Acta Crystallographica Section C
Crystal Structure
Communications
ISSN 0108-2701

Alkaline positions in $CsTiOAsO_4$

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Received 20 December 1999
Accepted 24 January 2000

The caesium titanyl arsenate structure has been studied to determine the status of the cation sites. At room temperature, residual charge density was accumulated at a distance of approximately 0.7 Å from the Cs sites. This could be attributed to partial occupancy of additional sites related by pseudo-symmetry. The occupancies of the split Cs positions were about 0.8 for the original site and 0.2 for the additional Cs position. The additional Cs positions were displaced from the two original sites along the polar *c* axis at distances of 0.366 (8) and 0.26 (2) Å, respectively.

Comment

Caesium titanyl arsenate, CTA, belongs to the $KTiOPO_4$ (KTP) isomorphic family of compounds, known for their excellent ferroelectric and non-linear optical properties (Stucky *et al.*, 1989). Arsenates such as $RbTiOAsO_4$ (RTA) and CTA have high transmission in the IR region, superior to that of KTP, and this property can be used to extend the optical range of lasers (Mangin *et al.*, 1989).

The general structure in CTA is a three-dimensional network of AsO_4 tetrahedra and distorted TiO_6 octahedra, with periodic bond chains of $-AsO_4-TiO_6-AsO_4-TiO_6-$ along the *a* and *b* directions and the *ac* diagonal (Protas *et al.*, 1989). In the octahedra, the Ti atoms are displaced, giving alternating shorter (Ti1—O12 and Ti2—O11) and longer (Ti2—O12 and Ti1—O11) bonds along the polar *c* axis. The three-dimensional network has open channels along **c**, with two different sites for the Cs cations. The ferroelectric phase transition for KTP isomorphs is continuous second order of both the displacive and order–disorder types (Belokoneva *et al.*, 1997). During the transformation from the paraelectric to the ferroelectric phase, the cations are displaced along the polarization vector to two independent sites. However, elements of the high-temperature structure are retained at room temperature (Thomas *et al.*, 1990; Thomas & Womersley, 1998).

Womersley *et al.* (1998) have reported some evidence of disorder of the cations over additional sites along the *c* direction for Cs-rich compounds of $Cs_xRb_{1-x}TiOAsO_4$ mixtures. Split alkaline positions had previously been refined for $KFeFPO_4$ at room temperature (Belokoneva *et al.*, 1990). The KTP and $RbTiOPO_4$ (RTP) structures have been studied at elevated temperatures by Delarue *et al.* (1998, 1999). The split cation sites model could be applied at temperatures higher than 473 K. For RTA, additional density at the Rb sites was noted in the 9.6 K structure, but refinement of the split positions model was not applicable (Almgren *et al.*, 1999). Recently, synchrotron data at room temperature by Streltsov *et al.* (2000) has shown that a combination of split Rb positions and multipole functions in the refinement gives the best description of the RTA structure. The question has been posed as to whether the split alkaline positions are universal for KTP isomorphs. Thus, it was desirable to conduct an accurate X-ray diffraction study of the CTA structure to investigate the status of the Cs positions and how these would change with temperature.

Flack parameter (Flack, 1983) refinements (see below) indicated that a single-domain crystal was used. Model I, with two fully occupied Cs sites, was first refined for the room-temperature structure. It resulted in significant residual electron density found along the *c* direction at both Cs sites at distances of approximately 0.67 and 0.75 Å from Cs1 and Cs2, respectively. The use of Model II, with split Cs positions, resulted in a better fit of the refined structure to experimental data and significantly reduced the excess electron density around the Cs atoms. The refined positions were found closer to the original Cs positions than the additional density resulting from the Model I refinement. The new Cs3 atom was positioned 0.366 (8) Å from Cs1 along the *c* axis. For the Cs2–Cs4 couple, the corresponding distance was 0.26 (2) Å. This could be compared with the interatomic distances in the *a* and *b* directions, which were an order of magnitude shorter. The occupancies of the split Cs positions were 0.800 (7) for Cs1 and 0.200 (7) for Cs3, and 0.80 (1) for Cs2 and 0.20 (1) for Cs4. This could be compared with the RTA room-temperature structure, where the Rb1 site has an occupancy of 0.885 (5) and Rb2 an occupancy of 0.872 (9). The shifts of the additional Rb positions are 0.303 (2) and 0.228 (3) Å for the Rb1–Rb3 and Rb2–Rb4 pairs, respectively (Streltsov *et al.*, 2000). In RTP at 473 K, the corresponding distances are 0.27 (1) and 0.19 (1) Å. It could therefore be concluded that the splitting is more pronounced in CTA than in the KTP isomorphs previously re-investigated.

An *ORTEP* plot (Johnson *et al.*, 1972) of the room-temperature structure in the *ac* plane is given in Fig. 1. The elongated isotropic displacement ellipsoid of Cs4 indicates that this additional site is in fact not one position but represents several Cs positions which cannot be resolved. The isotropic displacement parameters along the principal axes have been calculated using the program *ORFFE* modified for PC (Busing *et al.*, 1964; Gustafsson, 1993). For Cs4, the isotropic displacements along the principal axes r_1, r_2 and r_3 were 0.06 (3), 0.13 (1) and 0.24 (1) Å, respectively. The corresponding values for Cs2 were 0.093 (3), 0.107 (3) and 0.155 (3) Å, respectively. The r.m.s. parameters were more uniform for the Cs1–Cs3 pair, with displacements along r_1 and r_3 of 0.095 (1) and 0.172 (2), respectively, for Cs1, and 0.085 (9) and 0.17 (1) Å, respectively, for Cs3. The Cs1 and

Cs2 atoms vibrate predominately in the [001] direction at an angle to the *c* axis of 25 (5)°. Atoms Cs3 and Cs4 also vibrate mainly in this direction. This is correlated with the coordination of the Cs sites situated in the channels along **c** and with no oxygen bonds in the [001] direction.

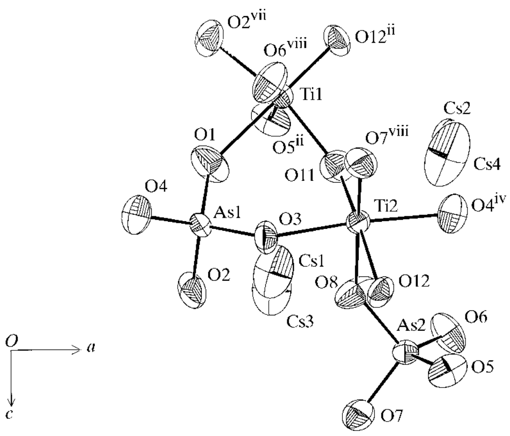

Figure 1
An *ORTEP* plot (Johnson *et al.*, 1972) of the room-temperature CTA structure in the plane perpendicular to the *b* axis. Split alkaline positions are shown by the Cs1–Cs3 and Cs2–Cs4 pairs, and all atoms are given as 99% probability displacement ellipsoids. The elongated ellipsoid of Cs4 indicates that this additional site comprises several positions that cannot be individually resolved [symmetry codes: (ii) $\frac{3}{2} - x, y - \frac{1}{2}, z - \frac{1}{2}$; (iv) $\frac{1}{2} + x, \frac{3}{2} - y, z$; (vii) $1 - x, 1 - y, z - \frac{1}{2}$; (viii) $\frac{3}{2} - x, \frac{1}{2} + y, z - \frac{1}{2}$].

At 183 K, the residual electron density near the Cs atoms could not be resolved to any specific split positions and for this temperature Model I was used in the refinement. The atomic coordinates for Cs1 and Cs2 were very similar to the coordinates for the same atoms at room temperature. This indicates that the additional Cs peaks have moved towards the dominant Cs sites. It should be noted that in the refinement of the room-temperature structure using Model I, the fractional *z* coordinates of Cs1 and Cs2 were in between those of the Cs1–Cs3 and Cs2–Cs4 pairs in Model II. For the RTA structure, on the other hand, the average *z* coordinates at room temperature of Rb1–Rb3 and Rb2–Rb4, respectively (Streltsov *et al.*, 2000), corresponded well with the 9.6 K coordinates of Rb1 and Rb2 (Almgren *et al.*, 1999). The thermal displacements along the principal axes r_1, r_2 and r_3 were 0.073 (2), 0.100 (1) and 0.150 (1) Å, respectively, for Cs1, and 0.072 (2), 0.091 (1) and 0.1255 (8) Å, respectively, for Cs2, at 183 K. Both cations vibrated in the [001] direction at an angle of 18 (1)° with respect to the *c* axis.

The original Cs sites are coordinated by nine O atoms and this is also true for the additional Cs4 site. Cs3 is, on the other hand, coordinated by six O atoms; selected atomic bond distances are given in Table 1. The three-dimensional network structure was little affected by the inclusion of additional Cs positions at room temperature. No significant differences were noted in the bond lengths, either in the Ti octahedra or in the As tetrahedra. As the Cs1 and Cs2 sites at room temperature correspond to those at 183 K, the Cs1—O and Cs2—O bonds did not change significantly with temperature (Table 2).

Experimental

CTA crystals were made from spontaneous growth using a self-flux of $Cs_5As_3O_{10}$, with 0.6 g CTA per 1 g flux, made from analytical grade Cs_2CO_3, As_2O_5 and TiO_2 (Cheng *et al.*, 1993). The powder starting materials were mixed thoroughly using an agate mortar and placed in a pure Pt crucible. This was inserted into a vertical tube furnace, which was heated rapidly to 470 K, where it was kept for 12 h to allow for dehydration of the hygroscopic powders. Then the flux was heated slowly to 1230 K, where it was maintained for 24 h as the flux melt was homogenized by stirring with a Pt spoon. Growth was accomplished by cooling from 1085 to 1066 K by 2 K per day, after which the flux containing crystals was cooled to room temperature at a rate of 200 K per day. Small clear crystals were recovered by dissolution in water; some crystals had a slightly yellow colour. Many of the smaller crystals had a needle-like morphology, which has been observed previously in supercooled melts of CTA (Cheng *et al.*, 1993), while some of the larger crystals had the typical KTP morphology (Bolt & Bennema, 1990). However, none of the crystals were small enough to reduce the extinction effect on the X-ray diffraction data efficiently. Therefore, the sample chosen for the present crystallographic study was cut from a small clear crystal of needle-like morphology.

Models I and II at room temperature

Crystal data (Models I and II)

$CsTiOAsO_4$	Mo $K\alpha$ radiation
$M_r = 335.7$	Cell parameters from 6935 reflections
Orthorhombic, $Pna2_1$	$\theta = 3.02$–$41.78°$
$a = 13.4892$ (3) Å	$\mu = 15.536$ mm^{-1}
$b = 6.8637$ (1) Å	$T = 297$ (2) K
$c = 10.6908$ (1) Å	Rectangular, colourless
$V = 989.82$ (3) Å^3	$0.03 \times 0.02 \times 0.02$ mm
$Z = 8$	
$D_x = 4.505$ Mg m^{-3}	

Data collection (Models I and II)

Siemens SMART CCD diffractometer	6720 independent reflections
ω scans	4208 reflections with $F^2 > 3\sigma(F^2)$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	$R_{\rm int} = 0.078$
$T_{\rm min} = 0.65$, $T_{\rm max} = 0.75$	$\theta_{\rm max} = 41.78°$
36 263 measured reflections	$h = -25 \rightarrow 25$
	$k = -12 \rightarrow 12$
	$l = -19 \rightarrow 19$

Table 1
Selected distances (Å) for Model II at room temperature.

Cs1—O1	3.408 (6)	Cs2—$O5^{vi}$	3.036 (7)
Cs1—O2	2.851 (7)	Cs2—Cs4	0.260 (18)
Cs1—$O3^{i}$	2.893 (6)	Cs3—O2	2.826 (15)
Cs1—O11	3.528 (6)	Cs3—$O3^{i}$	2.972 (13)
Cs1—$O12^{i}$	2.983 (7)	Cs3—$O12^{i}$	2.961 (15)
Cs1—$O5^{ii}$	3.233 (5)	Cs3—$O5^{ii}$	3.594 (9)
Cs1—$O6^{iii}$	3.303 (7)	Cs3—$O6^{iii}$	3.136 (15)
Cs1—$O7^{ii}$	3.473 (6)	Cs3—O8	2.952 (15)
Cs1—O8	2.934 (7)	Cs4—$O4^{iv}$	2.885 (16)
Cs1—Cs3	0.366 (8)	Cs4—O11	2.926 (17)
Cs2—$O4^{iv}$	3.043 (6)	Cs4—$O7^{ii}$	3.057 (17)
Cs2—O11	2.974 (7)	Cs4—$O2^{ii}$	3.515 (17)
Cs2—$O7^{ii}$	3.041 (6)	Cs4—$O8^{ii}$	3.49 (2)
Cs2—$O2^{ii}$	3.323 (7)	Cs4—$O3^{ii}$	3.594 (17)
Cs2—$O8^{ii}$	3.287 (7)	Cs4—$O12^{ii}$	3.486 (17)
Cs2—$O3^{ii}$	3.339 (7)	Cs4—$O1^{v}$	2.837 (17)
Cs2—$O12^{ii}$	3.318 (7)	Cs4—$O5^{vi}$	3.076 (17)
Cs2—$O1^{v}$	2.838 (7)		

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

Refinement (Model I)

Refinement on *F*
$R = 0.038$
$wR = 0.026$
$S = 1.993$
4208 reflections
146 parameters
$w = 1/\sigma^2$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 3.14$ e Å^{-3}
$\Delta\rho_{\min} = -2.39$ e Å^{-3}
Extinction correction: Zachariasen (1968)
Extinction coefficient: $6.2\ (3) \times 10^2$
Absolute structure: Flack (1983)
Flack parameter = 0.05 (2)

Refinement (Model II)

Refinement on *F*
$R = 0.034$
$wR = 0.023$
$S = 1.763$
4208 reflections
164 parameters
$w = 1/\sigma^2$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 1.41$ e Å^{-3}
$\Delta\rho_{\min} = -1.26$ e Å^{-3}
Extinction correction: Zachariasen (1968)
Extinction coefficient: $7.1\ (2) \times 10^2$
Absolute structure: Flack (1983)
Flack parameter = 0.05 (2)

Model I at low temperature

Crystal data

$CsTiOAsO_4$
$M_r = 335.7$
Orthorhombic, $Pna2_1$
$a = 13.4623\ (1)$ Å
$b = 6.8484\ (1)$ Å
$c = 10.7075\ (1)$ Å
$V = 987.18\ (2)$ Å^3
$Z = 8$
$D_x = 4.517$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 6293 reflections
$\theta = 3.03$–$45.35°$
$\mu = 15.578$ mm^{-1}
$T = 183\ (1)$ K
Rectangular, colourless
$0.03 \times 0.02 \times 0.02$ mm

Data collection

Siemens SMART CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.65$, $T_{\max} = 0.75$
30 621 measured reflections
6940 independent reflections
4282 reflections with $F^2 > 2\sigma(F^2)$
$R_{\rm int} = 0.087$
$\theta_{\max} = 45.35°$
$h = -26 \rightarrow 25$
$k = -13 \rightarrow 13$
$l = -16 \rightarrow 21$

Refinement

Refinement on *F*
$R = 0.043$
$wR = 0.03$
$S = 1.996$
4282 reflections
144 parameters
$w = 1/\sigma^2$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 2.54$ e Å^{-3}
$\Delta\rho_{\min} = -2.69$ e Å^{-3}
Extinction correction: Zachariasen (1968)
Extinction coefficient: $4.7\ (3) \times 10^2$
Absolute structure: Flack (1983)
Flack parameter = 0.06 (2)

Full-matrix least-squares refinements were made using the independent atom model. The Zachariasen extinction parameter r^* was refined in accordance with the Larson implementation (Larson, 1969). The minimum extinction correction parameter $y_{\min}$ was 0.85 (Model I) and 0.83 (Model II) at 297 K, and 0.88 at 183 K for the 013 reflection (the observed structure factor is $F_{\rm obs} = yF_{\rm kin}$, where $F_{\rm kin}$ is the kinematic value of the structure factor). The refined Flack (1983) parameter of 0.05 (2) at 297 K and 0.06 (2) at 183 K shows that the crystal is nearly single-domain. The Flack parameter refinement was made using 2188 Friedel pairs at 297 K and 2553 Friedel pairs at 183 K. For the 183 K data, the anisotropic displacement parameters for O8 and O12 showed peculiar values and isotropic parameters were used in the final refinements.

For all data sets, data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT* and *SADABS* (Sheldrick, 1996); program(s) used to refine structure: *Xtal*3.6 (Hall *et al.*, 1999); molecular graphics: *Xtal*3.6; software used to prepare material for publication: *Xtal*3.6.

Table 2
Selected distances (Å) for Model I at low temperature.

Cs1—O1	3.362 (7)	Cs2—O4$^{\rm iv}$	3.031 (6)
Cs1—O2	2.850 (6)	Cs2—O11	2.949 (6)
Cs1—O3$^{\rm i}$	2.882 (5)	Cs2—O7$^{\rm ii}$	3.060 (5)
Cs1—O11	3.521 (6)	Cs2—O2$^{\rm ii}$	3.275 (7)
Cs1—O12$^{\rm i}$	2.9813 (8)	Cs2—O8$^{\rm ii}$	3.296 (2)
Cs1—O5$^{\rm ii}$	3.214 (8)	Cs2—O3$^{\rm ii}$	3.312 (8)
Cs1—O6$^{\rm iii}$	3.310 (6)	Cs2—O12$^{\rm ii}$	3.304 (2)
Cs1—O7$^{\rm ii}$	3.468 (6)	Cs2—O1$^{\rm v}$	2.837 (6)
Cs1—O8	2.9224 (8)	Cs2—O5$^{\rm vi}$	3.025 (6)

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

Access to the SMART diffractometer and assistance in data collection by Dr Vratislav Langer and Mr Amir Mahmoudkhani, Göteborg University, and fruitful discussions with Dr Victor Streltsov, Crystallography Centre, and Dr Göran Svensson and Professor Jörgen Albertsson, Chalmers, are hereby gratefully acknowledged.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1106). Services for accessing these data are described at the back of the journal.

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