

**Douglas du Boulay,* Atsuko
Oono and Nobuo Ishizawa**Materials and Structures Laboratory, Tokyo
Institute of Technology, 4259 Nagatsuta Midori,
Yokohama 226-8503, JapanCorrespondence e-mail:
ddb@r3401.msl.titech.ac.jp**Key indicators**

Single-crystal X-ray study

 $T = 295\text{ K}$ Mean $\sigma(\text{Ta-O}) = 0.007\text{ \AA}$ R factor = 0.044 wR factor = 0.032

Data-to-parameter ratio = 19.4

For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.**A reinvestigation of the structure of $\text{Cs}_3\text{Ta}_5\text{O}_{14}$**

In a recent analysis of a new pyrochlore-like mesoporous phase $\text{Rb}_3\text{Ta}_5\text{O}_{14}$ (trirubidium pentatantalum tetradeca-oxide) [du Boulay *et al.* (2002). *Acta Cryst.* **C58**, i40–i44], the authors observed in the literature some rather large uncertainties in the vibrational motion and thereby atomic positions reported for the archetypal analogue structure $\text{Cs}_3\text{Ta}_5\text{O}_{14}$. New X-ray diffraction data for that compound were collected on an image plate diffractometer with an Mo $K\alpha$ source. The current study confirms the original structural model and modestly improves on its precision.

Comment

In the course of investigation of four layered $\text{Rb}_2\text{Ca}_2\text{Ta}_4\text{O}_{13}$ perovskites, a new mesoporous pyrochlore-like structural phase, $\text{Rb}_3\text{Ta}_5\text{O}_{14}$, was encountered by du Boulay *et al.* (2002). That phase turned out to be a variant of a $\text{Cs}_3\text{Ta}_5\text{O}_{14}$ archetype structure reported previously by Serafin & Hoppe (1982). In reviewing the two structures, the more recent authors were led to suspect some irregularities in the original $\text{Cs}_3\text{Ta}_5\text{O}_{14}$ structural model because, with the exception of three independent Cs sites, all atoms were refined with isotropic displacement parameters and, of the Cs sites, two exhibited unusually large U_{ij} values. The isotropic displacement parameters of the O atoms also varied considerably over the range 0.001–0.023 \AA^2 . The largest displacement parameter occurred for one atom, Cs3, located on one of two independent *Pbam* mirror planes, exhibiting very large displacements normal to that plane. Consequently du Boulay *et al.* (2002) speculated that the mirror symmetry could be broken, by analogy with two of the Rb atoms in the $\text{Rb}_3\text{Ta}_5\text{O}_{14}$ analogue. This could have led to doubling of the *Pbam* *c* axis and a Cs-atom sublattice in closer agreement with the Rb sublattice observed for the latter compound.

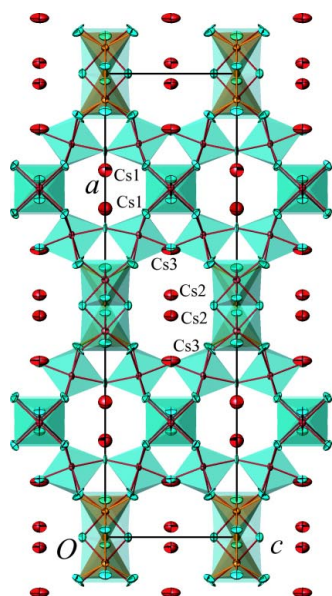
To remove any uncertainties the current authors crystallized and reanalysed $\text{Cs}_3\text{Ta}_5\text{O}_{14}$ via single-crystal X-ray diffraction. Here we confirm that the structure reported by Serafin & Hoppe (1982) was correct and, in addition, we report marginally more precise structural parameters accompanied by anisotropic displacement parameters determined for all atoms.

X-ray diffraction data for $\text{Cs}_3\text{Ta}_5\text{O}_{14}$ were measured on a Rigaku R-AXIS RAPID three-circle diffractometer. An Mo $K\alpha$ X-ray source and a semi-cylindrical image plate were used to measure the room-temperature single-crystal diffraction data. The initial orientation matrix and associated lattice parameters were determined from eight oscillation photographs measured at 120 s^{-1} with $\Delta\omega = 2^\circ$. A single 90 min duration X-ray image was taken, while rotating the crystal 30° about its *c* axis at 180 s^{-1} . That frame failed to reveal

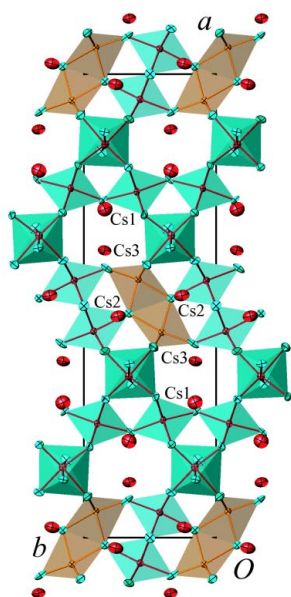
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(a)



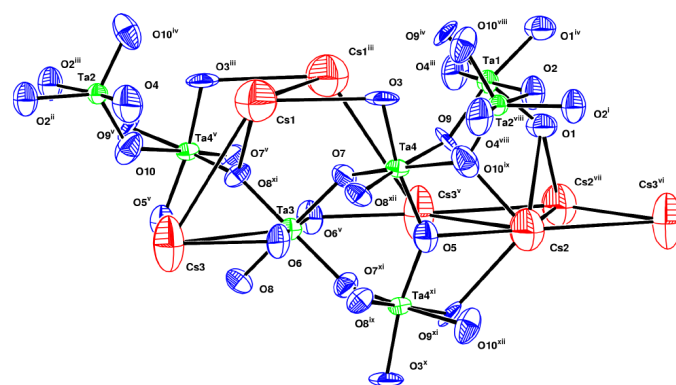
(b)

Figure 1

ATOMS (Dowty, 1999) polyhedral view of the *Pbam* $\text{Cs}_3\text{Ta}_5\text{O}_{14}$ structure projected along (a) the *b* axis and (b) the *c* axis. Ellipsoids are drawn at the 90% probability level. Fivefold polyhedra are coloured brown.

superlattice reflections of any kind corresponding to doubling of the *Pbam* *c* axis. The implications were that the originally reported lattice was quite correct, though not necessarily the symmetry.

The data measurement involved 275 image plate frames, measured with rotations of $\Delta\omega = 2^\circ$ at 500 s^{-1} , from which 20976 reflections were identified with $2\theta \leq 60.1^\circ$. Lattice parameters were refined with other apparatus parameters, using all 275 frames, and agree with those of Serafin & Hoppe (1982) to about 0.05 Å. The measured intensities were in good accord with the *b* glide along *a* and *a* glide along *b* reported by

**Figure 2**

ORTEP (*Xtal3.7*; Hall *et al.*, 2000) view of an extended asymmetric unit, with ellipsoids drawn at the 99% probability level. [Symmetry codes: (i) $-x, -y, z$; (ii) $\frac{1}{2} + x, \frac{1}{2} - y, -z$; (iii) $\frac{1}{2} - x, \frac{1}{2} + y, -z$; (iv) $x, y, -z$; (v) $\frac{1}{2} - x, \frac{1}{2} + y, z$; (vi) $-\frac{1}{2} + x, \frac{1}{2} - y, z$; (vii) $-x, 1 - y, z$; (viii) $\frac{1}{2} - x, -\frac{1}{2} + y, -z$; (ix) $\frac{1}{2} - x, -\frac{1}{2} + y, z$; (x) $x, y, 1 + z$; (xi) $x, y, 1 - z$; (xii) $\frac{1}{2} - x, -\frac{1}{2} + y, 1 - z$.]

the previous authors. The uncertainties remaining, therefore, primarily concern the degree of perfection of the *Pbam* mirror planes.

Structurally $\text{Cs}_3\text{Ta}_5\text{O}_{14}$ consists of four distinct TaO polyhedra, of which three are corner-sharing TaO_6 octahedra and one is an edge-sharing TaO_5 bicapped trigonal prism, as depicted in Fig. 1. Those TaO polyhedra form the backbone of a network of two symmetry-distinct, Cs-filled structural cavities, the larger containing four Cs atoms and the smaller cavity containing two. The underlying atomic coordination geometries were well examined by Serafin & Hoppe (1982), and the relationship of $\text{Cs}_3\text{Ta}_5\text{O}_{14}$ to the three-independent-cavity network of mesoporous $\text{Rb}_3\text{Ta}_5\text{O}_{14}$ was previously discussed by du Boulay *et al.* (2002).

Experimental

Reagent grade CsCl and Ta_2O_5 chemicals, 4.245 g in total, were combined to form 0.1 mol% $\text{Cs}_3\text{Ta}_5\text{O}_{14}$ in a 99.9 mol% CsCl flux. In a Pt crucible, the mixture was heated quickly to 1073 K, which was sustained for 2 h and followed by slow cooling at 2.8 K h^{-1} to 723 K. After rinsing in hot water, the residue contained transparent and colourless crystals of $\text{Cs}_3\text{Ta}_5\text{O}_{14}$ with rectangular shapes, as well as unidentified crystals with thin hexagonal shapes.

Crystal data

$\text{Cs}_3\text{Ta}_5\text{O}_{14}$
 $M_r = 1527.48$
 Orthorhombic, *Pbam*
 $a = 26.219$ (6) Å
 $b = 7.4283$ (10) Å
 $c = 7.3914$ (10) Å
 $V = 1439.6$ (4) Å³
 $Z = 4$
 $D_x = 7.048 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation
 Cell parameters from 20976 reflections
 $\theta = 1.6\text{--}30.0^\circ$
 $\mu = 45.17 \text{ mm}^{-1}$
 $T = 295 \text{ K}$
 Rectangular block, colourless
 $0.06 \times 0.06 \times 0.04 \text{ mm}$

Data collection

Rigaku Rapid image plate diffractometer
 ω scans
 Absorption correction: numerical (*NUMABS*; Higashi, 2000)
 $T_{\min} = 0.113, T_{\max} = 0.349$
 2269 measured reflections

2269 independent reflections
 2269 reflections with $F > 0$
 $R_{\text{int}} = 0.060$
 $\theta_{\max} = 30.0^\circ$
 $h = 0 \rightarrow 36$
 $k = -10 \rightarrow 0$
 $l = 0 \rightarrow 10$

Refinement

Refinement on F	117 parameters
$R = 0.044$	$w = 1/[\sigma(F)^2 + 0.2 + 10^{-4}F^2]$
$wR = 0.032$	$(\Delta/\sigma)_{\max} = 0.001$
$S = 0.91$	$\Delta\rho_{\max} = 3.69 \text{ e } \text{\AA}^{-3}$
2269 reflections	$\Delta\rho_{\min} = -4.25 \text{ e } \text{\AA}^{-3}$

Although minor difficulties were encountered while refining the structure, because of a tendency toward non-positive definite displacement parameters for two O atoms, the problems were suppressed after including all data satisfying $F^2 \geq 0$ in a refinement on F , in conjunction with a modified weighting scheme. This led to a larger, but acceptable, R factor $wR(F) = 0.032$. The refined atomic positions agree with those of Serafin & Hoppe (1982), typically within two of their reported s.u.'s, although the s.u.'s reported here are typically smaller by a factor of about 5. The mean atomic displacement parameters are also comparable in magnitude between the two studies, though here U_{eq} for the Ta atoms are about double those reported in the earlier work. In addition, U_{eq} values for the O atoms reported here have a considerably smaller range. The anisotropic displacement tensor elements for the Cs atoms are broadly comparable between the experiments, though disparities of up to a factor of 2 on some components are to be found. U_{eq} values reported here for the Cs atoms are typically half the magnitude of equivalent parameters determined for the four Rb atoms in $\text{Rb}_3\text{Ta}_5\text{O}_{14}$ by du Boulay *et al.* (2002). In particular, the largest displacement tensor component observed here ($U_{33} = 0.0472 \text{ \AA}^2$ for Cs3) is less than half that of the largest tensor element reported in the latter [$U_{22} = 0.1057$ (11) \AA^2 for Rb4]. The large Cs atom displacements are in good accord with the structural geometry, because these atoms occupy large structural cavities with asymmetric bonding environments. This is particularly true of Cs3, which has one short Cs3—O6 bond within the plane, that appears to act like a hinge on which the Cs3 atom can swing with greater freedom into two adjoining structural cavities.

A relatively large residual $\Delta\rho$ range was observed [-4 (1) to 4 (1) $\text{e } \text{\AA}^{-3}$]. The two largest peaks occur 0.7 \AA away from Cs1 and 0.8 \AA from O4 and both maxima occur on the $z = 0$ mirror plane. The two largest holes were also located on the mirror planes, 1.7 \AA from Cs1 and 1.5 \AA from Cs2. The positions and magnitudes of the extrema suggest a stochastic measurement noise origin, rather than a deficiency of the harmonic displacement model of the atoms. The experimental electron density does then seem to be in good accord with the $Pbam$ space group symmetry.

As a further check, the data were refined against a lower symmetry $Pba2$ structural model, yielding $wR(F) = 0.029$ from 199 parameters and 2269 reflections, with 14 of the 23 independent atoms exhibiting non-positive definite atomic displacement parameters and only minor changes in the atomic displacement parameters of the Cs atoms. Comparable results were obtained in $P2_12_12$, with $wR(F) = 0.032$ from 200 parameters and 12 atoms non-positive definite. Although $Pba2$ symmetry superficially reduces the R factor, it introduces around 25% more atoms and 70% more parameters which do not really improve the structural model. In particular, there was no significant damping effects on the mean squared displacement parameters of the Cs atoms.

We conclude therefore that the adoption of a symmetry lower than $Pbam$ gives no significant improvement over the structural model originally proposed by Serafin & Hoppe (1982), though the current confirmatory study has modestly improved upon the precision of the original, and full anisotropic displacement parameters are reported here for all atoms.

Data collection: *RAPID-AUTO* (Rigaku, 1999); cell refinement: *RAPID-AUTO*; data reduction: *RAPID-AUTO*; source or structural solution: Serafin & Hoppe (1982); program(s) used to refine structure: *CRYLSQ* in *Xtal3.7* (Hall *et al.*, 2000); molecular graphics: *ATOMS* (Dowty, 1999) and *ORTEP* in *Xtal3.7*; software used to prepare material for publication: *Xtal BONDLA CIFIO* in *Xtal3.7*.

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