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Crystal structures and polymorphism in compounds $Bi_{6+x}T_{1-x}P_2O_{15+y}$, $T=$ first row transition metals and Pb

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ABSTRACT

The compounds $Bi_{6+x}T_{1-x}P_2O_{15+y}$, $T=$ Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn and Pb display five polymorphic forms. Polymorph A is formed by the Ti, Mn, Fe and Ni phases. Polymorph B is exhibited by Co and Cu compounds. The Cr phase crystallizes as polymorphic form C and the Zn phase crystallizes as polymorph D. The Pb compound crystallizes in a new structure type designated as polymorph E. The transition metal crystal structures demonstrate a similar motive. OBi_4 tetrahedra share edges to form two-dimensional Bi_2O_2 layers that are spanned by PO_4 tetrahedra and TO_{6-y} octahedra, pyramids and a trigonal bipyramid to form a three-dimensional network. Polymorph A crystallizes in space group $C2$; polymorph B is centrosymmetric with space group $C2/c$, the unit cell parameters differ and the unit cell volume is about double. Polymorph C crystallizes in space group $P\bar{1}$ and polymorph D exhibits space group $C2$. $Bi_{6.4}Pb_{0.6}P_2O_{15.2}$ can be considered as polymorph E, space group $C2$, with a new crystal structure but related stoichiometry.

1. Introduction

The compound $Bi_6TiP_2O_{16}$ [1] is a new structure type in the complex phase space Bi–Pb–transition metals–phosphates, vanadates and arsenates. Its structure consists of OBi_4 tetrahedra that share edges to form two-dimensional (2-D) Bi_2O_2 layers that are spanned by PO_4 tetrahedra and TiO_6 octahedra to form a three-dimensional (3-D) network. Ion transport did not seem promising since all atomic sites were occupied and very little atomic disorder is present. However, the replacement of Ti^{4+} with trivalent or divalent transition metals should cause oxygen vacancies in order to preserve charge balance or possibly give rise to new compounds. We therefore synthesized compounds with the nominal stoichiometry $Bi_6TP_2O_{15+x}$, $T=$ first row transition metals, determined their crystal structures and physical properties. The compounds containing Mn, Fe, Ni and Zn have been reported and they are isomorphs (Mn, Fe, Ni phases) or a polymorph (Zn phase) of the Ti phase [2,3]. In all of these crystal structures Bi also partially occupies the octahedral transition metal site and since Pb^{2+} has approximately the same ionic radius as Bi^{3+} we also prepared the nominal phase $Bi_6PbP_2O_{15+x}$. Indeed it is a polymorph but with a new crystal structure [4]. We continued with this study and prepared compounds containing Cr, Co and Cu analogs to examine the effect of the substitution on the crystal structure and properties and report the results here. Table 1 summarizes the lattice parameters for the various polymorphs.

2. Experimental

2.1. Synthesis

The experimental conditions for the preparation and crystal growth have been described in detail for $Bi_6TiP_2O_{16}$ [1], $Bi_6(Mn_{0.6}Bi_{0.4})P_2O_{15}$ [2] and the Fe, Ni and Zn compounds [3] except that the corresponding transition metal oxides were used. The regimen of consecutive refiring and repelletizing is necessary to achieve single phase, or nearly single-phase material. X-ray powder diffraction patterns were obtained with a Philips diffractometer, Cu$K\alpha$ radiation, equipped with a diffracted beam monochromator, 45 kV, 40 mA, 2θ scan range 5–90°. The thermal behavior was determined by the use of a Perkin-Elmer Series 7 differential thermal analyzer (DTA) heating a small amount of the powder in air to 1000 °C with a heating and cooling rate of 10 °C min^{-1}. The Cr and Cu products were quantitatively analyzed by inductively coupled plasma optical emission spectroscopy (ICP) yielding: 78.2 wt% Bi, 7.34 wt% Cr, 3.54 wt% P; 74.6 wt% Bi, 7.80 wt% Cu, 3.74 wt% P. On the basis of two phosphorus per formula the stoichiometries are Bi6.55Cr2.47 and Bi5.90Cu2.03; evidently the products contained excess chromium and copper

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Table 1
Crystal parameters for $Bi_{6+x}T_{1-x}P_2O_{15\pm y}$ compounds

Compounds	Crystal system	Cell parameters
$Bi_6TiP_2O_{16}$	Monoclinic, $I2$ Monoclinic, $C2^a$	$a = 11.232$, $b = 5.410$, $c = 11.233$, $\beta = 95.13$, $V = 679.8$ $a = 15.159$, $b = 5.410$, $c = 11.233$, $\beta = 132.44$, $V = 679.8$
$Bi_{6.4}Mn_{0.6}P_2O_{15}$	Monoclinic, $I2$ Monoclinic, $C2^a$	$a = 11.284$, $b = 5.426$, $c = 11.112$, $\beta = 96.25$, $V = 676.3$ $a = 14.95$, $b = 5.426$, $c = 11.112$, $\beta = 131.38$, $V = 676.3$
$Bi_{6.32}Fe_{0.68}P_2O_{15.5}$	Monoclinic, $I2$ Monoclinic, $C2^a$	$a = 11.264$, $b = 5.438$, $c = 11.144$, $\beta = 96.16$, $V = 678.70$ $a = 14.972$, $b = 5.438$, $c = 11.144$, $\beta = 131.58$, $V = 678.7$
$Bi_{6.56}Ni_{0.44}P_2O_{15.2}$	Monoclinic, $I2$ Monoclinic, $C2^a$	$a = 11.259$, $b = 5.461$, $c = 11.109$, $\beta = 96.64$, $V = 678.5$ $a = 14.99$, $b = 5.461$, $c = 11.109$, $\beta = 131.58$, $V = 678.5$
$Bi_6ZnP_2O_{15}$	Monoclinic, $I2$ Monoclinic, $C2^a$	$a = 19.727$, $b = 5.438$, $c = 16.973$, $\beta = 131.93$, $V = 1354.46$ $a = 15.1573$, $b = 5.438$, $c = 16.973$, $\beta = 104.48$, $V = 1354.46$
$Bi_{6.24}Cr_{0.09}P_2O_{14.4}$	Primitive, $P\bar{1}$	$a = 19.312$, $b = 5.549$, $c = 9.499$ $\alpha = 103.814$, $\beta = 90.344$, $\gamma = 90.479$, $V = 988.48$
$Bi_{6.6}Co_{0.47}P_2O_{15.45}$	Monoclinic, $C2/c$	$a = 16.756$, $b = 5.476$, $c = 14.884$, $\beta = 91.09$, $V = 1365.5$
$Bi_{6.56}Cu_{0.4}P_2O_{15.35}$	Monoclinic, $C2/c$	$a = 16.727$, $b = 5.471$, $c = 14.889$, $\beta = 91.26$, $V = 1362.2$
$Bi_{6.4}Pb_{0.6}P_2O_{15.2}$	Monoclinic, $C2$	$a = 19.470$, $b = 11.369$, $c = 16.381$, $\beta = 101.17$, $V = 3557.35$

[a] Indicates standard orientation.

oxides. The Co-phase was not examined by ICP since the X-ray powder diffraction patterns indicated a mixture of phases. Several single crystals from these three products were selected upon examination with a polarizing binocular microscope. The crystals were mounted on an automated single-crystal diffractometer and the best ones used for the data collections. The Co-phase crystals were of poor quality. Repeated preparations of new material and variations in crystal growth conditions did not yield different results.

2.2. Crystallography

Single-crystal X-ray diffraction data were obtained using a Nonius κ automated CCD diffractometer equipped with a graphite monochromator with Mo$K\alpha$ radiation, $\lambda = 0.71073$ Å. The diffracted intensities were generated by multiple ω and ϕ scans. Data reduction and scaling were performed using DENZO-SMN [5]. For the Cr compound the intensities were collected on the basis of a $P1$ triclinic cell, $a = 5.5490(1)$ Å, $b = 9.4997(2)$ Å, $c = 19.3116(6)$ Å, $\alpha = 90.344(1)^\circ$, $\beta = 90.4794(12)^\circ$, $\gamma = 103.8138(15)^\circ$. For the structure solution the cell was reoriented as shown in Table 1. Details of crystal data, data collection and structure refinement are listed in Table 2. The structure was solved with the direct methods program SHELXS [6] in space group $P\bar{1}$ that yielded the Bi atom positions. Difference electron density maps revealed the Cr, P and oxygen atoms. The refinement proceeded by least squares using SHELXL [6], DENZO-style merged intensities, anisotropic displacement parameters for Bi and Cr, eventually converging to $R_1 = 0.0368$.

For Co the intensities were collected on the basis of a $C2$ monoclinic cell, $a = 16.7562(7)$ Å, $b = 5.4764(2)$ Å, $c = 14.8836(7)$ Å, $\beta = 91.09(3)^\circ$. Crystals were of poor quality. Repeated attempts to synthesize and grow new specimens did not yield better results and the data and ultimate refinement reflect the crystal quality. The structure was solved with the direct methods program SHELXS [6] in space group $C2/c$ that yielded the Bi atom positions. Difference electron density maps revealed the Co, P and oxygen atoms. The refinement proceeded by least squares using SHELXL [6]. Intensities were corrected for absorption using SADABS [7], anisotropic displacement parameters for Bi and Co, eventually converging to $R_1 = 0.072$. Similar processing and refinement of data for the Cu phase collected on the basis of a $C2$ monoclinic unit cell, $a = 16.7272(5)$ Å, $b = 5.4709(2)$ Å, $c = 14.8888(5)$ Å, $\beta = 91.259(2)^\circ$, converged to $R_1 = 0.054$. The unit cell volumes of the Co and Cu compounds are about 1360 Å^3 while the volumes for the other monoclinic transition metal phases are about 680 Å^3. The above C-centered unit cells can be transformed to the previously observed I-centered monoclinic cells (Table 1), by the matrix $(-0.5\ 0\ 0.5,\ 0\ \bar{1}\ 0,\ 0.5\ 0\ 0.5)$ but now a large number of observed intensities have fractional Miller indices. The larger C-centered unit cell is correct for the Co and Cu compounds. Table 2 summarizes the results and Tables 3 and 4 list the atomic coordinates.

3. Crystal structures

3.1. The Cr crystal structure

The crystal structure of the Cr phase is shown in Fig. 1. Two unit cells are shown to emphasize a chain of eight OBi_4 edge-sharing tetrahedra that are terminated at each end by two PO_4 tetrahedra. The chains are connected laterally by PO_4 tetrahedra and Cr polyhedra. The site occupancy of the apical oxygen, O22, of the Cr octahedron is 0.61(3) so that in a given unit cell the polyhedron switches between an octahedron and a rectangular pyramid. The compound displays disorder of some of the Bi ions and the octahedral site of Cr (Wyckoff notation 1h, point symmetry $\bar{1}$) has a sof of 0.137(4) with Bi occupying that site the rest of the time. The Bi ions are in irregular coordination to oxygen due to the presence of the $6s^2$ electrons. Bi1 is in a distorted rectangular pyramid; Bi2 is in a rectangular prism; Bi3, Bi4, Bi5, Bi8 are in a monocapped rectangular prism; Bi6, Bi7 Bi9 are in a monocapped rectangular pyramid. The Bi–O bond lengths vary from 2.11(2) to 3.10(3) Å. The crystal structure refinement yields the unit cell content $Bi_{18}(Bi_{0.72}Cr_{0.28})P_6O_{43.2}$ or $Bi_6(Bi_{0.24}Cr_{0.09})P_2O_{14.4}$ for comparison with the other stoichiometries. The structural change from a centered to a primitive unit cell leads to open channels that could increase anion transport over the relatively low values observed in related compounds [8–10].

Table 2
Crystal data and refinement for $Bi_{6.24}Cr_{0.09}P_2O_{14.4}$, $Bi_{6.6}Co_{0.47}P_2O_{15.45}$ and $Bi_{6.56}Cu_{0.4}P_2O_{15.35}$

	$Bi_{6.24}Cr_{0.09}P_2O_{14.4}$	$Bi_{6.6}Co_{0.47}P_2O_{15.45}$	$Bi_{6.56}Cu_{0.4}P_2O_{15.35}$
Empirical formula	$Bi_{18.71}Cr_{0.27}P_6O_{43.22}$	$Bi_{6.6}Co_{0.47}P_2O_{15.45}$	$Bi_{6.56}Cu_{0.4}P_2O_{15.35}$
Formula weight	4801.4	1674.58	1703.5
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system, space group	Triclinic, $P\bar{1}$	Monoclinic, $C2/c$	Monoclinic, $C2/c$
Unit cell dimensions (Å)			
a	19.3116(11)	16.756(3)	16.727(3)
b	5.549(10)	5.4764(11)	5.4709(11)
c	9.4997(2)	14.884(3)	14.889(3)
α (deg)	103.814(2)	–	–
β (deg)	90.344(10)	91.09(3)	91.26(3)
γ (deg)	90.4790(10)	–	–
Volume (Å^{-3})	988.48(6)	1365.5(5)	1362.2(5)
Z, Calculated density (g cm^{-3})	1, 8.066	4, 8.347	4, 8.306
Absorption coefficient (mm^{-1})	83.367	85.619	85.34
Absorption correction	SADABS	SADABS	Multiscan
Crystal size (mm)	$0.03 \times 0.045 \times 0.02$	$0.12 \times 0.04 \times 0.035$	$0.05 \times 0.06 \times 0.06$
Crystal color	Pale green	Black	Green
Theta range for data collection (deg)	2.11–27.44	2.43–27.44	2.44–27.5
Limiting indices	$-24\leqslant h\leqslant 25$, $0\leqslant k\leqslant 7$, $-12\leqslant l\leqslant 11$	$0\leqslant h\leqslant 21$, $0\leqslant k\leqslant 7$, $-19\leqslant l\leqslant 19$	$0\leqslant h\leqslant 21$, $0\leqslant k\leqslant 7$, $-19\leqslant l\leqslant 19$
Reflections total/accepted	1990/1990	1334/1334	1388/1388
Data completeness (%)	98.1	99.6	99.8
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	1990/1/198	1334/0/90	1308/0/86
Goodness-of-fit on F^2	1.119	1.115	1.026
Final R [$I>2\sigma(I)$]	$R_1 = 0.0368$, w$R_2 = 0.0821$	$R_1 = 0.072$, w$R_2 = 0.1944$	$R_1 = 0.0544$, w$R_2 = 0.1424$
R indices (all data)	$R_1 = 0.0368$, w$R_2 = 0.0821$	$R_1 = 0.072$, w$R_2 = 0.1944$	$R_1 = 0.0544$, w$R_2 = 0.1424$
Extinction coefficient	0.00058(5)	0.0003(6)	0.00019(3)
Largest diff. peak and hole e A^{-3}	2.588/−1.998	7.204/−5.221	5.863/−5.701

3.2. *The Co and Cu crystal structures*

The Co and Cu compound are polymorphic with the non-centrosymmetric phases and differ only because of the presence of a center of symmetry. Infinite chains of OBi_4 edge-sharing tetrahedra parallel to the *a*-axis are connected by PO_4 tetrahedra and Co or Cu octahedra into a 3-D framework in the *a*–*c* plane (Fig. 2). As has been observed in previous structures, Bi atoms are disordered (Table 2). The apical oxygen of the Cu octahedron, O9, has a sof of 0.72(6) and is also part of the Bi3, sof 0.59(2) or Bi3′, sof 0.41, polyhedron. Two domains exist in the crystal in which Cu is present about 70% of the time in an octahedral site and the apical O9 is bonded to Bi3, while in the second domain Cu is in rectangular pyramidal coordination and O9 is bonded to one Bi3′ (Fig. 3). Similar vacancies in this site have been observed in many of the other phases. The stoichiometry derived from the crystal structure refinement is $Bi_6(Cu_{0.4}Bi_{0.6})P_2O_{15.4}$. On the assumption that Cu is divalent the calculated oxygen stoichiometry is 15.4 in good agreement with the derived value. Bi1 and Bi2 are in a distorted, monocapped prismatic environment of seven oxygen atoms while the oxygen atoms around Bi3 form a monocapped rectangular pyramid. The Bi–O bond lengths <3 Å vary from 2.15(2) to 2.74(3) Å. The Cu/Bi occupant of the octahedral site is disordered around the center of symmetry, site 4*d* of space group $C2/c$. The structure shown in Fig. 2 has the disordered Bi atoms eliminated and the Cu atom has been placed at $\bar{1}$. Based on the X-ray diffraction data the stoichiometry of the Co-phase is $Bi_6(Co_{0.4}Bi_{0.6})P_2O_{15.5}$.

4. Discussion

The crystal chemical investigation of the phases existing for compounds $Bi_6TP_2O_{15+x}$, $T =$ first row transition metals, reveals the existence of four polymorphs. Polymorph A is exhibited by the Ti, Mn, Fe and Ni compounds (1–3). They are isomorphs crystallizing in space group $I2$ ($C2$ standard orientation) with unit cells nearly the same. The Bi atoms are almost in centrosymmetric positions; the lighter P and O atoms destroy the center. The coordination polyhedron around the transition metal consists of an octahedron or, due to structurally induced vacancies on the apical site, as a rectangular pyramid. Infinite chains of edge-sharing OBi_4 tetrahedra are present in the *a*–*c* plane.

Polymorph B is exhibited by the Co and Cu phases. They crystallize in space group $C2/c$ and the unit cell volume is doubled from those of the former transition metal compounds. The coordination polyhedron around the transition metals is similar to those in polymorph A and infinite chains of edge-sharing OBi_4 tetrahedra are present in the *a*–*c* plane. The Cr compound crystallizes in space group $P\bar{1}$ and forms a third polymorph C. Its structure is characterized by the termination of the OBi_4 chains after eight edge-sharing tetrahedra that are terminated on each end by two PO_4 tetrahedra. These chains are bridged laterally by PO_4 tetrahedra and by Cr polyhedra that are either octahedra or rectangular pyramids because the apical O22 has a sof equal to 0.61(6) (Fig. 1). The basic motif of polymorphs A–C is the same. OBi_4 tetrahedra form Bi_2O_2 sheets, chains in projection parallel to the *b*-axis (Fig. 2). The chains are connected laterally by PO_4 tetrahedra and transition metal octahedra in which an apical corner may only be partially occupied by oxygen. Since Bi^{3+} also occupies the octahedral site on a statistical basis and its coordination sphere is highly irregular due to the presence of the nonbonding $6s^2$ electrons it is not possible to say with certainty that in a domain where the site is occupied exclusively by the transition metal the apical oxygen vacancy actually exists. However, on the basis of charge balance only the Ti^{4+} phase can have an O_{16} stoichiometry, i.e. no oxygen vacancies. The other transition metal phases must have oxygen vacancies and the apical oxygen of the octahedron is a logical candidate resulting in a rectangular pyramidal coordination polyhedron. Five-fold coordination forming rectangular pyramidal or trigonal bipyramidal coordination around transition metals are common [11].

Table 3
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($A^2 \times 10^3$) for $Bi_{6.24}Cr_{0.09}P_2O_{14.4}$

Atoms	sof	x	y	z	U(eq)[a]
Bi(1)		−1070(1)	−3569(2)	−1062(1)	9(1)
Bi(2)	0.88(4)	−7814(1)	1013(3)	7407(2)	1(1)
Bi(2′)	0.12(4)	−8000(5)	860(20)	7265(13)	4(3)
Bi(3)		−3056(1)	−5283(2)	4502(1)	9(1)
Bi(4)		−8925(1)	−4892(2)	5071(1)	9(1)
Bi(5)		−5419(1)	2903(2)	1026(1)	6(1)
Bi(6)		−2113(1)	−9489(2)	−3410(1)	7(1)
Bi(7)		−9846(1)	−818(2)	3100(1)	8(1)
Bi(8)		−6580(1)	7180(2)	−477(1)	10(1)
Bi(9)	0.81(1)	−5907(1)	1461(3)	−2748(2)	16(1)
Bi(9′)	0.18(1)	−5894(3)	298(10)	−2955(7)	4
Bi	0.363(4)	−1/2	−1/2	1/2	16(1)
Cr	0.137(4)	−1/2	−1/2	1/2	16(1)
P(1)		−9230(3)	6703(11)	−1348(7)	7(1)
P(2)		−4073(3)	794(13)	−3417(8)	14(1)
P(3)		−7319(3)	3111(11)	1241(7)	7(1)
O(1)		−2141(8)	−12460(30)	−5413(18)	9(3)
O(2)		−1146(7)	−6320(30)	−3020(16)	0(2)
O(3)		−5589(8)	4670(30)	−819(18)	7(3)
O(4)		−6859(7)	3690(30)	−2495(17)	5(3)
O(5)		−3133(8)	−8640(30)	2640(20)	17(3)
O(6)		−7953(8)	−2350(30)	5435(19)	14(3)
O(7)		−5667(8)	−240(30)	−800(20)	16(3)
O(8)		−1142(8)	−11350(30)	−3200(20)	17(3)
O(9)		−9266(8)	6950(30)	333(19)	11(3)
O(10)		−7805(7)	4920(30)	710(18)	9(3)
O(11)		−4435(9)	3280(40)	−3410(20)	26(4)
O(12)		−10160(9)	2160(30)	4900(20)	22(4)
O(13)		−7445(9)	3330(40)	2880(20)	24(4)
O(14)		−9969(8)	6680(30)	−1930(20)	19(4)
O(15)		−6594(8)	3900(30)	980(19)	16(3)
O(16)		−3476(10)	470(40)	−4450(20)	31(4)
O(17)		−7488(12)	490(40)	410(30)	46(6)
O(18)		−4643(10)	−1270(40)	−3930(20)	29(4)
O(19)		−3868(10)	760(40)	−1900(20)	32(5)
O(20)		−8884(11)	8880(40)	−1740(30)	40(5)
O(21)		−8929(15)	4150(50)	−2100(30)	66(7)
O(22)		−5723(17)	−4580(60)	6230(40)	31(11)

[a] U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 4
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($A^2 \times 10^3$) for $Bi_{6.56}Cu_{0.4}P_2O_{15.35}$ and for $Bi_{6.6}Co_{0.47}P_2O_{15.45}$ in italics

Atoms	sof	x	y	z	U(eq)[a]
Bi(1)		879(1)	2817(1)	3312(1)	9(1)
	0.93(1)	*879(1)*	*2792(2)*	*3311(1)*	*11(1)*
Bi(1′)	–	–	–	–	–
	0.91(1)	*872(8)*	*1980(30)*	*3314(8)*	*4*
Bi(2)		4265(1)	2833(1)	3395(1)	10(1)
	0.95(1)	*4270(1)*	*2798(2)*	*3397(1)*	*11(1)*
Bi(2′)		–	–	–	–
	0.07(1)	*4278(9)*	*1850(30)*	*3446(10)*	*4*
Bi(3)	0.59(2)	2531(1)	3220(16)	1699(2)	20(1)
	0.57(2)	*2532(1)*	*3180(20)*	*1695(3)*	*22(2)*
Bi(3′)	0.40(2)	2526(1)	1997(19)	1645(4)	14(2)
	0.43(2)	*2527(2)*	*1990(20)*	*1650(5)*	*15(2)*
Cu	0.200(5)	2490(20)	2290(60)	4870(40)	4(1)
Co	*0.24(1)*	1/4	*1/4*	*1/2*	*20(20)*
Bi	0.300(5)	2470(5)	2440(17)	4869(9)	4(1)
	0.26(1)	*2470(3)*	*2409(9)*	*4853(8)*	*4(3)*
P		1040(3)	2578(8)	64(3)	6(1)
		1037(4)	*2557(12)*	*61(5)*	*7(1)*
O(1)		4192(10)	2360(30)	930(11)	25(3)
		4203(14)	*2360(40)*	*943(15)*	*24(5)*
O(2)		3375(7)	260(20)	2586(8)	7(2)
		3383(11)	*160(40)*	*2595(12)*	*10(3)*
O(3)		1616(7)	260(20)	2387(8)	10(3)
		1607(12)	*230(40)*	*2385(13)*	*17(4)*
O(4)		0	5210(30)	*1/4*	2(3)
		0	*5190(40)*	1/4	*6(5)*
O(5)		0	170(30)	*1/4*	4(3)
		0	*90(50)*	1/4	*10(3)*
O(6)		360(10)	2200(30)	703(11)	26(4)
		368(16)	*2310(50)*	*709(17)*	*33(6)*
O(7)		1646(11)	540(40)	250(13)	38(4)
		1633(16)	*530(50)*	*239(18)*	*36(6)*
O(8)		1481(10)	4970(30)	312(12)	31(4)
		1486(16)	*4890(50)*	*304(18)*	*35(6)*
O(9)	0.71(6)	2270(14)	2760(40)	3798(16)	27(8)
	0.74(9)	*2270(20)*	*2710(60)*	*3790(20)*	*35(12)*

[a] U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

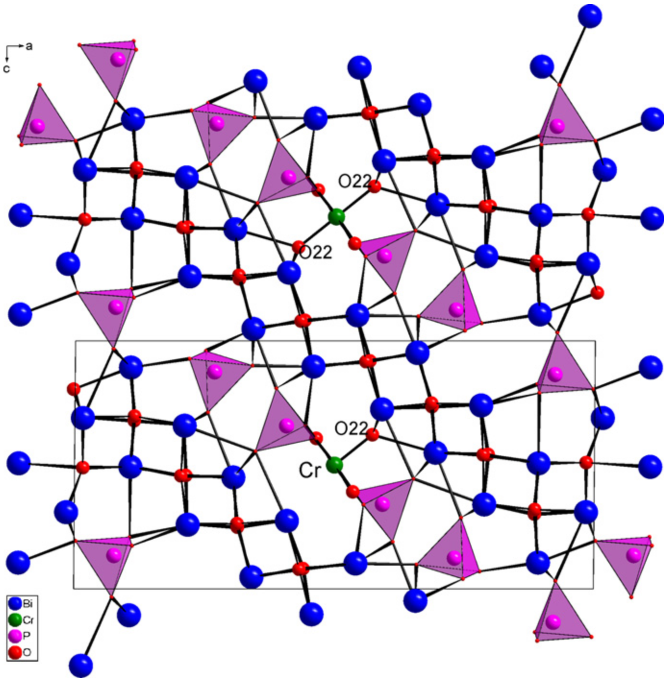

Fig. 1. The crystal structure of $Bi_6(Bi_{0.24}Cr_{0.09})P_2O_{14.4}$ perpendicular to [010]. Two unit cells are shown to illustrate the Cr environment as an oxygen octahedron and as a rectangular pyramid. Eight OBi_4 chains are terminated by two PO_4 tetrahedra at each end.

The structures can be considered as derivatives of the δ-Bi_2O_3 and CaF_2 motifs so that they are all pseudo-centrosymmetric. The crystals also show twinning and disorder of some of the Bi ions in the Bi_2O_2 layers.

The Zn phase can be assigned to a new polymorph D. The unit cell parameters differ, the volume is about double although the space group remains *I*2 (*C*2). The Zn ion is in distorted triangular bipyramidal coordination to oxygen, contrasting with the octahedral

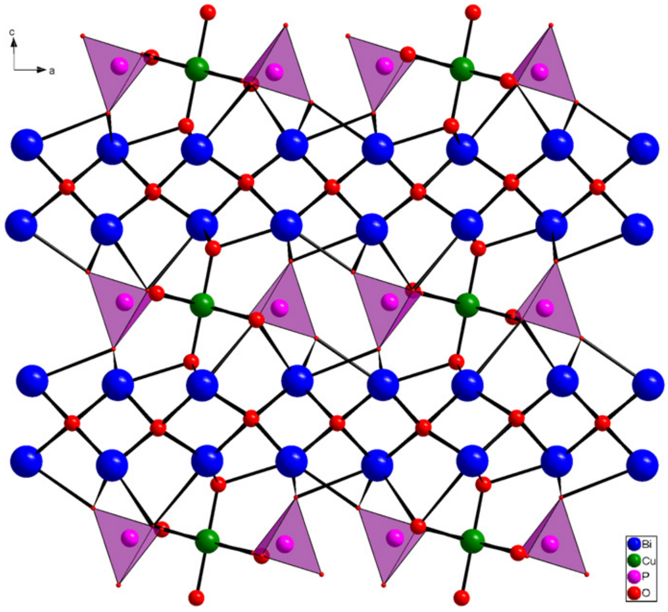

Fig. 2. The crystal structure of $Bi_6(Cu_{0.4}Bi_{0.6})P_2O_{15.4}$ perpendicular to [010]. Only one each of the disordered Bi atoms is shown and the Cu position is placed at $(\frac{1}{4}\frac{1}{4}\frac{1}{2})$, $\bar{1}$ of $C2/c$. The crystal structure of $Bi_6(Co_{0.4}Bi_{0.6})P_2O_{15.5}$ is the same.

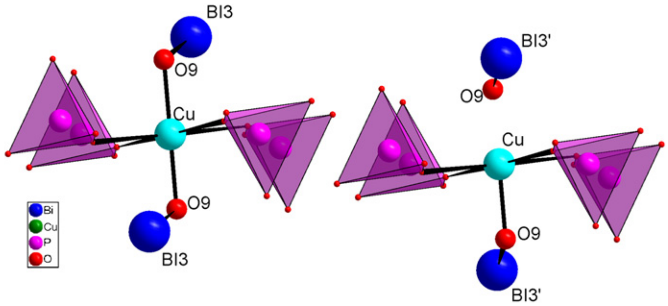

Fig. 3. Illustrating the two domains of the $Bi_6(Cu_{0.4}Bi_{0.6})P_2O_{15.4}$ structure. Note that the four equatorial oxygen atoms are part of PO_4 tetrahedra that are not visible in the [010] projections.

coordination of the previous transition metal ions. No oxygen vacancies exist in this structure and the oxygen stoichiometry is reduced to 15. The tetrahedral site preference of Zn^{2+} is evident; the average of four Zn–O bond length is 1.97(10) Å but an additional long bond, Zn–O of 2.71(2) Å, changes the tetrahedron to a trigonal bipyramid. The zinc ion has also been displaced from the center of the tetrahedron to be coplanar with the three oxygen ions of the basal plane lengthening the opposite Zn–O apical bond to 2.12(2) Å. A chain of five OBi_4 edge-sharing tetrahedra is terminated by a PO_4 tetrahedron at each end of the chain [3].

In summary when moving across the periodic table from Ti to Zn in these compounds the change in the octahedral site occupancy varies from a slight admixture of Bi in the Ti phase and no oxygen vacancies to about a 50% presence of Bi in the other compositions except for the Zn phase. The introduction of oxygen vacancies changes the coordination polyhedron of the transition metal ion from an octahedron to a rectangular pyramid or a trigonal bipyramid. The strong tetrahedral site preference of Zn^{2+} gives rise to a distorted trigonal bipyramid and no Bi substitution or oxygen vacancy are observed.

The compound $Bi_{6.4}Pb_{0.6}P_2O_{15.2}$ can be considered as polymorph E with a new crystal structure but related stoichiometry [4].

Supplementary materials

The crystallographic cif files for all the compounds were deposited with FIZ Karlsruhe and the CSD numbers are 419138 for $Bi_{6.24}Cr_{0.09}P_2O_{14.4}$; 419139 for $Bi_{6.6}Co_{0.47}P_2O_{15.45}$; 419140 for $Bi_{6.56}Cu_{0.4}P_2O_{15.35}$. The data may be obtained without charge from FIZ Karlsruhe, fax: +497247 808 666 crysdata@fiz-karlsruhe.de.

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