

# Neutron and X-Ray Diffraction Study of the Crystal Structure of CsTiSi<sub>2</sub>O<sub>6.5</sub>

M. L. Balmer,\* Q. Huang,†,‡ W. Wong-Ng,‡ R. S. Roth,‡ and A. Santoro‡

\*Battelle, Pacific Northwest National Laboratory, Richland, Washington 99352; †University of Maryland, College Park, Maryland 20742; and ‡National Institute of Standards and Technology, Gaithersburg, Maryland 20899

Received June 19, 1996; in revised form January 16, 1997; accepted January 22, 1997

The structure of the silicotitanate CsTiSi<sub>2</sub>O<sub>6.5</sub> has been analyzed with neutron powder and X-ray single crystal diffraction techniques. The compound crystallizes with the symmetry of space group *Ia* $\bar{3}$ *d* and lattice parameter *a* = 13.8417(7) Å. There are 16 formula units in the unit cell. The basic structure of the silicotitanate is similar to that of pollucite and consists of a framework of corner-sharing TO<sub>4</sub> tetrahedra (*T* = 1/3 Ti + 2/3 Si) forming large voids in which the Cs<sup>+</sup> cations are located. Titanium and silicon are disordered over the 48g sites of the cubic space group. Compared to pollucite, there are eight extra oxygen atoms in the unit cell. These atoms partially occupy two sets of general sites and are bonded to both the cesium and the *T* cations of neighboring tetrahedra. © 1997 Academic Press

## 1. INTRODUCTION

The discovery of silicotitanate ion exchangers for removal of Cs from radioactive, Na-rich wastes has stimulated research efforts in the preparation and characterization of new silicotitanate materials (1, 2). One of the new compounds recently synthesized is a derivative of the cesium aluminosilicate pollucite, CsAlSi<sub>2</sub>O<sub>6</sub>, in which the titanium replaces aluminum (3, 4). This substitution requires a mechanism for charge compensation, such as the presence of trivalent titanium cations, or the incorporation of oxygen in excess of six atoms per formula unit into the structure. Since the title silicotitanate was synthesized at 800°C in air (vide infra), and since Ti<sup>3+</sup> is typically only present in materials that are prepared in highly reducing environments, it is unlikely that a significant quantity of Ti<sup>3+</sup> is present in the samples considered in this study (it is also worth noting that these samples have a white color, typical of Ti<sup>4+</sup> compounds). Additional evidence for the presence of Ti<sup>4+</sup> was obtained by X-ray photoelectron spectroscopy data which show a broad, symmetric peak centered at -464 eV, typical of Ti<sup>4+</sup> (4). Since the binding energy of Ti<sup>3+</sup> is about 2 eV higher than that of Ti<sup>4+</sup> (5), this peak would be asymmetric, with a shoulder at higher binding energies, if Ti<sup>3+</sup> were

present in any appreciable quantities in the samples used in this study. Finally, in X-ray absorption spectra, the energy of the absorption edge for the title compound was found to be 3.4 eV. This value is in agreement with those found for K<sub>2</sub>Ti<sub>2</sub>O<sub>5</sub> (3.8 eV) and Ba<sub>2</sub>TiSi<sub>2</sub>O<sub>8</sub> (4.1 eV), which contain Ti<sup>4+</sup>(V), and with those obtained for CsAlTiO<sub>4</sub> (3.4 eV) and Ba<sub>2</sub>TiO<sub>4</sub> (3.5 eV), which contain Ti<sup>4+</sup>(IV) (6). According to Waychunas (7), we should expect shifts of about 2 eV if Ti<sup>3+</sup> were present in our compound. These results show that the mechanism of charge compensation is incorporation of excess oxygen in the pollucite structure resulting in the stoichiometry CsTiSi<sub>2</sub>O<sub>6.5</sub>.

Based on the atomic scattering amplitudes for neutrons, neutron diffraction analysis is expected to clarify oxygen positions. A neutron powder diffraction experiment was undertaken to elucidate the complete crystal structure, and in particular, to determine the location of the extra oxygen in the unit cell of CsTiSi<sub>2</sub>O<sub>6.5</sub>. X-ray diffraction, on the other hand, is relatively insensitive to small changes in oxygen composition, but can more precisely measure cation positions and temperature factors. A single crystal X-ray analysis was therefore carried out to complement the neutron experiment.

A complete description of the structure and clarification of the cation environments will facilitate the determination of structure–property relationships and the development of new materials with tailored properties.

## 2. EXPERIMENTAL

### A. Preparation of the Sample

Crystalline CsTiSi<sub>2</sub>O<sub>6.5</sub> was prepared via a sol–gel processing route. First, an amorphous, homogeneous precursor was synthesized using tetraisopropyl orthotitanate (TIOT), tetraethyl orthosilicate (TEOS), and cesium hydroxide. The alkoxides were mixed in a glove bag under nitrogen and then a mixture of CsOH, water, and ethanol was added. The resulting hydrolyzed precursor was stirred for a minimum of 15 h and then dried in air at room temperature. X-ray

diffraction and TEM/EDS analysis showed that the precursor was both homogeneous and amorphous. Approximately 0.5 g of this material was then heat treated in a platinum crucible to produce crystalline  $\text{CsTiSi}_2\text{O}_{6.5}$ .

Two heat treatment schemes were applied to the precursor. In the first, the material was heated from room temperature to  $800^\circ\text{C}$  at the rate of  $5^\circ\text{C}/\text{min}$  and then held at  $800^\circ\text{C}$  in air for at least 1 h. In this procedure, the onset of the formation of crystalline  $\text{CsTiSi}_2\text{O}_{6.5}$  was observed at  $750^\circ\text{C}$  and full crystallization occurred at  $800^\circ\text{C}$ . Upon further heating the sample melted at  $980^\circ\text{C}$ . In the second scheme, the stoichiometric precursor was melted at  $1200^\circ\text{C}$  and then quenched to form a clear glass. The quenched glass was then ground to fine powder and heat treated at  $800^\circ\text{C}$  in air for 30 h. Both these methods produced the same crystallized material. The sample used in the neutron diffraction experiment was produced with the first scheme previously described.

Single crystals of  $\text{CsTiSi}_2\text{O}_{6.5}$  were grown from a powdered sample of the compound, using  $\text{CsVO}_3$  as a flux. A mixture of  $\text{CsTiSi}_2\text{O}_{6.5}$  and  $\text{CsVO}_3$  was placed into a Pt tube which was then sealed at both ends, heated in a vertical tube furnace at the rate of  $50^\circ\text{C}/\text{h}$  to  $1100^\circ\text{C}$ , held for 1 h at this temperature, cooled to  $650^\circ\text{C}$  at the rate of  $1^\circ\text{C}/\text{h}$ , and finally cooled to room temperature. The flux was dissolved in warm  $\text{H}_2\text{O}$  and crystals of the title compound were isolated from a mixture of phases comprising  $\text{TiO}_2$ , cristobalite, and a new Cs–Ti silicate. Samples of quality suitable for single crystal work were selected using a polarizing microscope and were checked for stoichiometry by atomic absorption spectroscopy.

### B. Neutron Powder Diffraction Data

The neutron powder diffraction measurements were made with the new high-resolution powder diffractometer at the National Institute of Standards and Technology reactor, using the experimental conditions listed in Table 1. The profile refinements were carried out using the General Structure Analysis System (GSAS) program of Larson and Von Dreele (8). The observed diffraction lines could be readily indexed in terms of a cubic unit cell of lattice parameter close to that reported for cubic pollucite (9–11),

giving a strong indication that the structures of  $\text{CsTiSi}_2\text{O}_{6.5}$  and  $\text{CsAlSi}_2\text{O}_6$  are basically the same. A few extra reflections, the strongest of which had less than 5% the intensity of the strongest peak in the powder pattern, could not be indexed in terms of any of the derivative lattices of the cubic cell and were therefore attributed to impurities in the sample and excluded from all subsequent calculations. The first structural refinement was carried out assuming the cubic atomic arrangement of pollucite, with the  $\text{Ti}^{4+}$  and  $\text{Si}^{4+}$  cations disordered over the sites  $48g$  of space group  $Ia\bar{3}d$ ,  $\text{Cs}^+$  located in  $16b$ , oxygen in the general position  $96h$ , and ignoring the presence of the extra oxygen atoms in the structure. This first set of calculations gave reasonable agreement between observed and calculated intensities and acceptable bond distances, thus confirming the previous observation that the structure of the title compound is indeed similar to that of pollucite. The sites of space group  $Ia\bar{3}d$  split into sets of crystallographically distinct positions when the symmetry is lowered to  $I4_1/acd$  and  $I4_1/a$ , thus making it possible to check if the  $\text{Ti}^{4+}$  and  $\text{Si}^{4+}$  cations are ordered. Attempts to refine models based on these space groups, however, were unsuccessful due to the high correlations between the structural parameters varied in the refinements. These results strongly indicate that  $\text{Ti}^{4+}$  and  $\text{Si}^{4+}$  are indeed disordered, and they further confirm that the symmetry of the sample used in the experiment is cubic.

The additional eight oxygen atoms contained in the unit cell of  $\text{CsTiSi}_2\text{O}_{6.5}$  can be distributed over any of the positions available in space group  $Ia\bar{3}d$ . Special position  $24c$  ( $\frac{1}{4}, \frac{1}{8}, 0$ ) (which was found to be partially occupied by  $\text{Na}^+$  cations in the structure of  $\text{Cs}_{12}\text{Na}_4\text{Al}_{16}\text{Si}_{32}\text{O}_{96} \cdot 4\text{H}_2\text{O}$ , (9)) is an unlikely site for the extra oxygen because it results in unrealistically short Cs–O distances of about 2.45 Å. Not surprisingly, a refinement of this model did not give an agreement factor between observed and calculated intensities significantly lower than that obtained for the model with  $\text{O}_6$  stoichiometry (see Table 2), and, more importantly, attempts to refine the occupancy of the extra oxygen resulted in a negative value of the occupancy factor. The position  $24d$  ( $\frac{3}{4}, \frac{1}{8}, 0$ ) was eliminated because of similar crystal–chemical arguments and because of unsatisfactory refinement results.

TABLE 1  
Collection of Neutron Powder Diffraction Data

Monochromatic beam	311 reflection of a Cu monochromator
Wavelength	1.5396 Å
Horizontal divergences	15', 20, 7' of arc for the inpile, monochromatic, and diffracted beam collimators, respectively
2θ angular range	3°–168°; steps, 0.05°
Scattering amplitudes ( $10^{-12}$ cm)	$b(\text{Cs}) = 0.542$ , $b(\text{Si}) = 0.415$ , $b(\text{Ti}) = -0.344$ , and $b(\text{O}) = 0.581$

**TABLE 2**  
**Refinement of Different Structural Models**

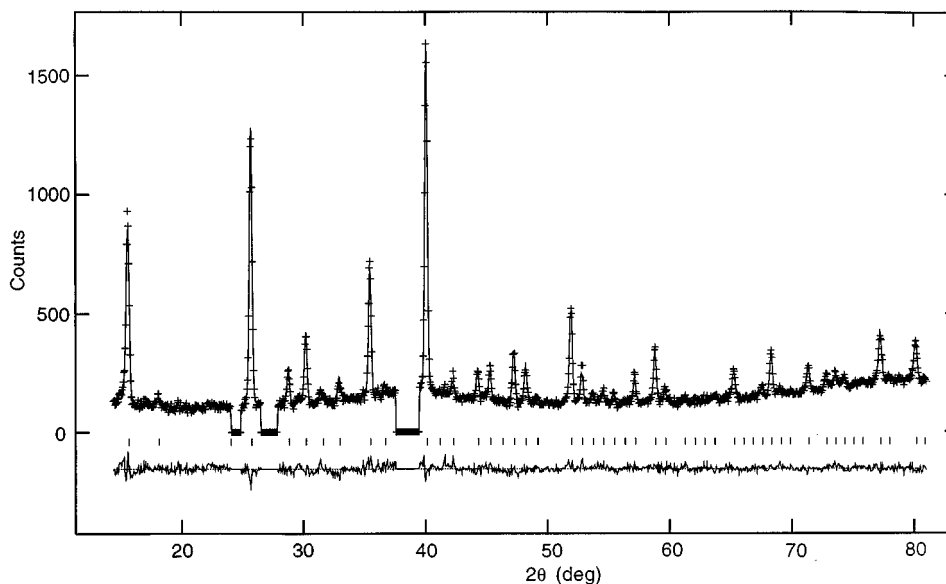
	No extra oxygen	Extra O at (1/4, 1/8, 0)	Extra O at (3/4, 1/8, 0)	O(3)	O(2)	O(3) + O(2)
$R_p$	6.70	6.52	6.25	6.03	5.73	5.66
$R_{wp}$	7.75	7.62	7.41	7.07	6.90	6.79
$\chi^2$	1.38	1.33	1.26	1.15	1.09	1.06
$a$ (Å)	13.8418(8)	13.8418(7)	13.8417(7)	13.8418(7)	13.8417(7)	13.8417(7)

To determine possible locations of the extra oxygen atoms, a Fourier difference map (based on the neutron powder data) was calculated after refining the structural model in which these atoms had not been included. Of the several weak peaks present in the map, only two (with approximate  $x, y, z$  coordinates equal to 0.79, 0.21, 0.24 and 0.71, 0.06, 0.02, indicated as O(3) and O(2), respectively, in Table 2) gave acceptable Cs–O and T–O distances ( $T = 1/3$  Ti +  $2/3$  Si). As shown in Table 2, the  $\chi^2$  factors for the models with the extra oxygen located only in positions O(3) or in positions O(2), are both significantly lower than the value of  $\chi^2$  corresponding to the structure with O<sub>6</sub> stoichiometry (1.15 and 1.09 for O(3) and O(2), respectively, versus 1.38 for the structure with no oxygen), indicating that neither set of positions can be excluded *a priori* from the structural model. For this reason the excess oxygen was

distributed over both sets of sites in the subsequent calculations. Because of the strong correlation between occupancy and thermal parameters, in the final refinement based on the neutron experiment, only the occupancies of O(3) and O(2) were allowed to vary, while their thermal factors were kept fixed at a value of  $4.8 \text{ \AA}^2$  (i.e., of the same order of that of O(1)). The results of the final neutron refinement are given in Table 4 and the agreement between observed and calculated neutron intensities is shown in the plot of Fig. 1.

### C. X-Ray Single Crystal Data

Since the  $T$  cations have a low value of the scattering amplitude compared to Cs and O ( $b(T) = 0.162 \times 10^{-12} \text{ cm}$ , versus  $b(\text{Cs}) = 0.542$  and  $b(\text{O}) = 0.581 \times$



**FIG. 1.** Observed (crosses) and calculated (continuous line) intensities in the neutron powder pattern of CsTiSi<sub>2</sub>O<sub>6.5</sub>. The difference  $I(\text{obs}) - I(\text{cal})$  is shown in the plot in the lower part of figure. The short vertical lines mark the  $2\theta$  angles of the Bragg reflections. The three angular intervals with no data shown are the regions affected by weak peaks attributed to impurities in the sample. These regions were excluded from the refinement.

**TABLE 3**  
**Crystal Data and Summary of Intensity Data Collection and Structure Refinement**

Color	Colorless
Formula weight	340.97
Temp., °C	≈ 25
Radiation, graphic monochromator	Mo, 0.71073
Crystal dimensions, mm	0.12 × 0.10 × 0.06
Crystal data	
Space group	$Ia\bar{3}d$
Cell constants, Å <sup>a</sup>	13.8359(14)
Formula units/unit cell	16
Data collection	
Total reflections measured	3598
Independent reflections	703
Observed reflections <sup>a</sup>	158
$\theta$ range, °	28
Range of transm. factors, % <sup>b</sup>	82.4 to 100, Ave. 92.1
Refinements	
$R = \sum   F_o  -  F_c   / \sum  F_o $	0.032
$R_w$	0.048
No. parameters varied	13
Weights <sup>b</sup>	non-Poisson, $p = 0.4$
Extinction coefficient	$1.279 \times 10^{-7}$
GOF	1.5
Largest shift/error	0.01

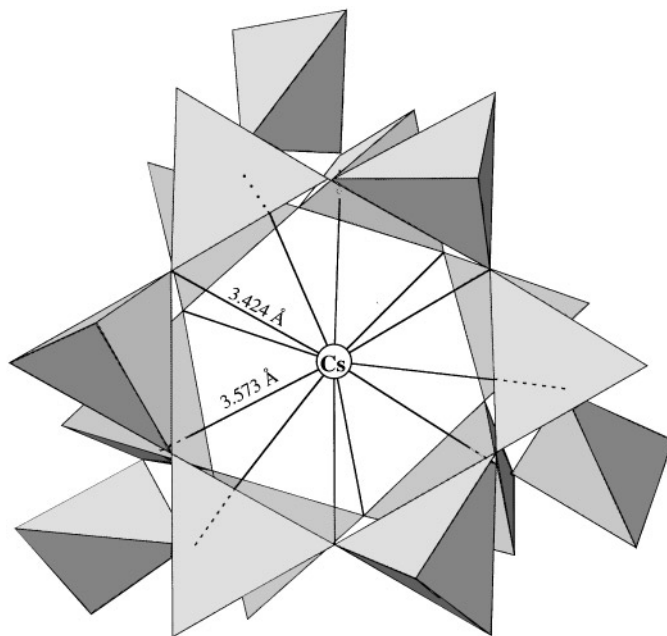
<sup>a</sup> CAD4 operation manual, Enraf-Nonius, Delft, The Netherlands, 1977.

<sup>b</sup> Molen, Structure solution package provided by Enraf-Nonius, Inc., 1991. Scattering factors from: D. T. Cromer and J. T. Waber, "International Tables for X-Ray Crystallography," Vol. IV. The Kynoch Press, Birmingham, UK, 1974.

$10^{-12}$  cm), their positional parameters and temperature factors could only be determined with low precision from the neutron powder pattern. For this reason it was decided to refine the structure also using X-ray single crystal intensity data.

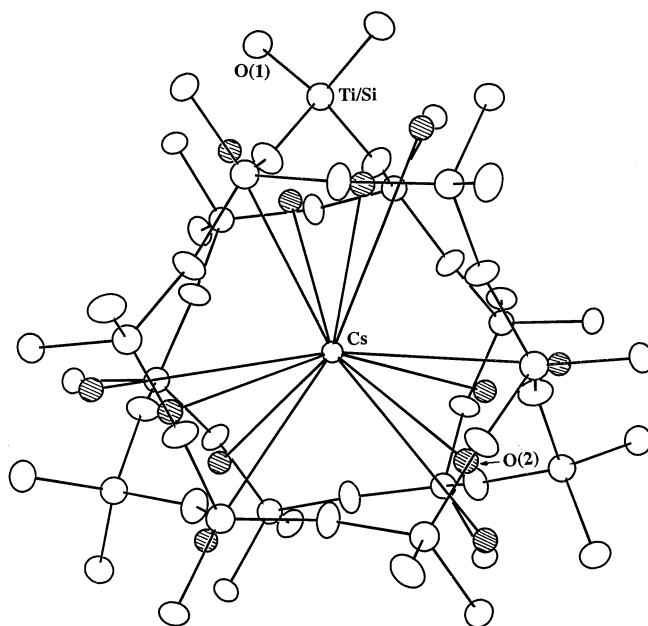
The X-ray intensities were measured with a DAD4 diffractometer, using the conditions listed in Table 3.<sup>1</sup> Twenty five reflections with  $13^\circ < \theta < 19^\circ$  were employed in the least squares determination of the lattice constant. Crystal stability and orientation were monitored throughout the experiment by periodically checking the intensities of six standard reflections. The raw intensities were corrected for Lorentz and polarization effects, and the absorption correction was evaluated with the psi absorption scheme. The initial parameters used in the X-ray refinements were those obtained previously in the neutron experiment. The initial structural model, which did not include the extra oxygen

<sup>1</sup> The purpose of identifying the X-ray equipment in this article is to specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology.



**FIG. 2.** View along one of the  $\langle 111 \rangle$  axes of the distribution of the  $TO_4$  tetrahedra around a  $Cs^+$  cation. The oxygen atoms O(1) bonded to the cesium are indicated by the Cs–O lines.

atoms, yielded a value of the  $R$  factor of 3.4%, confirming again the general features of the structure. Due to the low value of the scattering factors of oxygen compared to that of the other elements in the structure, and to the small fraction



**FIG. 3.** Locations of the O(2) oxygen atoms (hatched circles) around a  $Cs^+$  cation. This figure is a projection along one of the threefold axes. On the average, each O(2) site is occupied by 0.063 atoms.

of oxygen in excess of the O<sub>6</sub> stoichiometry, no attempts were made to locate the extra oxygen atoms in the X-ray analysis. These atoms were therefore included in the final refinement at the positions determined from the neutron data and their positional and thermal parameters were not allowed to vary. Not surprisingly, the inclusion of the extra oxygen resulted in an *R* factor of 3.2%, i.e., insignificantly lower than that obtained previously.

The results of the X-ray analysis are shown in Table 4.

### 3. DISCUSSION

The structural parameters listed in Table 4 show that all the atoms in the structure of CsTiSi<sub>2</sub>O<sub>6.5</sub> have unusually high temperature factors. This result is not surprising, since the presence of eight extra oxygen atoms in the unit cell combined with the disordering of the Si<sup>4+</sup> and Ti<sup>4+</sup> cations over the same crystallographic sites is, in general, associated with local shifts of some of the atoms and, consequently, with high thermal parameters. Similar results have been

reported previously for compounds with similar structures. In the case of Cs<sub>12</sub>Na<sub>4</sub>Al<sub>16</sub>Si<sub>32</sub>O<sub>96</sub>·4H<sub>2</sub>O, water molecules and Cs<sup>+</sup> cations are disordered over the same crystallographic sites (9). In our case, the presence of water in the structure can be excluded since the neutron powder pattern does not show abnormally high background.

The oxygen atoms O(1) form a network of corner-sharing tetrahedra practically identical to that described for pollucite (9, 10). The configuration of the tetrahedra in the immediate vicinity of a central cesium atom is schematically represented in Fig. 2 in projection along the [111] axis of the cubic unit cell. As indicated in the figure, six-membered loops of tetrahedra form channels along the [111] direction (as well as along the other threefold axes), with the Cs<sup>+</sup> cations located in the channels and bonded to 12 O(1) oxygen atoms with distances of 3.424(4) and 3.573(4) Å. These bond distances, as well as the T–O separations reported in Table 4, agree very closely with the corresponding values reported for pollucite (9). The distribution of the O(2) atoms around cesium is illustrated in Fig. 3, and the

TABLE 4  
Structural Parameters and Selected Bond Distances (Å) of CsTiSi<sub>2</sub>O<sub>6.5</sub> at 295 K

Atom	Site	x	y	z	<i>B</i> (Å <sup>2</sup> )	Occup.	
Cs	16b . 32	1/8	1/8	1/8	4.0(2)	1	
		1/8	1/8	1.8	3.645(7)	1	
Ti	48g . . 2	0.661(1)	0.589(1)	1/8	6.3(5)	1/3	
		0.6639(2)	0.5861(2)	1/8	2.85(4)	1/3	
Si	48g . . 2	0.661(1)	0.589(1)	1/8	6.3(5)	2/3	
		0.6639(2)	0.5861(2)	1/8	2.85(4)	2/3	
O(1)	96h 1	0.1042(3)	0.1349(3)	0.7175(3)		1	
		0.1047(5)	0.1353(5)	0.7171(7)	6.3(2)	1	
		[B(11)	B(22)	B(33)	B(12)	B(13)	B(23)]
		[8.8(3)	8.0(3)	4.2(2)	1.6(2)	1.6(2)	0.5(2)]
O(2)	96h 1	0.706	0.062	0.021	4.8	0.060(4)	
		0.706	0.062	0.021	4.8	0.060(4)	
O(3)	96h 1	0.791	0.205	0.235	4.8	0.023(4)	
		0.791	0.205	0.235	4.8	0.023(4)	
Selected bond distances (Å)							
Cs–O(1)	× 6	3.424(4)		Ti/Si–O(1)	× 2	1.70(1)	
		3.427(9)				1.67(1)	
Cs–O(1)	× 6	3.573(4)		Ti/Si–O(1)	× 2	1.63(1)	
		3.564(8)				1.66(1)	
Cs–O(2)		3.17		Ti/Si–O(2)		2.00	
		3.17				2.01	
Cs–O(2)		4.03		Ti/Si–O(2)		2.14	
		4.03				2.13	
Cs–O(3)		3.03		Ti/Si–O(2)		2.37	
		3.03				2.33	
Cs–O(3)		3.20		Ti/Si–O(3)		2.31	
		3.20				2.33	
				Ti/Si–O(3)		2.46	
					2.46		

Note. Space group, *Ia* $\bar{3}d$ ; neutron (first line) *a* = 13.8417(7) Å; X-ray (second line) *a* = 13.8359(14) Å; *z* = 16. *R*<sub>p</sub> = 5.66, *R*<sub>wp</sub> = 6.80,  $\chi^2$  = 1.06.

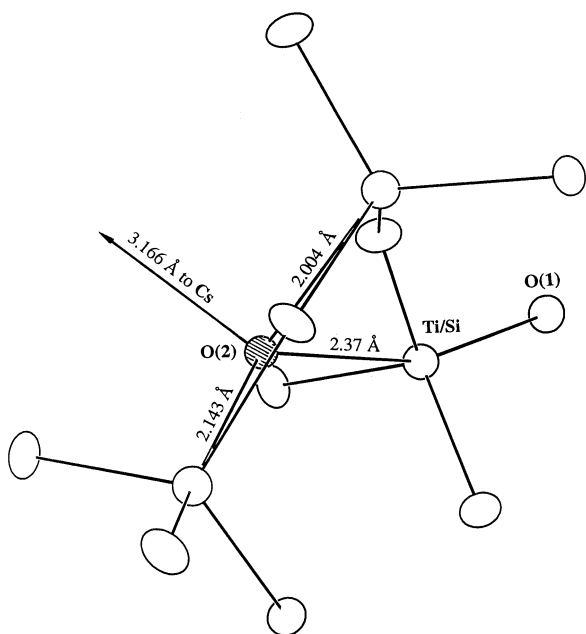


FIG. 4. Environment of one of the O(2) extra oxygens (the atom represented in this figure is the one identified by an arrow in Fig. 3).

environment of one of these atoms is shown in greater detail in Fig. 4, where the Cs–O(2) and T–O(2) distances are also indicated. We have to point out, however, that the distances reported in Table 4 represent average values and that, on a local level, these separations may be significantly different due to shifts of the atoms involved in the bonding. It is reasonable to assume that a site O(2) is occupied by an oxygen atom only when the centers of neighboring tetrahedra are occupied by titanium, rather than silicon. This is in agreement with  $^{29}\text{Si}$  NMR studies and Ti-EXAF results published elsewhere which show that both four- and five-coordinated Ti is present in the structure (6, 12). The O(3) sites are clustered above and below the cesium along the threefold axes, as shown in Fig. 5, and form rings within which O(3)–O(3) separations are as short as 0.8 Å. Consequently, only one atom of oxygen can be present in each ring, located on any one of the available sites. The distances reported in Table 4 show that O(3) has strong bond with cesium and a weak bond with T. As a consequence of the presence of extra oxygen in the unit cell of  $\text{CsTiSi}_2\text{O}_{6.5}$ , the average coordination of the central  $\text{Cs}^+$  cation is 13-fold, rather than 12-fold as in pollucite. In addition, when an O(2) site is occupied by oxygen, the coordination of the T cations located at the centers of the neighboring tetrahedra is five-fold, rather than fourfold, as shown in Fig. 4.

Some O(1)–O(2) and O(1)–O(3) distances in this structure are unreasonably short (on the order of 1.7–1.8 Å). As

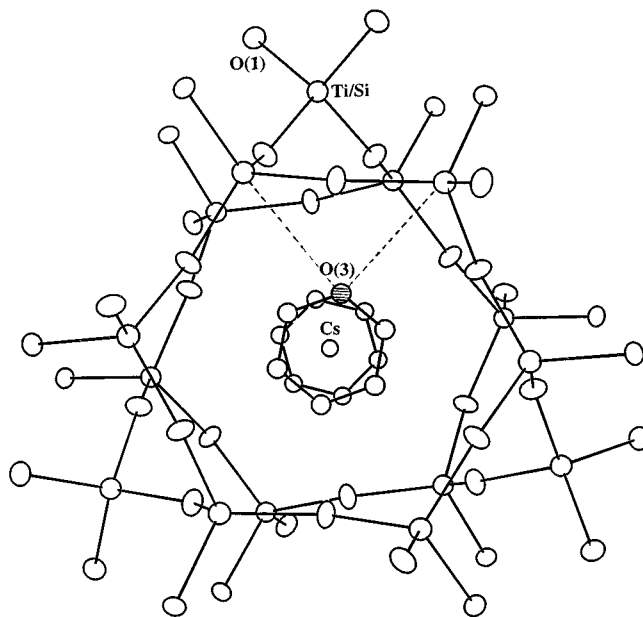


FIG. 5. Distribution of the O(3) sites around a central  $\text{Cs}^+$  cation. The two O(3) rings are located above and below the cesium. On average each O(3) site is occupied by 0.023 atoms.

mentioned previously, however, the thermal parameters obtained in the refinement indicate that large distortions are possible, with some of the atoms locally shifted from their average positions by about 0.3 Å. It is the existence of these shifts that makes the positions given in Table 4 for O(2) and O(3) acceptable as possible locations of the extra oxygen in the unit cell.

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