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# The crystal structure of a bimuth–transition metal phosphate $Bi_6TiP_2O_{16}$

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**Abstract**

A single-crystal was selected from the reaction product of a stoichiometric mixture of $Bi_3PO_7$ to which was added 10% $TiO_2$ and its crystal structure determined from three-dimensional X-ray diffraction data. The structure is monoclinic, $a = 11.233(2)$ Å, $b = 5.410(1)$ Å, $c = 11.233(2)$ Å, $\beta = 95.13(3)^\circ$, space group $I2$, $Z = 2$; least squares refinement was on $F^2$ and converged to $R1 = 0.0514$, $wR2 = 0.146$ for 833 unique reflections. The crystal was twinned by a 180° rotoinversion about the $[\bar{1}01]$ direction of the direct lattice, resulting in the interchange of the $a$ and $c$ axes. The structure consists of chains formed by edge sharing of $OBi_4$ tetrahedra. The stacking along [100] consists of these chains bridged by layers formed by $TiO_6$ octahedra and $PO_4$ tetrahedra. The three crystallographically independent Bi ions are surrounded by eight oxygen ions that form two bicapped trigonal prisms and one distorted cubic environment, respectively. The Bi–O distances vary from 2.20(4) to 3.16(4) Å. Ti is in octahedral environment in which the equatorial distances are 1.82(3) and 2.00(5) Å and the apical distances are 2.14(4) Å. The $PO_4$ tetrahedron is nearly regular.

*Keywords:* Bismuth–transition metal phosphates; Structure of $Bi_6TiP_2O_{16}$

## 1. Introduction

The discovery of the oxygen ion conductor $Bi_4V_2O_{11}$ [1] has given rise to a large crystal chemical literature describing structures and properties of compounds resulting from the substitution of other cations for Bi and V [2–11]. The articulations of the polyhedra are not only influenced by the $6s^2$ lone-pair electrons of the group IVB and VB metals but also by vacancies, mixed valence states and domain variations of the chemical composition within single crystals that usually manifest themselves as disorder, twinning or superstructures. The appearance of these complex phases has given rise to commensurate and incommensurate structures but the deviations from three-dimensional periodicities are frequently small, the X-ray diffraction intensities are dominated by the regular lattice of the heavy atoms that mimic the structure of $\delta$-$Bi_2O_3$ [12] so that superlattice reflections are very few and structures are solved on the basis of subcells [13].

Many of these structures can be described in terms of the articulations of chains of $O(BiM)_4$ tetrahedra that are linked by $PO_4$ moieties into three-dimensional frameworks [13,14]. The structural description based on linked $O(BiM)_4$ tetrahedra is especially advantageous for compounds exhibiting disorder. The exploration of possible Bi–Ti–P oxides in the systems Bi–$M$–$X$ oxides ($M$ = transition metal, $X$ = P, V, As) has yielded a new compound with the composition $Bi_6TiP_2O_{16}$ and we describe here its crystal structure. The ternary compounds $Bi_6PbM_2O_{15}$, $M$ = P, As and V, are reported in [3] but their crystal structures are unknown.

## 2. Experimental

Analytical grade $Bi_2O_3$, $TiO_2$ and $NH_4H_2PO_4$ were thoroughly ground under acetone in various proportions in an agate mortar. The mixtures were preheated at 400°C for 4 h, the temperature was raised to 600°C for about 8 h and then raised to 900°C for 12 h. The products were examined with an X-ray powder diffractometer equipped with a diffracted beam monochromator

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and Cu$K\alpha$ radiation. The diffraction patterns indicated that the materials were polyphasic even after repeated grinding and firing. Some of the specimens contained $BiPO_4$ and $TiO_2$ in addition to one or more unknown constituents. Examination of the products under a polarizing binocular microscope showed no evidence of single crystals suitable for structure analysis. We then decided to prepare the phase $Bi_3PO_7$ [15] from a mixture of $Bi_2O_3$ and $NH_4H_2PO_4$ that was prepared and processed as described above. The product was polyphasic. To this product was added $TiO_2$ in increments of 5%, 10%, 15% and 20% by weight. Products prepared from mixtures containing more that 10% $TiO_2$ showed the presence of rutile. The diffraction patterns of the products did not appear to be from single-phase material. Microscopic examination of the 10% product showed the presence of yellowish crystals with columnar and platy habits. One such crystal was selected and Weissenberg and precession photographs showed the crystal had a metrically orthorhombic unit cell with lattice parameters about $a = 15.2$ Å, $b = 16.1$ Å, $c = 5.41$ Å. The systematic absences were consistent with a face centered space group. Semiquantitative energy dispersive X-ray analysis, EDX, of several single crystals showed the approximate composition $Bi_8TiP_2$ in fair agreement with the eventual stoichiometry determined by the structure analysis.

A crystal was mounted on a Nonius $\kappa$ automated CCD diffractometer and three-dimensional X-ray intensities were collected in P1 and the orthogonal lattice parameters $a = 5.4096(2)$ Å, $b = 15.1593(5)$ Å, $c = 16.5801(6)$ Å. After processing of the data and an analytical absorption correction the lowest $R_{\text{int}}$ was for a monoclinic crystal system and space group $I2$ had the lowest FOM. The nonstandard space group orientation was selected because previous, related structures had been described in this space group [10,14,16]. The data collection and results of the refinement are shown in Table 1. The transformation matrix between the monoclinic cell shown in Table 1 and the orthogonal cell for the data collection is (010, 101, $10\bar{1}$). The two diagonals of the monoclinic cell are 15.16 and 16.58 Å, respectively, the $b$ and $c$ axes of the orthorhombic cell.

Table 1
Crystal data and structure refinement for $Bi_6TiP_2O_{16}$

| | |
|---|---|
| Empirical formula | Bi6 O16 P2 Ti |
| Formula weight | 1619.72 |
| Temperature | 293(2) K |
| Wavelength (Å) | 0.71073 |
| Crystal system, space group | Monoclinic, $I2$ |
| Unit cell dimensions | |
| $a$ (Å) | 11.233(2) |
| $b$ (Å) | 5.4096(11) |
| $c$ (Å) | 11.233(2) |
| $\beta$ (deg) | 95.13(3) |
| Volume (Å$^3$) | 679.8(2) |
| Z, Calculated density (g/cm$^3$) | 2, 7.913 |
| Color | Pale yellow |
| Absorption coefficient (mm$^{-1}$) | 78.255 |
| Absorption correction | Analytical |
| Crystal faces $h\,k\,l$/dimension (mm) | 1 0 1/0.065, −1 0−1/0.065, −1 0 1/0.16, −3−6 3/0.10, 1 1−1/0.09, 4−1−4/0.13 |
| Transmission max/min | 0.0277/0.0019 |
| $\theta$ range for data collection (deg) | 3.64 to 27.40 |
| Limiting indices | $-14 \leqslant h \leqslant 14$, $-6 \leqslant k \leqslant 6$, $0 \leqslant l \leqslant 14$ |
| Reflections collected/unique | 1468/833 [$R$(int) = 0.0766] |
| Completeness to theta (%) | 97.2 |
| Twin matrix | 0 0 1/0 1 0/1 0 0 |
| Twin fraction | 0.61 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data/restraints/parameters | 833/1/66 |
| Goodness-of-fit on $F^2$ | 1.098 |
| Final $R$ indices [$I > 2\sigma(I)$] $R1$, w$R2$ | 0.0514, 0.1460 |
| $R$ indices (all data) $R1$ | 0.0515, w$R2$ = 0.1458 |
| Absolute structure parameter | 0.01(7) |
| Extinction coefficient | 0.00043(16) |
| Largest diff. peak and hole (e.A$^{-3}$) | 4.209–7.567 |

## 3. Structure solution

The direct method using the SHELXS suite of programs contained in WINGX [17] yielded Bi positional parameters. Least squares refinements used the SHELXL software [17]. The Bi atoms were used for phasing the structure factors to calculate difference electron density maps that revealed the Ti, P and some of the oxygen atoms. It became evident that the composition of the compound was $Bi_6TiP_2$ and with the assumption of the usual valence states, O16. Further examinations of difference electron density maps revealed all the required oxygen ions.

During the refinement the site occupancy for Ti was consistently greater than unity. Therefore refinements were calculated in which a mixed occupancy of Ti and Bi was introduced with the restraints that the site occupancy sum to unity and that the positional and displacement parameters are the same. 84% of Ti and 16% Bi occupies the site, Table 2, and for the purposes of the structural description the site occupancy can be considered as solely occupied by Ti. The heavy-metal–transition metal mixed site occupancy was also encountered in the structure of $Bi_{1.5}(Pb_{7.3}Mn_{0.7})(PO_4)_6O_{1.3}$ [18]. The atomic environments of O1, O2, O3 and O4 are essentially identical and for the least squares refinements their atomic displacement parameters were therefore constrained to be the same. The crystal used for the data collection was twinned by a 180° rotoinversion about the $[\bar{1}01]$ direction of the direct lattice, resulting in the interchange of the $a$ and $c$ axes. 61% of the crystal volume had coordinates as shown in Table 2.

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($A^2 \times 10^3$) for $Bi_6TiP_2O_{16}$*

| Sof | $x$ | $y$ | $z$ | $U$(eq) |
|---|---|---|---|---|
| Bi(1) | 3313(2) | −320(7) | 86(2) | 13(1) |
| Bi(2) | −1740(2) | −4897(1) | −1620(2) | 10(1) |
| Bi(3) | 107(2) | −306(7) | −3375(2) | 14(1) |
| Ti 0.423(8) | 0 | −386(17) | 0 | 10(2) |
| Bi 0.077 | 0 | −386 | 0 | 10 |
| P | 1326(14) | 4560(30) | −1415(13) | 19(3) |
| O(1) | 0 | −2690(90) | −1/2 | 5(3) |
| O(2) | 0 | 2270(90) | −1/2 | 5(3) |
| O(3) | 1520(30) | 2170(80) | 3290(30) | 5(3) |
| O(4) | 3500(30) | 2180(80) | 1740(30) | 5(3) |
| O(5) | 2570(20) | 4520(70) | −710(20) | 11(5) |
| O(6) | −3650(40) | −700(1 2 0) | 2280(30) | 40(9) |
| O(7) | 670(40) | 2140(90) | −1060(30) | 31(9) |
| O(8) | −1410(30) | −830(80) | −900(20) | 22(7) |
| O(9) | −600(30) | −3250(70) | 1120(30) | 18(8) |

* $U$(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

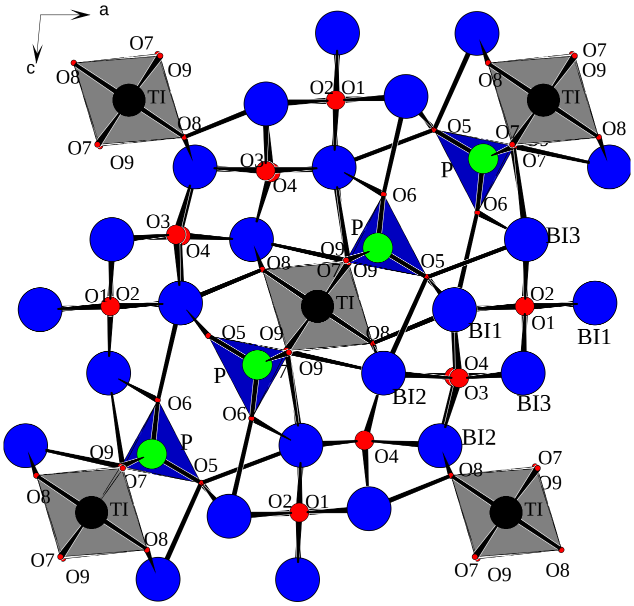

Fig. 1. View of the crystal structure of $Bi_6TiP_2O_{16}$ along [010].

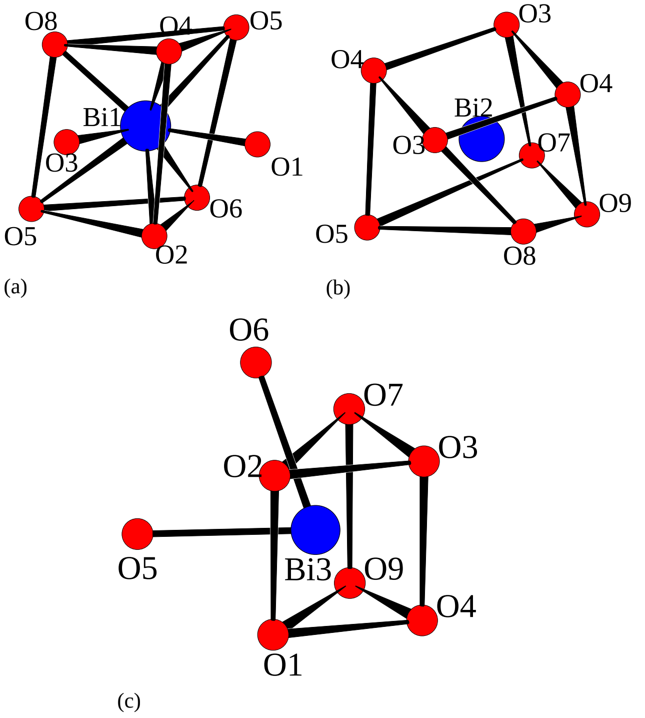

Fig. 2. The oxygen polyhedra around the bismuth ions. Some Bi–O bonds have been omitted for the sake of clarity.

## 4. Discussion

The structure consists of chains formed by edge sharing of $OBi_4$ tetrahedra [13]. O1 and O2 are in the tetrahedral interstice formed by 2Bi1 and 2Bi3, while Bi1, 2Bi2 and Bi3 surround O3 and O4, Fig. 1. The chains are parallel to the $[\bar{1}01]$, the 16.58 Å $c$-axis of the metric, orthogonal cell. The stacking along [100] consists of Bi–O–Bi chains bridged by layers formed by $TiO_6$ octahedra and $PO_4$ tetrahedra.

The description of the Bi–O coordination polyhedra includes all oxygen ions less than or equal to 3.16 Å. Bi1 is surrounded by eight oxygen ions that form a nearly regular trigonal prism in which two rectangular faces are capped, Fig. 2a. Bi2 is in a distorted cubic environment, Fig. 2b. Bi3 also is surrounded by eight oxygen ions but one rectangular and one triangular face of the trigonal prism are capped, Fig. 2c. The respective valence bond sums are 3.09, 3.00 and 3.00. Ti is in octahedral environment in which the equatorial distances are 1.82(3) and 2.00(5) Å and the apical distances are 2.14(4) Å. The valence bond sum is 4.02 [19]. In rutile there are four equatorial distances at 1.944(4) Å and two apical distances at 1.988(6) Å. On the basis of the esd's of these distances they must be considered equal but nevertheless the lengthening of the apical bond is qualitatively the same in both compounds. The $PO_4$ moiety is a nearly regular tetrahedron.

The differences of the atomic displacement parameters of the oxygen ions can be connected to their bonding in the structure. The oxygen ions O1 to O4 are in tetrahedral coordination to four Bi and are tightly bound with bond lengths between 2.20 and 2.54 Å. The valence bond strength is about 0.6. The small value of the displacement parameter is indicative of this environment. The $PO_4$ coordination polyhedron consists of O5 O6, O7 and O9 and their displacement parameters are significantly larger. O5 is bonded to Bi1, Bi2 and Bi3 at about 2.88 Å, O6 is bonded to Bi1 and Bi3 at about 2.8 Å, O7 is bonded to Bi3 at 2.9 Å and O9 is bonded to Bi2 and Bi3 at about 2.9 Å, Table 3. These are significantly longer distances and the valence bond values are much weaker at about 0.1. This weaker

Table 3
Bond lengths (Å) and angles (deg) for $Bi_6TiP_2O_{16}$

| | | | | | |
|---|---|---|---|---|---|
| Bi(1)–O(3)#1 | 2.27(4) | Bi(2)–O(3)#6 | 2.25(3) | Bi(3)–O(4)#6 | 2.27(4) |
| Bi(1)–O(2)#2 | 2.31(3) | Bi(2)–O(4)#6 | 2.20(4) | Bi(3)–O(1) | 2.23(3) |
| Bi(1)–O(4) | 2.29(3) | Bi(2)–O(8) | 2.36(4) | Bi(3)–O(3)#4 | 2.27(4) |
| Bi(1)–O(1)#3 | 2.38(3) | Bi(2)–O(3)#7 | 2.48(3) | Bi(3)–O(2) | 2.29(3) |
| Bi(1)–O(8)#4 | 2.41(3) | Bi(2)–O(4)#7 | 2.54(4) | Bi(3)–O5#9 | 2.89(3) |
| Bi(1)–O(6)#4 | 2.73(4) | Bi(2)–O9#4 | 2.78(3) | Bi(3)–O6#10 | 2.92(6) |
| Bi(1)–O5 | 2.87(4) | Bi(2)–O5#7 | 2.88(3) | Bi(3)–O7 | 2.93(4) |
| Bi(1)–O5#5 | 3.02(4) | Bi(2)–O7#5 | 3.16(4) | Bi(3)–O9#4 | 3.00(3) |
| Ti–O(8)#4 | 1.82(3) | P–O(6)#10 | 1.47(4) | O(6)#10-P–O(9)#11 | 111(3) |
| Ti–O(8) | 1.82(3) | P–O(9)#13 | 1.49(4) | O(6)#10-P–O(5) | 114(2) |
| Ti–O(7)#4 | 2.00(5) | P–O(5) | 1.55(3) | O(9)#11-P–O(5) | 113(2) |
| Ti–O(7) | 2.00(5) | P–O(7) | 1.57(5) | O(6)#10-P–O(7) | 102(3) |
| Ti–O(9)#4 | 2.14(4) | | | O(9)#11-P–O(7) | 108(2) |
| Ti–O(9) | 2.14(4) | | | O(5)–P–O(7) | 107(2) |

#1 $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$; #2 $x+\frac{1}{2}, y-\frac{1}{2}, z+\frac{1}{2}$; #3 $x+\frac{1}{2}, y-\frac{1}{2}, z+\frac{1}{2}$; #4 $-x, y, -z$; #5 $x, y-1, z$; #6 $x-\frac{1}{2}, y-\frac{1}{2}, z-\frac{1}{2}$; #7 $-x, y-1, -z$; #8 $-x-\frac{1}{2}, y-\frac{1}{2}, -z-\frac{1}{2}$; #9 $-x+\frac{1}{2}, y-\frac{1}{2}, -z-\frac{1}{2}$; #10 $x+\frac{1}{2}, y-\frac{1}{2}, z-\frac{1}{2}$; #11 $x+\frac{1}{2}, y-\frac{1}{2}, z--z-\frac{1}{2}$; #12 $-x, y, -z-1$; #13 $-x, y+1, -z$; #14 $x-\frac{1}{2}, y-\frac{1}{2}, z-\frac{1}{2}$; #15 $-x+\frac{1}{2}, y-\frac{1}{2}, -z-\frac{1}{2}$; #16 $x, y, z-1$; #17 $x, y+1, z$; #18 $-x-\frac{1}{2}, y-\frac{1}{2}, -z-\frac{1}{2}$; #19 $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$ #20 $x, y, z+1$; #21 $x-\frac{1}{2}, y-\frac{1}{2}, z+\frac{1}{2}$; #22 $-x-\frac{1}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$; #23 $x-\frac{1}{2}, y-\frac{1}{2}, z+\frac{1}{2}$; #24 $-x-\frac{1}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$.

bonding allows greater vibrational amplitudes and that is reflected in their larger ADP's. An additional factor for an increased value of the ADP exists for O7, O8 and O9 because they are bonded to Ti. This site is disordered and some Bi is also present. Even though bond lengthening is not observed in the averaged structure it must be present when Bi occupies this site.

The crystal structure is nearly centrosymmetric. Small adjustments in the positional parameters would place Bi1, Bi2, Bi3 and P into the 4*i*, $x\,0\,z$, position of space group $I2/m$, Ti would be at the origin, 2*a*. The oxygen parameters develop a centrosymmetric relationship except for O9. Numerous attempts to refine in a centrosymmetric space group did not converge to acceptable *R*-values. Also the lowest value of $R_{\text{int}}$ was obtained for $I2$.

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