycnometry
Mo $K\alpha$ radiation
Cell parameters from 7305 reflections
θ = 1.0–27.5°
μ = 8.67 mm^{-1}
T = 293 (2) K
Block, colourless
0.08 × 0.08 × 0.07 mm

Data collection

Nonius KappaCCD area-detector diffractometer
ψ and ω scans
4088 measured reflections
1024 independent reflections
979 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.067
$\theta_{\max}$ = 27.5°
$h = -7 \rightarrow 7$
$k = -14 \rightarrow 14$
$l = -8 \rightarrow 8$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.018
$wR(F^2)$ = 0.043
S = 1.08
1024 reflections
74 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0170P)^2 + 1.1723P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = 0.002
$\Delta\rho_{\max}$ = 0.90 e Å^{-3}
$\Delta\rho_{\min}$ = −1.09 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0163 (8)

Table 2
Selected geometric parameters (Å, °) for NaVTeO.

Te—O5	1.891 (2)	Na—O2	2.418 (3)
Te—O1$^{\rm i}$	1.913 (2)	Na—O2$^{\rm iii}$	2.512 (3)
Te—O4	2.057 (2)	Na—O3$^{\rm iv}$	2.527 (3)
Te—O5$^{\rm ii}$	2.158 (2)	Na—O5	2.537 (3)
V—O2	1.639 (2)	Na—O1$^{\rm v}$	2.642 (3)
V—O3	1.649 (2)	Na—O5$^{\rm vi}$	2.703 (3)
V—O4	1.789 (2)	Na—O3$^{\rm v}$	2.709 (3)
V—O1	1.828 (2)	Na—O4$^{\rm vii}$	2.903 (3)
O5—Te—O1$^{\rm i}$	94.88 (9)	O2—V—O3	109.11 (12)
O5—Te—O4	90.07 (9)	O2—V—O4	110.71 (11)
O1$^{\rm i}$—Te—O4	88.89 (9)	O3—V—O4	109.14 (11)
O5—Te—O5$^{\rm ii}$	77.78 (10)	O2—V—O1	109.72 (11)
O1$^{\rm i}$—Te—O5$^{\rm ii}$	85.05 (9)	O3—V—O1	106.36 (11)
O4—Te—O5$^{\rm ii}$	165.88 (9)	O4—V—O1	111.68 (10)

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

For both compounds, data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*III (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1380). Services for accessing these data are described at the back of the journal.

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