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A single-crystal neutron diffraction study of $RbTiOAsO_4$

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A rubidium titanyl arsenate single-crystal has been studied by neutron diffraction (λ = 1.207 Å). The polished sample used was 5 × 3 × 2 mm and was cut from a crystal made by top-seeded solution growth. The crystal showed severe extinction. It was, however, possible to obtain a structural model with well defined oxygen sites and reasonable anisotropic displacement parameters.

Comment

Rubidium titanyl arsenate (RTA) belongs to the $KTiOPO_4$ (KTP) family of compounds well known for their non-linear optical and ferroelectric properties (Stucky *et al.*, 1989). The structure is based on a three-dimensional network of arsenic tetrahedra and titanium octahedra with open channels along the *c* axis where the Rb atoms are situated at two independent sites (Thomas *et al.*, 1992). Additional alkaline positions were detected as 'ghost' sites in Cs-rich mixtures of RTA and $CsTiOAsO_4$ (CTA) (Womersley *et al.*, 1998). The original and additional sites are related by pseudosymmetry retained at room temperature from the high-temperature paraelectric phase (Thomas *et al.*, 1990; Thomas & Womersley, 1998). The evolution towards centrosymmetry for the KTP and $RbTiOPO_4$ structures has been studied extensively by Delarue *et al.* (1998, 1999). For these isomorphs, split alkaline positions could be refined for structures above 473 K.

A study of the RTA structure at 9.6 K showed additional electron density near the Rb atoms but a structural model with split Rb positions was not applicable (Almgren *et al.*, 1999). However, using synchrotron-radiation data, it is currently shown that there is a partial occupancy of additional sites in RTA at room temperature, which is reported separately (Streltsov *et al.*, 2000). A parallel study of the CTA structure confirms splitting of the alkaline sites in CTA (Nordborg, 2000). In the present study, single-crystal neutron diffraction has been used to improve the structural model for RTA as concerns the O sites. The aim was to get well defined nuclear positions for the O atoms together with reasonable displacement parameters.

The displacement ellipsoids for O atoms have an average value for $U_{\rm min}/U_{\rm max}$ of about 0.7. These are more uniform than those obtained previously from X-ray tube data, for which the $U_{\rm min}/U_{\rm max}$ average was approximately 0.5 (Almgren *et al.*, 1999). The values presently obtained from a common independent atomic model refinement are comparable to those obtained by multipole refinements in the parallel synchrotron study (Streltsov *et al.*, 2000). The atomic displacement parameters along the principal axes have been calculated using the program *ORFFE* modified for PC (Busing *et al.*, 1964; Gustafsson, 1993). The Rb1 atom predominantly vibrates in the [−101] direction with an angle to the *c* axis of 33 (4)°, while the Rb2 atom vibrates in the [001] direction deviating by 18 (7)°. The anisotropy of the ellipsoids is markedly pronounced for the Rb atoms. The displacements along principal axes r_1, r_2 and r_3 are 0.09 (1), 0.138 (9) and 0.201 (6) Å for Rb1, and 0.109 (8), 0.130 (7) and 0.171 (6) Å for Rb2. This is consistent with the r.m.s. parameters obtained from X-ray data.

More uniform r.m.s. displacements of the O atoms have been obtained compared to those from X-ray data previously reported by Almgren *et al.* (1999). This is represented, for example, by the displacements for O2 along principal axes r_1 and r_3, which are 0.09 (1) and 0.13 (1) Å when derived from neutron data, and 0.06 (2) and 0.134 (9) Å when derived from X-ray data. The corresponding values for O7 are 0.07 (1) and 0.13 (1) Å, and 0.05 (2) and 0.13 (1) Å, respectively. The Rb—O and bond distances are given in Table 1. In CTA, the Cs3 site, which is the additional site at Cs1, is coordinated by six O atoms and not binding to O1, O11 and O7 (Nordborg, 2000). This is propably the case also for the Rb1—Rb3 pair as splitting is seen in the *c* direction which is the direction of the Rb1—O1, Rb1—O11 and Rb1—O7 bonds.

Experimental

The RTA crystals were grown by the top-seeded solution growth technique (Nordborg *et al.*, 2000) using the $Rb_5As_3O_{10}$ self-flux (Cheng *et al.*, 1994). The starting material for both flux and crystals were prepared simultaneously from powder mixtures of analytical grade Rb_2CO_3, TiO_2 and As_2O_5. A batch of approximately 0.5 g RTA per 1 g $Rb_5As_3O_{10}$ flux was mixed in a platinum crucible and inserted in a vertical tube furnace. The mixture was homogenized at 1270 K, then the seed was set just below the flux surface and growth was accomplished with the subsequent cooling of 2 K d^{-1} from the crystallization temperature at 1190 K. The as-grown RTA crystal had the size of 10 × 12 × 20 mm.

Crystal data

$RbTiOAsO_4$	Neutron radiation
M_r = 288.27	λ = 1.207 Å
Orthorhombic, $Pna2_1$	Cell parameters from 11 reflections
a = 13.26 (2) Å	θ = 24.78–32.12°
b = 6.677 (7) Å	μ = 0.009 mm^{-1}
c = 10.766 (7) Å	T = 295 K
V = 953.5 (18) Å^3	Rectangular, colourless
Z = 8	5 × 3 × 2 mm
D_x = 4.016 Mg m^{-3}	

Data collection

Huber four-circle diffractometer
$\omega/2\theta$ scans
1174 measured reflections
1153 independent reflections
1153 reflections with $F > 0$
$\theta_{\max} = 51.97°$

$h = -17 \rightarrow 0$
$k = 0 \rightarrow 8$
$l = 0 \rightarrow 14$
3 standard reflections
every 36 reflections
intensity decay: none

Refinement

Refinement on F
$R = 0.034$
$wR = 0.033$
$S = 1.361$
1153 reflections
145 parameters
$w = 1/\sigma^2$

$(\Delta/\sigma)_{\max} = 0.003$
$\Delta\rho_{\max} = 0.06$ e Å^{-3}
$\Delta\rho_{\min} = -0.06$ e Å^{-3}
Extinction correction: Becker–Coppens (1974)
Extinction coefficient: 7219 (45)

Table 1
Selected geometric parameters (Å).

Rb1—O1	3.138 (6)	Rb2—O4$^{\rm iv}$	3.025 (5)
Rb1—O2	2.812 (6)	Rb2—O11	2.879 (6)
Rb1—O3$^{\rm i}$	2.762 (6)	Rb2—O7$^{\rm ii}$	2.992 (5)
Rb1—O11	3.283 (6)	Rb2—O3$^{\rm ii}$	3.193 (6)
Rb1—O12$^{\rm i}$	2.933 (6)	Rb2—O12$^{\rm ii}$	3.177 (6)
Rb1—O5$^{\rm ii}$	3.031 (6)	Rb2—O2$^{\rm ii}$	3.118 (6)
Rb1—O6$^{\rm iii}$	3.392 (6)	Rb2—O8$^{\rm ii}$	3.198 (12)
Rb1—O7$^{\rm ii}$	3.318 (6)	Rb2—O1$^{\rm v}$	2.753 (6)
Rb1—O8	2.812 (7)	Rb2—O5$^{\rm vi}$	2.926 (6)

Symmetry codes: (i) $x, 1+y, z$; (ii) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}+z$; (iii) $\frac{1}{2}+x, \frac{3}{2}-y, z$; (iv) $x-\frac{1}{2}, \frac{1}{2}-y, z$; (v) $x-\frac{1}{2}, \frac{3}{2}-y, z$; (vi) $-x, 1-y, \frac{1}{2}+z$.

Data were collected at beam channel No. H8 at NFL, the Studsvik Neutron Research Laboratory, Sweden. The three standard reflections, (-534), (-733) and (-543), were remeasured every 36 reflections to monitor the experimental stability, no significant variations were noted during the data collection. Intensity profiles were measured for 1/8 of a sphere, with a step size of 0.1° and a scan time of 10 s per step. Each reflection was sampled with 40 steps. Independent structural parameters, including scale factor, positional and displacement parameters for all atoms were refined by conventional full-matrix least squares. Extinction was severe and the best correction was made by refinement of the isotropic parameter for a type-I crystal with Lorentzian mosaic spread implemented by Becker & Coppens (1974). Still, six reflections with extinction correction parameters less than 0.45 had to be excluded from the refinement (the observed structure factor is $F_{\rm obs} = yF_{\rm kin}$, where $F_{\rm kin}$ is the kinematical value of the structure factor). The minimum extinction correction parameter $y_{\min}$ was then 0.52 for the (220) reflection.

Data collection: Huber diffractometer software; cell refinement: Huber diffractometer software; data reduction: *Xtal*3.6 *DIFDAT ADDREF SORTRF* (Hall *et al.*, 1999); program(s) used to refine structure: *Xtal*3.6 *CRYLSQ*; software used to prepare material for publication: *Xtal*3.6 *CIFIO*.

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e74 Jenni Nordborg *et al.* • RbTiOAsO$_4$ *Acta Cryst.* (2000). C**56**, e73–e74