# CsTi$_2$As$_3$O$_{12}$:  A Cesium Titanium(IV) Arsenate with an Open Framework Structure

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A new ternary titanium(IV) arsenate, CsTi$_2$As$_3$O$_{12}$, has been synthesized by a flux method and structurally characterized by single-crystal X-ray diffraction. It crystallizes in the cubic space group $Ia\bar{3}d$ (No. 230) with $a$ = 20.495(3) Å, $V$ = 8609(2) Å$^3$, $Z$ = 32, and $R$ = 0.0242. The framework consists of vertex-sharing TiO$_6$ octahedra and AsO$_4$ tetrahedra, enclosing large cavities in which the cesium atom sites are partially occupied. The cavities are interconnected to form 3-dimensional channels. The structure is considerably different from those of NASICON and langbeinite.

## Introduction

Alkali metal titanium phosphates are of interest for their technological applications. For example, NaTi$_2$(PO$_4$)$_3$ belongs to the NASICON family of compounds which exhibit fast ion conduction and low thermal expansion.[1−4] Potassium titanyl phosphate (KTiOPO$_4$, or KTP) has been recognized as an outstanding nonlinear optical crystal for frequency conversion and electrooptic applications.[5,6] The structure of KTP contains TiO$_6$ octahedra and PO$_4$ tetrahedra which are linked into a three-dimensional framework through shared corners.[7,8] The resulting structure contains infinite chains of −Ti−O−Ti−O− atoms, while the K atoms occupy sites in hexagonal channels. The KTP structure is particularly accommodating with respect to isomorphous substitution. For example, Na, Rb, Cs, Tl, and NH$_4$ can be substituted for K; Ge, Zr, and Sn for Ti; and As for P. Phosphates of the stoichiometry A$_x$M$_2$(PO$_4$)$_3$ crystallize mainly in the NASICON [Na$_3$Zr$_2$PSi$_2$O$_{12}$] and the langbeinite [K$_2$Mg$_2$(SO$_4$)$_3$] structures.[9−11] The NASICON structure is characterized by interconnected tunnels which are responsible for fast Na$^+$ ionic conductivity, whereas langbeinite has a cage structure. In view of the potential technological interest in phases containing octahedral Ti$^{IV}$O$_6$ and tetrahedral XO$_4$ groups, we are currently making efforts to synthesize other new phases in the A$_2$O−TiO$_2$−X$_2$O$_5$ (A = alkali metals; X = P, As) systems. In contrast to the phosphates, few compounds are known in the ternary arsenate phase space. To our knowledge, the KTP isostructures ATiOAsO$_4$ (A = Na, K, Rb, Cs, Tl, NH$_4$)[6,12] and Cs$_3$Ti$_3$As$_5$O$_{20}$[13] are the only structurally characterized compounds in the system. It is surprising to find that

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**Table 1.**  Crystallographic Data for CsTi$_2$As$_3$O$_{12}$

| formula | As$_3$CsO$_{12}$Ti$_2$ | $\mu$(Mo K$\alpha$), cm$^{-1}$ | 140.3 |
|---|---|---|---|
| fw | 645.47 | $\varrho_{calcd}$, g·cm$^{-1}$ | 3.984 |
| space group | $Ia\bar{3}d$ | $\lambda$, Å | 0.709 30 |
| $a$, Å | 20.495(3) | $T$, °C | 23 |
| $V$, Å$^3$ | 8609(2) | $R^a$ | 0.0242 |
| $Z$ | 32 | $R_w{}^b$ | 0.0207 |

$^a$ $R = \sum ||F_o| - |F_c||/\sum |F_o|$. $^b$ $R_w = [\sum_w(|F_o| - |F_c|)^2/\sum_w|F_o|^2]^{1/2}$, $w^{-1} = \sigma^2(F)$.

**Table 2.**  Atomic Coordinates and Thermal Parameters (Å$^2 \times 100$) for CsTi$_2$As$_3$O$_{12}$

| atom | $x$ | $y$ | $z$ | $U_{eq}{}^a$ |
|---|---|---|---|---|
| Cs(1)$^b$ | 0.125 | 0.125 | 0.125 | 4.17(4) |
| Cs(2)$^b$ | 0.01916(5) | −0.23084(5) | 0.375 | 3.88(4) |
| Ti(1) | 0.28550(5) | 0.03550(5) | 0.375 | 0.59(3) |
| Ti(2) | 0 | 0 | 0 | 0.35(3) |
| As(1) | 0.03109(3) | 0.34699(3) | 0.45232(3) | 0.57(2) |
| O(1) | 0.0117(2) | 0.4630(2) | 0.3180(2) | 0.9(1) |
| O(2) | 0.2796(2) | 0.1209(2) | 0.4072(2) | 1.0(1) |
| O(3) | 0.1953(2) | 0.0196(2) | 0.4049(2) | 0.8(1) |
| O(4) | 0.5758(2) | −0.0269(2) | 0.4521(2) | 1.0(1) |

$^a$ $U_{eq}$ is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor. $^b$ Site occupancy is 0.5.
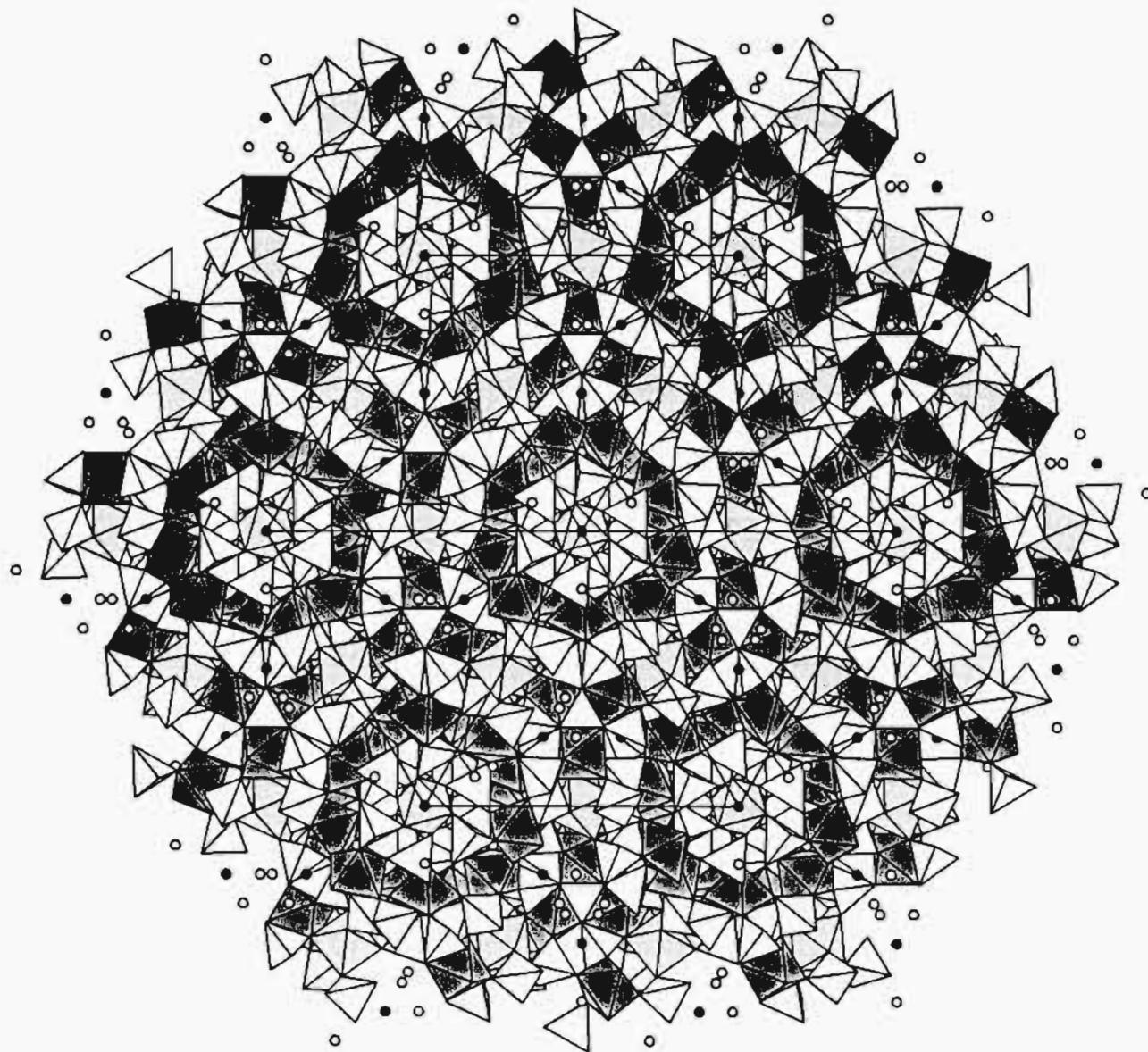
arsenates with the composition ATi$_2$As$_3$O$_{12}$ have not been reported, although the NASICON type structure was first determined in 1968. This paper reports the result of our exploratory synthesis and single-crystal X-ray structural characterization of a cesium titanium arsenate, CsTi$_2$As$_3$O$_{12}$. It adopts an open framework structure, which is rather different from those of NASICON and langbeinite.

## Experimental Section

**Synthesis.**  CsH$_2$AsO$_4$ was prepared from a solution of As$_2$O$_3$ dissolved in H$_2$O$_2$ with cesium hydroxide. NH$_4$H$_2$AsO$_4$ was prepared in a similar way with ammonium hydroxide. A mixture of 1.650 g of CsH$_2$AsO$_4$, 0.957 g of NH$_4$H$_2$AsO$_4$, and 0.160 g of TiO$_2$ (Cs:As:Ti mole ratio = 3:6:1) was thoroughly mixed and slowly heated to 850 °C in a 15 cm$^3$ platinum crucible. It was then cooled to 650 °C at a rate of 10 °C h$^{-1}$ and 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 colorless chunks of the title compound, colorless rod-like crystals, and a yellow crystalline solid. Some of the chunk crystals are pseudo-dodecahedral. The rod crystal is Cs$_3$Ti$_3$As$_5$O$_{20}$,[13] but the yellow solid was not characterized. Energy dispersive X-ray fluorescence analysis on four colorless chunk crystals gave an average Cs:Ti:As mole ratio of 0.93:

**Figure 1.** Polyhedral representation of the CsTi₂As₃O₁₂ structure along the [111] direction. In this representation the corners of octahedra and tetrahedra are O atoms and the Ti and As atoms are at the center of each octahedron and tetrahedron, respectively. Solid circles, Cs(1); open circles, Cs(2). The octahedra with darker and lighter shades are Ti(1)O₆ and Ti(2)O₆, respectively.

2.07:3, which is close to the results from the single-crystal X-ray diffraction (vide infra). On the basis of X-ray analysis using a Rigaku powder diffractometer with filtered copper radiation, polycrystalline CsTi₂As₃O₁₂ was prepared in nearly pure form by reaction of CsH₂-AsO₄, NH₄H₂AsO₄, and TiO₂ in a mole ratio of 1:2:2 at 700 °C for 36 h with an intermediate grinding. The colorless products were always contaminated with a small amount of unidentified impurities. The intensity of the most intense reflection of the impurities ($2\theta = 26.1°$) was about 7.5% that of the major phase, and all other observed reflections in the diffraction pattern corresponded very well with that calculated from the single-crystal data.

**Single-Crystal X-ray Diffraction.** Peak profile analysis of the colorless chunk crystals of the title compound using an Enraf-nonius CAD4 diffractometer indicated that many of them were not single crystals. Many were selected before a single crystal was obtained. The crystal used was a colorless chunk of dimensions $0.15 \times 0.15 \times 0.17$ mm. Indexing and intensity data collection were done on the same diffractometer with graphite-monochromated Mo Kα radiation. Unit cell parameters and orientation matrix were determined by a least-squares fit of 20 peak maxima with $2\theta$ ranging from 24 to 33°. Axial

oscillation photographs were taken to check the unit cell parameters. Of the 1818 reflections collected ($2\theta_{max} = 50°$, scan mode $2\theta-\theta$), 505 reflections were considered observed ($I > 2.5\sigma(I)$) after $Lp$ and empirical absorption correction ($R_{int} = 0.030$). Corrections for absorption were based on $\varphi$ scans of several suitable reflections with $\chi$ values close to 90° using the NRCVAX program package.[14] 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 $Ia\bar{3}d$ (No. 230). The structure was solved by direct methods and successive Fourier synthesis, and was refined by full-matrix least-squares refinement based on $F$ values. Cs(1) was located at 16$b$ special positions, Cs(2) and Ti(1) at 48$g$, Ti(2) at 16$a$, and all other atoms at 96$h$ general positions. We earlier refined the structure with both Cs atom sites fully occupied. Both Cs atoms showed very large thermal parameters, indicative of partial occupancy or positional disorder. The Cs··Cs distances are very short (Cs(1)··Cs-(2) = 3.07 Å, Cs(2)··Cs(2) = 1.11 Å), precluding simultaneous Cs occupancy of these sites. The multiplicities of both Cs atom were allowed to refine. The Cs(1) and Cs(2) positions respectively refined to multiplicities of 0.0808(6) and 0.249(1), indicating that both Cs

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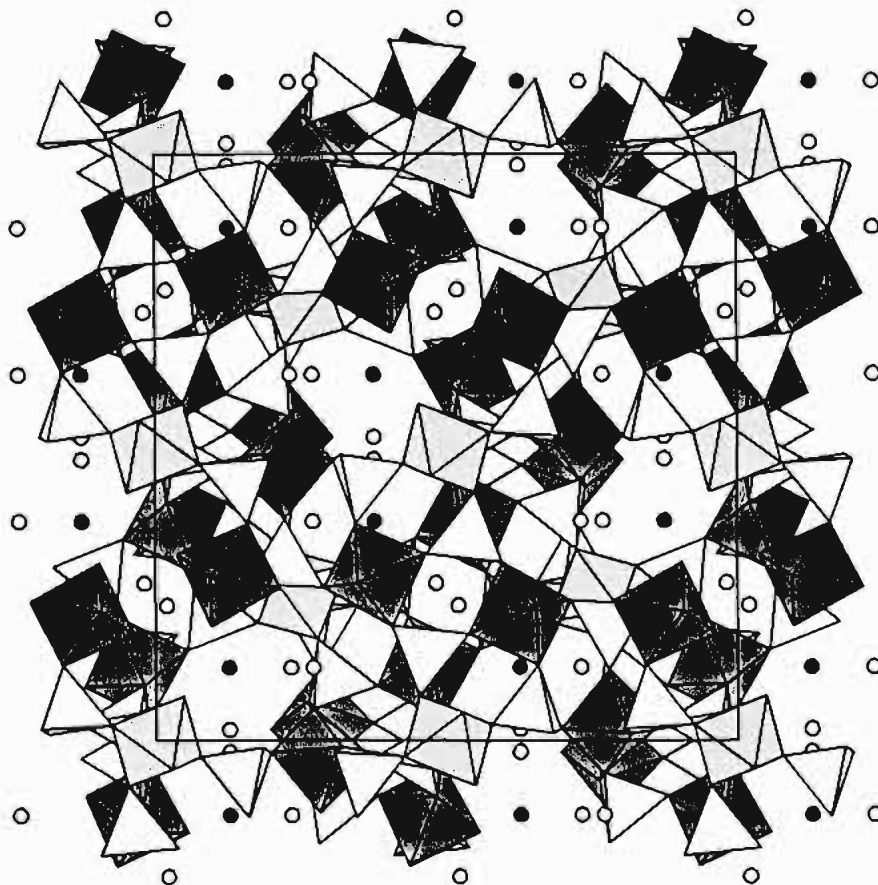(18) Donnay, G.; Allmann, R. *Am. Mineral.* **1970**, *55*, 1003.

**Figure 2.** Slice of the $CsTi_2As_3O_{12}$ structure parallel to (001) showing the large open windows in the framework.

**Table 3.** Bond Lengths (Å), Bond Valence Sums ($\sum s$), and Bond Angles (deg) for $CsTi_2As_3O_{12}$

Bond Lengths and Bond Valence Sums

| | | | |
|---|---|---|---|
| Cs(1)−O(3) | 3.352(4) (6×) | Cs(1)−O(4) | 3.635(4) (6×) |
| $\sum s$(Cs(1)−O) = 0.70 | | | |
| Cs(2)−O(1) | 3.189(4) (2×) | Cs(2)−O(1) | 3.342(4) (2×) |
| Cs(2)−O(3) | 3.232(4) (2×) | Cs(2)−O(3) | 3.426(4) (2×) |
| $\sum s$(Cs(2)−O) = 0.76 | | | |
| Ti(1)−O(1) | 1.984(3) (2×) | Ti(1)−O(2) | 1.874(4) (2×) |
| Ti(1)−O(3) | 1.974(4) (2×) | | |
| $\sum s$(Ti(1)−O) = 4.27 | | | |
| Ti(2)−O(4) | 1.918(4) (6×) | | |
| $\sum s$(Ti(2)−O) = 4.54 | | | |
| As(1)−O(1) | 1.687(4) | As(1)−O(2) | 1.672(4) |
| As(1)−O(3) | 1.675(4) | As(1)−O(4) | 1.674(4) |
| $\sum s$(As(1)−O) = 5.10 | | | |
| $\sum s$(O(1)) = 2.08 | | $\sum s$(O(2)) = 2.14 | |
| $\sum s$(O(3)) = 2.19 | | $\sum s$(O(4)) = 2.08 | |

Bond Angles

| | | | |
|---|---|---|---|
| O(1)−Ti(1)−O(2) | 86.1(2) (2×) | O(1)−Ti(1)−O(2) | 89.5(2) (2×) |
| O(1)−Ti(1)−O(3) | 89.5(2) (2×) | O(1)−Ti(1)−O(3) | 96.1(2) (2×) |
| O(2)−Ti(1)−O(3) | 89.1(2) (2×) | O(2)−Ti(1)−O(2) | 104.2(2) |
| O(3)−Ti(1)−O(3) | 77.7(2) | O(4)−Ti(2)−O(4) | 88.1(2) (6×) |
| O(4)−Ti(2)−O(4) | 91.9(2) (6×) | O(1)−As(1)−O(2) | 113.8(2) |
| O(1)−As(1)−O(3) | 108.4(2) | O(1)−As(1)−O(4) | 113.1(2) |
| O(2)−As(2)−O(3) | 109.3(2) | O(2)−As(2)−O(4) | 107.8(2) |
| O(3)−As(2)−O(4) | 104.0(2) | | |

positions are half-occupied. The final cycle of full-matrix least-squares refinement including atomic coordinates, anisotropic thermal parameters, and fixed multiplicities for half-occupied Cs positions converged at $R = 0.0242$, $R_w = 0.0207$, and GOF = 1.393. The final difference electron density map was featureless and the highest peak and deepest hole were 1.10 and −0.77 e/Å³, respectively. Neutral-atom scattering factors for all atoms were used.[15] Anomalous dispersion and secondary extinction corrections were applied. Structure solution and refinement
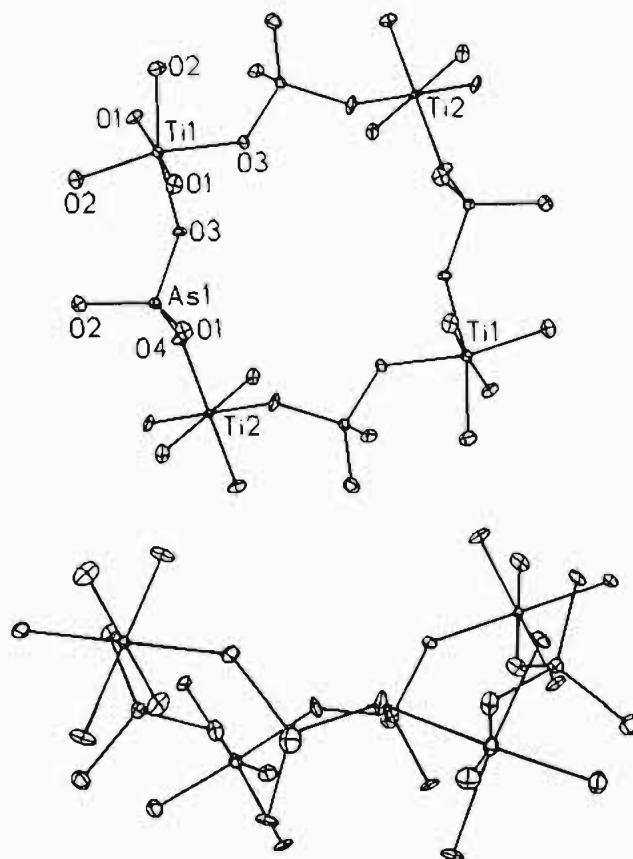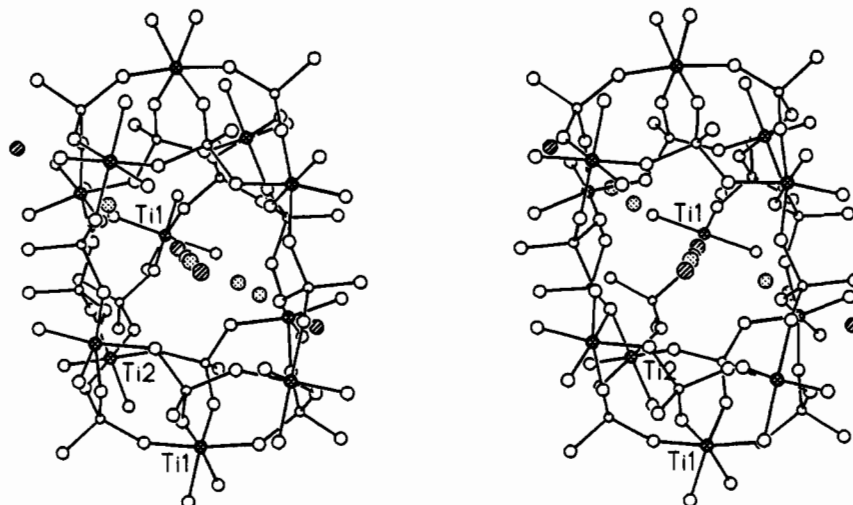


**Figure 3.** Eight-sided window in the $CsTi_2As_3O_{12}$ structure viewed perpendicular to (0$\bar{1}$1) (top) and along [100] (bottom).

were performed on a DEC MicroVAX computer system using SHELXTL-Plus programs.[16]

**Figure 4.** Stereoscopic view of a section of the CsTi$_2$As$_3$O$_{12}$ structure in a direction perpendicular to (110). Shaded, stippled, cross-hatched, small open circles, and large open circles represent Cs(1), Cs(2), Ti, As, and O atoms, respectively.

## Results and Discussion

The crystallographic data are listed in Table 1, atomic coordinates and thermal parameters in Table 2, and selected bond distances, bond angles and bond valence sums[17] in Table 3.

Atoms Ti(1) and Cs(2) sit on 2-fold axes (special positions 48$g$), Cs(1) has a local symmetry of 32 (16$b$), Ti(2) is located at 3 (16$a$), and As and all O atoms are at general positions. The Ti and As atoms are six- and four-coordinated, respectively. The coordination number of each Cs atom was determined on the basis of the maximum gap in the Cs−O distances ranked in increasing order. The maximum cation−anion distance, $L_{max}$, according to Donnay and Allmann, was also considered.[18] Therefore, Cs(1) and Cs(2) are coordinated by 12 and eight oxygen atoms with the 13th Cs(1)−O and the ninth Cs(2)−O distances at 4.50 and 3.85 Å, respectively. The valence sums for Cs(1) and Cs(2) are significantly lower than 1, indicating that they are loosely bound. The values for As and O atoms are in good agreement with their formal oxidation states. The values for both Ti(1) and Ti(2) are somewhat higher. Bond-valence calculation on the following alkali-metal titanium(IV) phosphates or arsenates have also been performed with the assessed valence sums for Ti in parentheses: α-CsTi$_3$P$_5$O$_{19}$ (4.48, 4.41);[19] β-CsTi$_3$P$_5$O$_{19}$ (4.50, 4.38);[19] Cs$_2$TiOP$_2$O$_7$ (4.14);[20] Cs$_3$Ti$_5$P$_7$O$_{29}$ (4.31, 4.14, 4.56, 4.15, 4.39);[21] Cs$_3$Ti$_3$As$_5$O$_{20}$ (4.37, 4.30);[13] CsTiOAsO$_4$ (4.02, 4.04);[22] RbTiOPO$_4$ (4.15, 4.04);[23] Rb$_3$Ti$_3$P$_5$O$_{20}$ (4.26, 4.44, 4.42);[24] KTiOPO$_4$ (4.15, 4.16);[8] KTi$_2$P$_3$O$_{12}$ (4.40);[25] α-NaTiOPO$_4$ (4.24);[12] LiTiOPO$_4$ (4.24).[26] It can be concluded that the assessment of the valences of the Ti atoms in alkali-metal titanium(IV) phosphates or arsenates using the bond-length bond-strength formula $s = \exp[(1.185 - r)/0.37]$ by Brown and Altermatt in many cases yields values significantly greater than +4.

A projection of the crystal structure of CsTi$_2$As$_3$O$_{12}$ along the [111] direction is illustrated in Figure 1. The compound
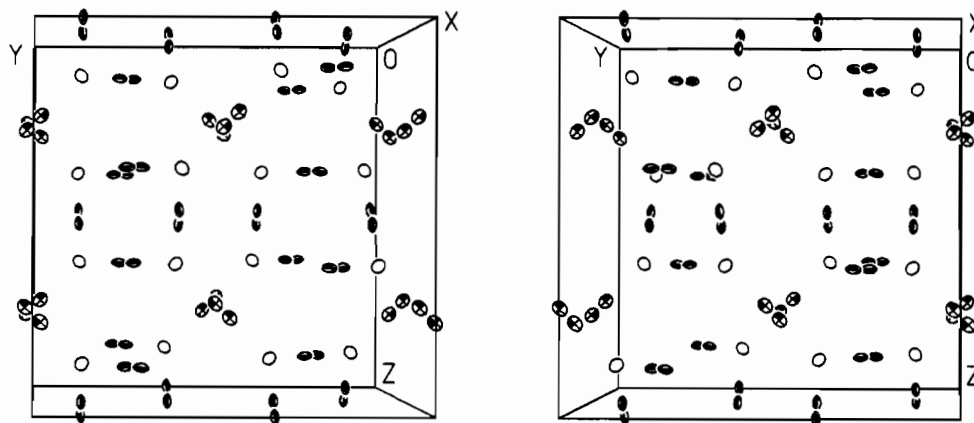
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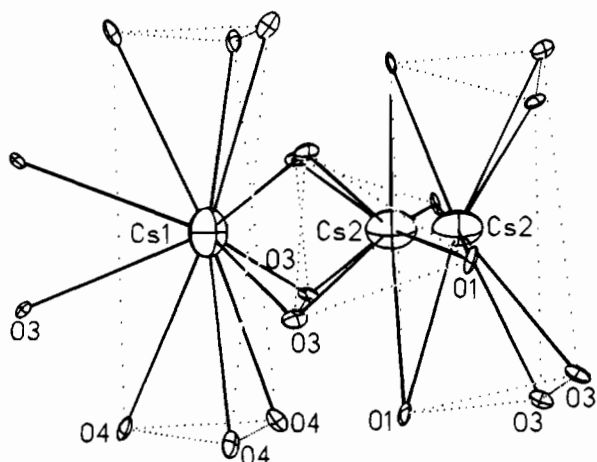(22) Protas, J.; Menaert, G.; Boulanger, B.; Menaert, B. *Acta Crystallogr.* **1989**, *C45*, 1123.
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adopts a new structure type, which appears rather different from those of NASICON ($R\bar{3}c$, $a \approx 8$, $c \approx 22$ Å) and langbeinite ($P2_13$, $a \approx 10$ Å). The structure of CsTi$_2$As$_3$O$_{12}$ can be described in terms of close-packed columns. Each column consists of a core of alternating Ti(2)O$_6$ octahedra and 12-coordinated Cs(1) atoms along the trigonal axis of $Ia\bar{3}d$. The core is surrounded by successive rings of AsO$_4$ tetrahedra, Ti-(1)O$_6$ octahedra, and AsO$_4$ tetrahedra. Between these columns, there are octahedral sites occupied by Ti(1) and Ti(2) atoms. The complex framework contains large interstitial space for the cesium ions. A slice of the structure parallel to the (001) plane reveals large open windows within the framework (Figure 2). These window are mainly parallel to the {$\bar{1}$10} planes, namely ($\bar{1}$10) and its symmetry-related planes. Each window is puckered and formed by the edges of four TiO$_6$ octahedra and four AsO$_4$ tetrahedra (Figure 3). The shortest oxygen−oxygen distance across this eight-sided window is 5.82 Å, which is smaller than twice the sum of the radii for $^{VIII}$Cs$^+$ (1.74 Å) and $^{IV}$O$^{2-}$ (1.38 Å). A stereoview of a portion of the unit cell, which permits visualization of the empty interstitial space inside the network, is shown in Figure 4. Two windows are stacked to form a large cavity, which is related to the other two by a 3-fold axis. These cavities are interconnected to form open channels which are undulating through the framework. Atom Cs(1) is located at the intersection of the three-way channel. Cs(2) is disordered over two sites in the cavity, which are related by the point symmetry 222. Both Cs(1) and Cs(2) sites are half-occupied. The disposition of Cs$^+$ cations in a unit cell shows that there are two sets of intertwined channels within the framework (Figure 5). The two sets of channels do not intersect and are related by the symmetry element $\bar{3}$.

The framework consists of vertex-sharing TiO$_6$ octahedra and AsO$_4$ tetrahedra. Each Ti(2)O$_6$ octahedron shares corners with six different AsO$_4$ tetrahedra, which are further coordinated to 12 Ti(1) atoms. Each Ti(1)O$_6$ also shares corners with six different AsO$_4$ tetrahedra, which further knit together three Ti-(1)O$_6$ and six Ti(2)O$_6$ octahedra by corner-sharing. Each AsO$_4$ shares corners with one Ti(2)O$_6$ and three Ti(1)O$_6$ octahedra. Every oxygen atom belongs simultaneously within a TiO$_6$ octahedron and a AsO$_4$ tetrahedron. Adjacent two TiO$_6$ octahedra are connected through two AsO$_4$ tetrahedra. In contrast both the NASICON and langbeinite structures contain [Ti$_2$P$_3$O$_{18}$] structural units composed of two TiO$_6$ octahedra linked to each other through three PO$_4$ tetrahedra. The AsO$_4$ tetrahedron is nearly regular. Ti(2)O$_6$ is regular, but Ti(1)O$_6$

**Figure 5.** Stereoscopic view of the cesium cations in the $CsTi_2As_3O_{12}$ structure showing the disposition of channels in the framework. Key: ellipsolid with shaded segments, Cs(2); ellipsoid boundary ellipse, Cs(1). Thermal ellipsoids are shown at 60% probability.



**Figure 6.** Coordination environment of Cs(1) and Cs(2) in $CsTi_2As_3O_{12}$ viewed in a direction approximately parallel to [111]. The edges of polyhedra are shown in dotted lines. Cs(2) is disordered over two sites. All Cs sites are half-occupied. Thermal ellipsoids are shown at 60% probability.

is significantly distorted. The two Ti(1)−O(2) bonds, which are in cis positions, are about 0.1 Å shorter than the other Ti-(1)−O bonds since O(2) is not involved in Cs−O coordination.

The framework of $CsTi_2As_3O_{12}$ delimits large sites for the $Cs^+$ cations. The coordination of the oxide ions around Cs(1) and Cs(2) is shown in Figure 6. Cs(1) is in a hexacapped trigonal prismatic site, which is formed by placing additional two oxygen ligands above each side edge of the prism. Cs(2) is in an eight-coordinated site, and the coordination polyhedron approximates a trigonal prism with two of the square faces being capped by oxide ions. These Cs sites are arranged in the following way $\cdots[Cs(1)\cdots Cs(2)\cdots Cs(2)]_\infty\cdots$. The distances between adjacent Cs sites are too short to allow simultaneous

occupancy. Both Cs(1) and Cs(2) sites are half occupied. The interconnected space of partially occupied lattice sites indicates the possibility of ionic mobility. However, the structure does not meet all the structural characteristics that are required for fast ion transport. For instances, the two Cs sites may have significantly different potential energies and the smaller cross-sectional area of a channel, which is located between Cs(1) and Cs(2), is smaller than twice the sum of the anion and cation radii. Namely, the site binding energy may preferentially stabilize the cation at a particular set of lattice sites and the bottleneck of the channel is not open enough for easy ion passage. Accordingly, the ion exchange experiments in molten salts were performed to hope that smaller cations could be exchanged for $Cs^+$ in $CsTi_2As_3O_{12}$. Powders of the title compound were held for 15 h in molten $NaNO_3$ and $KNO_3$. The products were washed with water to remove the excess nitrates, dried, and analyzed by X-ray powder diffraction and EDX. It was found that $Cs^+$ ions were partially exchanged with $K^+$ ions and the $CsTi_2As_3O_{12}$ framework was retained. For $Na^+$ exchange with $CsTi_2As_3O_{12}$, the network collapsed although a complete replacement of $Cs^+$ ions by $Na^+$ ions was achieved. Presumably, the $Na^+$ ion is too small to stabilize the structure. Further investigation of ion-exchange properties and ionic conductivity study are in progress.