# Synthesis and Structure of $Cs_3Ti_3As_5O_{20}$ *

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A new ternary titanium arsenate, $Cs_3Ti_3As_5O_{20}$, has been synthesized and structurally characterized by single-crystal X-ray diffraction. It crystallizes in the orthorhombic space group *Pbcm* (no. 57) with $a = 6.5084(9)$, $b = 19.167(1)$, $c = 15.377(1)$ Å, $Z = 4$ and $R = 0.0259$. The structure consists of tunnels where the caesium cations are located. The framework is formed by corner-sharing monomeric $TiO_6$ octahedra, dimeric $Ti_2O_{11}$ units consisting of two corner-sharing $TiO_6$ octahedra, $AsO_4$ tetrahedra, and $As_2O_7$ groups. The structural formula is $Cs_3Ti(Ti_2O)(AsO_4)_3(As_2O_7)$. The structure is compared with that of $\alpha$-$CsTi_3P_5O_{19}$.

Recently $\alpha$- and $\beta$-$CsTi_3P_5O_{19}$ were synthesized and structurally characterized during the course of studying caesium–titanium–phosphate phases.[1] These two polymorphs have different three-dimensional frameworks of vertex-sharing octahedra and tetrahedra. Both frameworks have tunnels where the caesium cations are located. These two polymorphs and $Cs_2TiOP_2O_7$[2] are the only structurally characterized compounds in this phase. Airapetyan *et al.*[3] reported the crystallization of $CsTiPO_5$ from melt solutions, but the compound was not characterized and its X-ray powder pattern could not be indexed based on the $KTiOPO_4$ structure. This potassium titanium phosphate is a well known second-harmonic generation crystal for transforming infrared radiation from a Nd:YAG laser into the green part of the optical spectrum. Preliminary work indicates that $CsTiOPO_4$ with the $KTiOPO_4$ structure does not exist. In contrast, crystals of the arsenate analogue, $CsTiOAsO_4$, an excellent non-linear optical material, have been grown and structurally characterized.[4–6] It would be interesting to know whether the arsenate analogues of $CsTi_3P_5O_{19}$ exist. Therefore, the system Cs–Ti–As–O was investigated. Cheng *et al.*[6] reported the presence of $Cs_3Ti_3(AsO_4)_5$ and a cubic $Cs_xTiAsO_x$ compound in the study of the $Cs_2O$–$TiO_2$–$As_2O_5$ ternary system, but the structures of these two new arsenates were not reported. This paper deals with the synthesis and single-crystal structure of $Cs_3Ti_3As_5O_{20}$, which has the structural formula $Cs_3Ti(Ti_2O)(AsO_4)_3(As_2O_7)$. The structure is compared with that of $\alpha$-$CsTi_3P_5O_{19}$.

## Experimental

*Synthesis.*—A mixture of $Cs(H_2AsO_4)$ (1.649 g), $NH_4(H_2AsO_4)$ (0.957 g) and $TiO_2$ (0.160 g) (Cs:As mole ratio = 1:2) was placed in a 15 cm$^3$ platinum crucible and heated from room temperature to 850 °C for 8 h. It was then cooled to 650 °C at a rate of 10 °C h$^{-1}$, maintained at 650 °C overnight, followed by quenching to room temperature on removal of the crucible from the furnace. The flux was dissolved with hot water and the solid product was obtained by suction filtration. The product contained colourless rod-like crystals of $Cs_3Ti_3As_5O_{20}$, colourless crystalline chunks and a yellow polycrystalline solid. A structural study on the crystalline chunks is in progress. The yellow polycrystalline solid was not characterized. Energy-dispersive X-ray fluorescence analysis on a colourless rod crystal showed that the Cs:Ti:As mole ratio was 3:3.02:4.99, which is in good agreement with the results from the single-crystal X-ray diffraction. Based on powder X-ray diffraction data a single phase of $Cs_3Ti_3As_5O_{20}$ was prepared by heating a mixture containing a stoichiometric quantity of the starting materials at 700 °C for one day with an intermediate grinding. Thermogravimetric and differential thermal analysis showed that the compound gave an endothermic peak with weight loss at *ca.* 850 °C. Below 850 °C, the sample did not show either exothermic or endothermic peaks. The decomposition product was not characterized.

*Single-crystal X-Ray Diffraction.*—A colourless crystal of dimensions 0.05 × 0.05 × 0.37 mm was selected for indexing and intensity data collection on an Enraf–Nonius CAD4 diffractometer using graphite-monochromated Mo-K$\alpha$ radiation. Axial oscillation photographs were taken to check the symmetry properties and unit-cell parameters. The intensity data were corrected for Lorentz polarization and absorption effects. The latter were based on $\psi$ scans of several suitable reflections with the $\chi$ values close to 90° using the NRCVAX program package.[7] On the basis of systematic absences, statistical analysis of the intensity distribution, and successful solution and refinement of the structure, the space group was determined to be *Pbcm* (no. 57). The structure was solved by the Patterson method and successive Fourier syntheses, and was refined by full-matrix least-squares refinement based on $F$ values. First the bridging oxygen atom of the diarsenate group, O(12), was placed on a two-fold axis. This showed a large thermal parameter and a large nearby residual electron density of 2.8 e Å$^{-3}$. A difference synthesis based on the atomic coordinates of all the atoms except O(12) revealed two equally occupied oxygen sites which are related by a two-fold axis. Therefore, the structure was refined with O(12) at a general position having an occupancy factor of 0.5. The final cycle of refinement, including atomic coordinates, isotropic thermal parameters for O(12) and O(3), anisotropic thermal parameters for all other atoms, and a secondary extinction coefficient, converged at $R = 0.0259$ and $R' = 0.0294$. The largest residual electron density in the final difference map is 1.3 e Å$^{-3}$, which is at a distance of 0.99 Å away from Cs(2). Structure solution and least-squares refinement were performed by using programs from the SHELXTL PLUS program package.[8] Neutral-atom scattering factors were used and correction for anomalous dispersion was applied.[9] The crystallographic data are listed in Table 1.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

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* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

## Results and Discussion

Atomic coordinates and selected interatomic distances for $Cs_3Ti_3As_5O_{20}$ are listed in Tables 2 and 3, respectively. As shown in Figs. 1 and 2, the structure consists of infinite tunnels where the caesium cations are located, and the framework is formed by $Ti(2)_2O_{11}$ units consisting of two corner-sharing $Ti(2)O_6$ octahedra, discrete $Ti(1)O_6$ octahedra, $As(1)O_4$ and $As(3)O_4$ tetrahedra, and $As(2)_2O_7$ groups. Atoms Ti(1), As(1), O(1), O(3), and the bridging oxygen, O(10), in the $Ti_2O_{11}$ unit sit on mirror planes. All other atoms are at general positions. Atom O(12) is disordered over two sites which are related by a two-fold axis. Each $Ti(1)O_6$ octahedron shares its six corners with two $As(1)O_4$, two $As(3)O_4$ and two $As(2)_2O_7$ groups. Each $Ti_2O_{11}$ dimer shares ten corners with one $As(1)O_4$, six $As(3)O_4$ and two $As_2O_7$ groups. The $As(1)O_4$ tetrahedron bridges over two Ti atoms within a $Ti_2O_{11}$ dimer and connects two $Ti(1)O_6$ monomers. Each $As(3)O_4$ co-ordinates to one monomer and three dimers. The $As_2O_7$ group co-ordinates to two dimers and two monomers with the remaining two O atoms being co-ordinated to Cs atoms only. Accordingly, the structural formula is $Cs_3Ti(Ti_2O)(AsO_4)_3(As_2O_7)$. The framework has two different pentagonal tunnels along the *a* axis, both of which are filled with Cs atoms. One type of tunnel, which has pentagonal windows formed by the edges of two octahedra and three tetrahedra, is filled with Cs(1), and the other type of tunnel, formed by three octahedra and two tetrahedra, is filled with Cs(2). As shown in Fig. 3, similar tunnels are found in α-$CsTi_3P_5O_{19}$ which has the structural formula $CsTi(Ti_2O)(PO_4)(P_2O_7)_2$. In this phosphate the tunnel formed by the edges of three $TiO_6$ octahedra and two $PO_4$ tetrahedra is filled with Cs atoms, but the other type of tunnel is empty. The larger size of $AsO_4$ relative to $PO_4$ allows the empty tunnels to accommodate the $Cs^+$ cations. To balance the charge one of the $As_2O_7^{4-}$ groups is replaced by two $AsO_4^{3-}$ groups, thus

**Table 1** Crystallographic data and intensity data collection parameters for $Cs_3Ti_3As_5O_{20}$

| | |
|---|---|
| Formula | $As_5Cs_3O_{20}Ti_3$ |
| *M* | 1237.03 |
| Crystal system | Orthorhombic |
| Space group | *Pbcm* (no. 57) |
| *a*/Å | 6.5084(9) |
| *b*/Å | 19.167(1) |
| *c*/Å | 15.377(1) |
| *U*/Å$^3$ | 1918.2(2) |
| *Z* | 4 |
| $D_c$/g cm$^{-3}$ | 4.284 |
| *F*(000) | 2224 |
| λ(Mo-Kα)/Å | 0.709 30 |
| μ(Mo-Kα)/cm$^{-1}$ | 154.9 |
| *T*/°C | 23 |
| Scan rate/° min$^{-1}$ | 16.48 |
| Scan mode | θ–2θ |
| Scan width/° | 0.56 + 0.44 tan θ |
| 2θ range/° | 4–55 |
| Unique reflections [$I > 2.5\sigma(I)$] | 1862 |
| Refined parameters | 147 |
| $R^a$ | 0.0259 |
| $R'^b$ | 0.0294 |
| Goodness of fit | 0.8959 |
| $(\Delta\rho)_{max, min}$/e Å$^{-3}$ | 1.34, −1.21 |

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{\frac{1}{2}}$. Weighting scheme, $w^{-1} = 1/[\sigma^2(F) + 0.0012\,F^2]$.

**Table 2** Positional parameters for $Cs_3Ti_3As_5O_{20}$

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Cs(1) | 0.130 58(5) | 0.150 96(2) | 0.026 07(2) |
| Cs(2) | 0.144 70(7) | 0.173 79(3) | 0.75 |
| Ti(1) | 0.239 6(2) | 0.647 11(6) | 0.25 |
| Ti(2) | 0.260 7(1) | 0.547 53(4) | 0.663 76(5) |
| As(1) | 0.268 62(9) | 0.099 73(3) | 0.25 |
| As(2) | 0.645 80(7) | 0.274 85(2) | 0.099 91(3) |
| As(3) | −0.246 02(7) | 0.004 92(3) | 0.101 38(3) |
| O(1) | −0.529 9(7) | 0.345 6(2) | 0.75 |
| O(2) | −0.242 6(6) | 0.421 3(2) | 0.659 1(3) |
| O(3) | 0.062 7(7) | 0.348 6(2) | 0.75 |
| O(4) | −0.219 7(7) | 0.278 5(2) | 0.663 7(3) |
| O(5) | −0.243 7(6) | 0.146 9(2) | 0.892 0(3) |
| O(6) | −0.270 9(5) | −0.052 5(2) | 0.841 8(2) |
| O(7) | −0.556 5(5) | 0.047 8(2) | 0.873 4(2) |
| O(8) | −0.246 6(6) | 0.024 4(2) | 0.996 4(2) |
| O(9) | 0.040 5(5) | 0.043 7(2) | 0.871 5(2) |
| O(10) | −0.255 9(7) | 0.065 0(3) | 0.75 |
| O(11) | 0.395 8(5) | 0.271 5(2) | 0.102 3(2) |
| O(12)* | −0.255 7(8) | 0.262 3(3) | −0.008 4(5) |

* Occupancy factor for O(12) is 0.5.

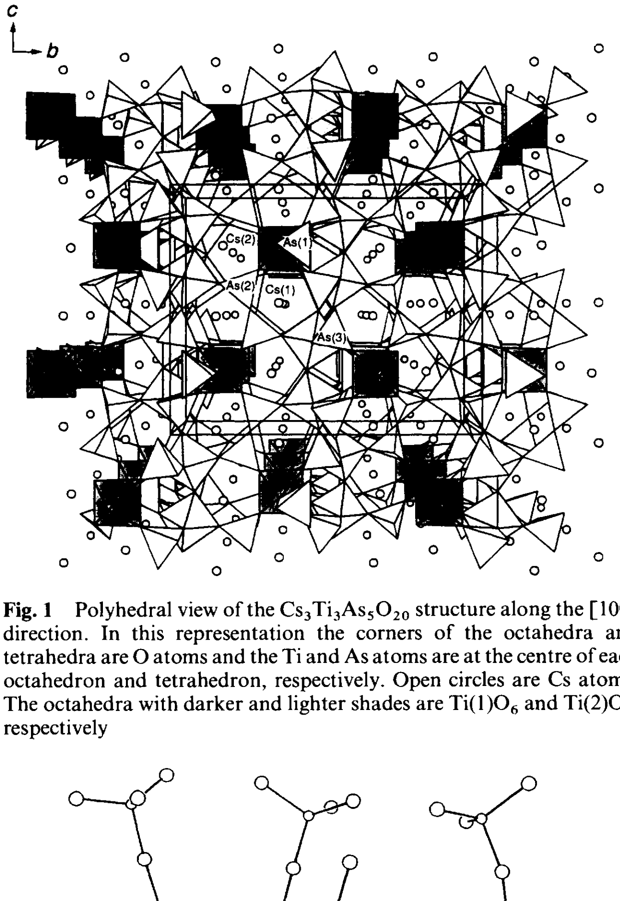

**Fig. 1** Polyhedral view of the $Cs_3Ti_3As_5O_{20}$ structure along the [100] direction. In this representation the corners of the octahedra and tetrahedra are O atoms and the Ti and As atoms are at the centre of each octahedron and tetrahedron, respectively. Open circles are Cs atoms. The octahedra with darker and lighter shades are $Ti(1)O_6$ and $Ti(2)O_6$, respectively

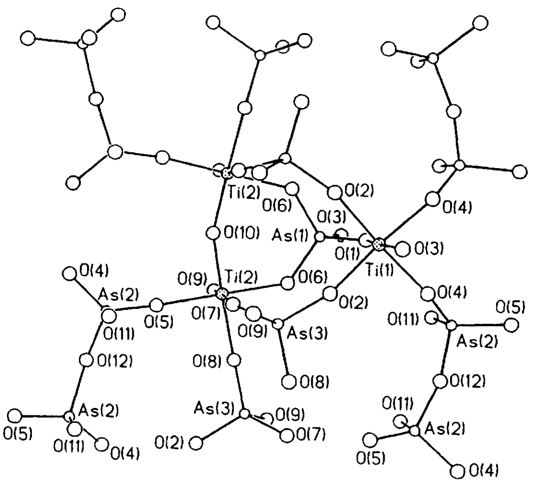

**Fig. 2** The co-ordination of the arsenate ligands around the dimeric $Ti_2O_{11}$ unit and monomeric $TiO_6$ octahedron in $Cs_3Ti_3As_5O_{20}$. For clarity the disordering of the bridging oxygen of the diarsenate group, O(12), is not shown

**Table 3** Selected interatomic distances (Å) for $Cs_3Ti_3As_5O_{20}$

| | | | |
|---|---|---|---|
| Cs(1)–O(2) | 3.464(4) | Cs(1)–O(3) | 3.472(1) |
| Cs(1)–O(4) | 3.392(5) | Cs(1)–O(5) | 3.192(4) |
| Cs(1)–O(6) | 2.919(3) | Cs(1)–O(7) | 3.684(4) |
| Cs(1)–O(8) | 3.481(4) | Cs(1)–O(8) | 3.462(4) |
| Cs(1)–O(9) | 3.197(4) | Cs(1)–O(11) | 3.113(4) |
| Cs(1)–O(11) | 3.014(4) | Cs(1)–O(12) | 3.340(6) |
| Cs(1)–O(12) | 3.026(6) | Cs(2)–O(3) | 3.394(5) |
| Cs(2)–O(4) | 3.379(5) (2 × ) | Cs(2)–O(5) | 3.380(4) (2 × ) |
| Cs(2)–O(7) | 3.634(4) (2 × ) | Cs(2)–O(9) | 3.188(4) (2 × ) |
| Cs(2)–O(10) | 3.339(5) | Cs(2)–O(11) | 2.988(4) (2 × ) |
| Ti(1)–O(1) | 1.894(5) | Ti(1)–O(2) | 1.917(4) (2 × ) |
| Ti(1)–O(3) | 1.969(5) | Ti(1)–O(4) | 1.952(5) (2 × ) |
| Ti(2)–O(5) | 1.948(4) | Ti(2)–O(6) | 1.956(3) |
| Ti(2)–O(7) | 1.928(3) | Ti(2)–O(8) | 2.052(4) |
| Ti(2)–O(9) | 1.964(4) | Ti(2)–O(10) | 1.819(1) |
| As(1)–O(1) | 1.679(5) | As(1)–O(3) | 1.666(5) |
| As(1)–O(6) | 1.676(3) (2 × ) | As(2)–O(4) | 1.666(5) |
| As(2)–O(5) | 1.668(4) | As(2)–O(11) | 1.629(4) |
| As(2)–O(12)* | 1.800(7) | As(2)–O(12′) | 1.703(7) |
| O(12) · · · O(12′) | 0.54(1) | As(3)–O(2) | 1.670(4) |
| As(3)–O(7) | 1.681(4) | As(3)–O(8) | 1.657(4) |
| As(3)–O(9) | 1.683(4) | | |

* O(12) is disordered over two sites.

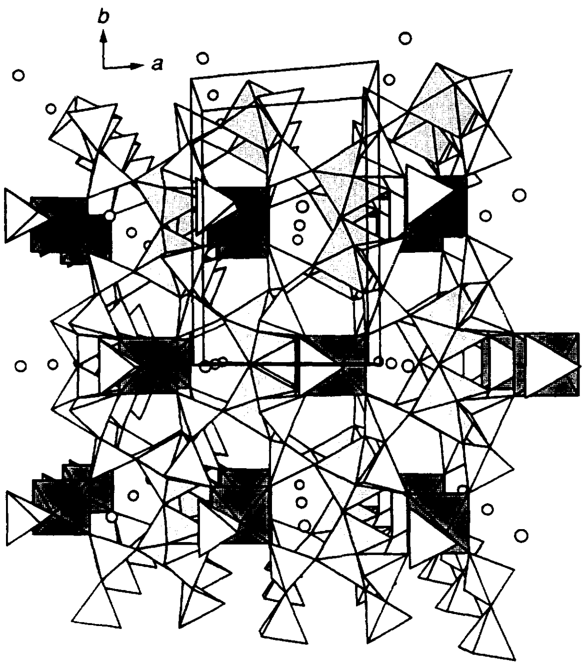

**Fig. 3** Polyhedral view of the α-$CsTi_3P_5O_{19}$ structure along the [001] direction

resulting in a different stoichiometry with a new structure as observed in $Cs_3Ti_3As_5O_{20}$.

Each Ti atom in the dimeric $Ti_2O_{11}$ unit is in a distorted octahedral co-ordination of one bridging oxide ion, O(10), and five phosphate oxygens. The titanium–oxide (bridging) distance is considerably shorter than the other Ti–O distances. The bond *trans* to the titanyl bridge is the longest. The titanyl bridge is symmetric and the two $Ti(2)O_6$ octahedra are in an eclipsed configuration. The Ti–O–Ti bond angle is 158.7° which is greater than the corresponding angle in α-$CsTi_3P_5O_{19}$ (147.9°). The $Ti(1)O_6$ octahedron is significantly distorted compared to the monomeric $TiO_6$ in α-$CsTi_3P_5O_{19}$. Both the $As(1)O_4$ and $As(3)O_4$ tetrahedra are quite regular. The $AsO_4$ tetrahedra of the $As_2O_7$ group are in a nearly eclipsed configuration. The As atoms are displaced away from the bridging oxygen so that one longer and three shorter As–O bonds are formed. The As–O–As bond angle is 133.3°. The Cs(1) and Cs(2) ions are co-ordinated by 13 and 12 oxygen atoms, respectively. The Cs co-ordination number is determined by the maximum cation–anion distance suggested by Donnay and Allmann.[10] Bond valence sums for Cs(1) and Cs(2) are 1.43 and 1.13, respectively. The value for Cs(1) indicates that the atom is tightly bound in $Cs_3Ti_3As_5O_{20}$ and explains why the tunnel formed by the edges of two octahedra and three tetrahedra in α-$CsTi_3P_5O_{19}$ is empty.

Few ternary compounds in the $A_2O$–$TiO_2$–$As_2O_5$ (A = akali metal) ternary system have been reported. To our knowledge, prior to this work $ATiOAsO_4$ (A = K, Rb or Cs)[4,11] and $LiTiAsO_5$[12] were the only examples of structurally characterized compounds in the system. The former compounds have the $KTiOPO_4$ structure and the latter is essentially isostructural with α-$Fe_2PO_5$. The phosphate $LiTiOPO_4$ is isostructural with β-$LiVOPO_4$.[13,14] The arsenates $Cs_3Ti_3As_5O_{20}$ and cubic $CsTi_2As_3O_{12}$[15] were isolated and characterized in an attempt to synthesize the arsenate analogue of $CsTi_3P_5O_{19}$. In contrast, the existence of $CsTi_2P_3O_{12}$ has not been reported. This study signals a rich crystal chemistry in the alkali-metal titanium arsenate system, indicating that many new structures will be forthcoming.

## Acknowledgements

Financial support of this investigation by the National Science Council and the Institute of Chemistry, Academia Sinica, is gratefully acknowledged.

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*Received* 12*th April* 1994; *Paper* 4/02164I