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Mn substitution in the solid solution series $Bi_2Pb_{8-x}(PO_4)_6O_{2-x}$. The crystal structure of $Bi_{1.5}(Pb_{7.3}Mn_{0.7})(PO_4)_6O_{1.3}$ a member of a new solid solution series $Bi_{2-x}Pb_8(PO_4)_6O_{2-1.5x}$

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Abstract

A single-crystal from a solid solution $Bi(Pb_{4-x}Mn_x)P_3O_y$ was selected and its crystal structure determined from 3-dimensional X-ray diffraction data. The crystal is orthorhombic, *Pnma*, $a = 12.967(3)$ Å, $b = 10.294(2)$ Å, $c = 8.9994(18)$ Å. The 1460 unique reflections were refined by least squares on F^2 to $R_1 = 0.0352$. The stoichiometry based on the atomic parameters is $Bi_{1.5}Pb_{7.3}Mn_{0.7}(PO_4)_6O_{1.3}$ $Z = 2$. Of the two crystallographically independent PO_4 groups one tetrahedron is regular while the oxygen ions of the other one are disordered, giving rise to two tetrahedral orientations. One of the crystallographic Pb sites contains vacancies that are filled by Mn. The structure is formed by the 3-dimensional articulations of one Bi–6O and three Pb–7O polyhedra and two PO_4 tetrahedra one of which is disordered. In addition to the previously reported solid solution $Pb_{8-x}Bi_2(PO_4)_6O_{2-x}$ there exists also a second type of solid solution, $Pb_8Bi_{2-x}(PO_4)_6O_{2-1.5x}$.

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1. Introduction

The discovery that $Bi_4V_2O_{11}$ was a very good oxygen ion conductor [1] ignited extensive exploration of the crystal chemistry and physical properties of the pseudo-ternary Bi–*M*–*X* and quaternary Bi–Pb–*M*–*X*—oxide systems (*M* = transition metals, *X* = P, V, As). Recent studies of the system Bi–Pb–Mn–P–O led to the discovery of a cubic phase with composition $BiMn_6PO_{12}$ and $Bi_2PbMnO_4(PO_4)_2$ [2,3]. The reaction products in which these compounds were discovered contained other unknown phases. The latter were selected for atomic analyses in a Philips CM30 transmission electron microscope equipped with an energy dispersive spectrometer. Two different solid solutions were observed, one high in Bi and one high in Pb content. The average composition from 13 crystals of the Bi-rich phase was $Bi_{0.74}Pb_{0.20}Mn_{0.41}P_{0.59}$ or approximately $(BiPb)_3MnP_2O_x$. The crystal structure of the Bi-rich phase was determined and yielded the formula $Bi_2PbMnO_4(PO_4)_2$, a member of a new solid solution series in the Bi–Pb–Mn–P oxide system [3]. The average composition of the Pb-rich phase based on seven analyses was $Bi_{0.28}Pb_{0.57}Mn_{0.32}P_{0.68}$ or approximately $(BiPb)_4MnP_3O_x$. We report here the structure of the Pb-rich phase.

2. Experimental

A mixture of analytical grade Bi_2O_3, PbO, MnO_2 and $(NH_4)H_2(PO_4)$ in the atom ratio Bi:Pb:Mn:P = 1:3:1:3 was prepared and ground for 1 h in acetone. The mixture was dried, placed into an alumina boat and preheated at 600°C for 4 h. The preheated mixture was reground and heated at 950°C for 8 h, well above the melting point. The melt was cooled at a rate of 2.5°C/h to 900°C and was maintained at that temperature for 30 h and then furnace cooled to room temperature. Powder X-ray diffraction patterns of the product were obtained with a diffractometer equipped with a diffracted-beam graphite monochrometer and Cu*K*α radiation. The powder pattern showed that the material was polyphasic and also contained amorphous material. The use of a search–match (SM) routine did not yield useful results. Standardless semi quantitative X-ray

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energy dispersive analysis (EDX) results showed that the overall composition of the product was BiPb3MnP3. An acicular single crystal with approximate dimensions $0.05 \times 0.05 \times 0.14$ mm was selected under a polarizing, optical microscope and subjected to an EDX analysis. The resultant composition was approximately $BiPb_{3.1}Mn_{0.9}P_{3.2}$. Weissenberg and precession photographs showed that it was a good quality crystal with orthorhombic symmetry, approximate lattice parameters $a = 12.8$ Å, $b = 10.33$ Å, $c = 9.02$ Å, space group *Pnma* (62) or $Pna2_1$ (33). Data were collected at room temperature on a Nonius Kappa CCD diffractometer using a graphite monochromator with Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å). A total of 304 frames of data, in four framesets, were collected using ω-scans with a scan range of 1° and a counting time of 182 s per frame. Data reduction was performed using DENZO-SMN [4]. Because of the large value for the absorption coefficient for the crystal, interframe scaling of the data was not employed so that an absorption correction could be applied to the data. R_{int} for the raw data was 0.222. A Gaussian face-indexed absorption correction was made and R_{int} became 0.090(3). The unit cell dimensions were refined using 2072 reflections with θ ranging from 2.9° to 27.5°. The crystal data and refinement are shown in Table 1.

Table 1
Crystal data and structure refinement for $Bi_{1.5}(Pb_{7.3}Mn_{0.7})(PO_4)_6O_{1.3}$

Formula weight	2455.1
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	orthorhombic, *Pnma*
Unit cell dimensions, Å	
a	12.967(3)
b	10.294(2)
c	8.9994(18)
Volume $Å^3$	1201.3(4)
Z, Calculated density	2, 6.79 g/cm^3
Absorption coefficient	62.5 mm^{-1}
Crystal size mm	$0.05 \times 0.05 \times 0.14$
Minimum/maximum transmission	0.00367/0.05048
Theta range for data collection	3.01–27.52°
Limiting indices	$-14 \leqslant h \leqslant 16$, $-12 \leqslant k \leqslant 13$, $-11 \leqslant l \leqslant 11$
Reflections collected/unique	18,800/1460 [$R_{\mathrm{int}} = 0.0898$]
Completeness to $\theta = 27.52°$	99.9%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1460/10/84
Goodness-of-fit on F^2	1.00
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0352$, w$R_2 = 0.0877$
R indices (all data)	$R_1 = 0.0387$, w$R_2 = 0.0898$
Extinction coefficient	0.00054(7)
Largest diff. peak and hole eÅ^{-3}	2.845 and −2.373

The crystal structure was determined by the Patterson superposition method using the Wingx program package, [5]. The positions of the four, crystallographically independent, heavy atoms were found; one in the general 8*d* position and three on the mirror plane in 4*c* of *Pnma*. The atomic ratio of Pb/Bi = 3/1 meant that one Pb occupied the 8*d* site. Because Pb and Bi X-ray scattering factors are nearly the same the single, crystallographically distinct Bi atom was initially assigned the position of Bi in a previously published crystal structure, $Pb_8Bi_2(PO_4)_6O_2$, by Moore, et al. [6]. Least-squares refinements and difference electron density maps provided the positions of the remaining atoms. At this stage the structure did not show separate atomic positions corresponding to Mn. Least-squares refinements in which the site occupancies of the heavy atoms and of P and their displacement parameters were alternately fixed during refinement eventually converged to values for most that were either equal to or within 1σ of full site occupancy. These sites were then fixed at full occupancies. The exceptions were the Pb atom in the 8*d* position and one Pb atom in a 4*c* position. Their sof's were respectively 0.828(5) and 0.315(3) instead of 1 and 0.5. Calculations with these positions fully occupied resulted in a significant increase in *R*. The coordination polyhedron around Pb2 exhibited the typical severe distortion of an oxygen octahedron around an atom with active crystal-chemical 6s^2 lone-pair electrons [7], Fig. 1. The introduction of Mn atoms into the vacancies of the Pb positions, with the restraint that their sums add to full occupancies and with the same positional and anisotropic displacement parameters for the respective Pb atoms, led to $R = 0.0381$. A valence bond sum calculation [8] showed that it was 1.75 for Bi, low for Bi^{3+}, and 2.82 for Pb1, in the sites corresponding to those given by Moore et al. [6]. The oxygen atoms coordinating to P2 also showed very large values of the displacement parameters.

3. Discussion

The stoichiometry $BiPb_{3.3}Mn_{0.7}O(PO_4)_3$ based on the parameters that yielded $R = 0.0381$ is in good agreement with the EDX results. A literature search for compounds containing Bi, Pb and P oxides within a narrow range of the above composition yielded the publications by Durif [9] reporting on the structures of compositions isomorphous with eulytite, $Bi_4(SiO_4)_3$, and by Moore, et al. [6] who reported the crystal structure of $Pb_8Bi_2(PO_4)_6O_2$. They also investigated the compositions $Pb_{8-x}Bi_2(PO_4)_6O_{2-x}$, for $x = 0$, 0.5, 1.0 and 1.5. The expectation was that the phase for $x = 0$ might be isostructural with apatite, $Pb_5(PO_4)_3O$, while for $x = 2$, $Pb_3Bi(PO_4)_3$, one might expect it to be isostructural with eulytite, $Bi_4(SiO_4)_3$. Instead the $x = 0$ phase, $BiPb_4(PO_4)_3O$ was a new structure with space group *Pnma* and its crystal structure was determined [6]. The compositions with $x > 0$ showed a distorted eulytite

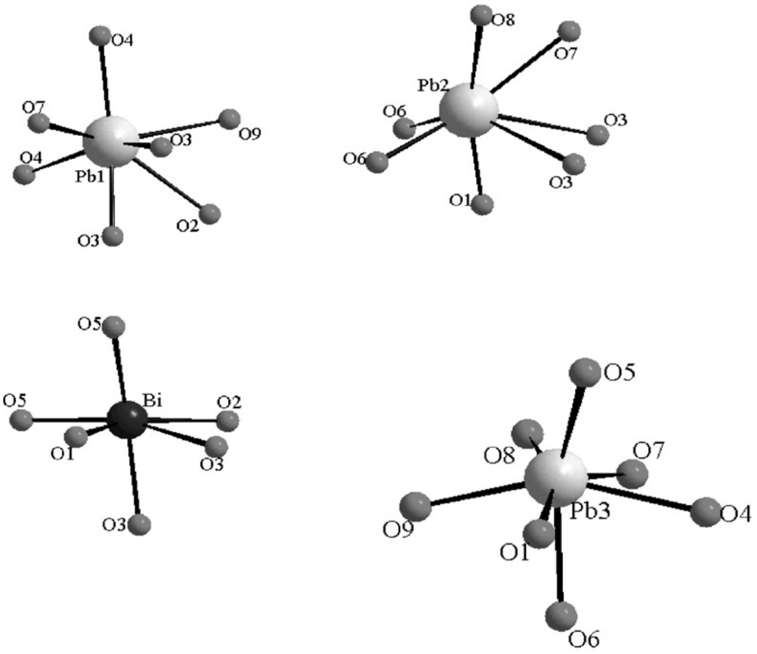

Fig. 1. The cation polyhedra of $Bi_{1.5}(Pb_{7.3}Mn_{0.7})(PO_4)_6O_{1.3}$. When an oxygen atom is disordered only one is shown.

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $Bi_{1.5}(Pb_{7.3}Mn_{0.7})(PO_4)_6O_{1.3}$

	sof	x	y	z	U(eq)
Bi	0.366(2)	9824(1)	2500	9761(1)	26(1)
Pb(1)		2311(1)	7500	3030(1)	21(1)
Pb(2)		2219(1)	2500	3402(1)	35(1)
Pb(3)	0.823(5)	4316(1)	4447(1)	1968(1)	28(1)
Mn(3)	0.177	4316	4447	1968	28
P(1)		1653(2)	4721(3)	0625(4)	24(1)
P(2)		9769(4)	7500	4154(6)	30(1)
O(1)		3964(9)	2500	3072(12)	21(2)
O(2)	0.42(6)	10180(30)	6810(40)	2800(40)	170(40)
O(3)		1653(9)	6167(12)	0927(13)	53(3)
O(4)		3316(13)	5424(17)	3933(19)	83(4)
O(5)		0672(13)	4089(17)	1140(19)	82(5)
O(6)		2573(10)	4038(13)	1297(15)	58(3)
O(7)	0.47(4)	3750(20)	6900(30)	1180(30)	82(13)
O(8)	0.47(4)	4610(20)	8480(30)	−0350(30)	94(11)
O(9)	0.47(4)	10530(20)	8480(30)	4660(40)	91(11)

The anisotropic displacement exponent takes the form $-2\pi^2(U_{11}h^2a^{*2} + \cdots + 2U_{13}hla^*c^*)$. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor. For the oxygen atoms it is the isotropic value.

structure but none of those structures was studied. No gradual transition between an eulytite and apatite structure was observed. The crystal structure reported here for the phase corresponding to $x = 1.0$ but containing Mn and for $x = 0$ by Moore et al. [6], are similar. The valence bond sums, however, strongly indicated that the positions of Bi and of one Pb in the 4*c* position that was not fully occupied, should be interchanged and are listed that way in Table 2. The valence bond sums now are 3.4 for Bi and 2.3 for Pb1. In the Mn-containing solid solution phase, the Mn atom fills the vacancy present in the Pb3 position. Attempts to raise the value of the site occupancy of Bi to unity increased R1 to 0.060 from 0.035.

The greatly distorted oxygen environment around Pb2 permits the filling of this site by Pb only, Fig. 1. It is noteworthy that the $P1O_4$ moiety is a nearly regular tetrahedron while the $P2O_4$ tetrahedron is quite distorted. The large atomic displacement parameters for oxygen ions in this tetrahedron are indicative either of disorder or large vibrational amplitude in the

Table 3
Bond lengths (Å), valence bond values and angles (deg) for $Bi_{1.5}(Pb_{7.3}Mn_{0.7})(PO_4)_6O_{1.3}$

Bi–O(1)#1	2.246(11)	0.663	Pb(1)–O(3)	2.489(12)	0.361	Pb(2)–O(1)	2.282(12)	0.632
Bi–O(5)#2	2.329(17)	0.53	Pb(1)–O(3)#11	2.489(12)	0.361	Pb(2)–O(6)#16	2.511(13)	0.34
Bi–O(5)#3	2.329(17)	0.53	Pb(1)–O(7)	2.58(3)[a]	0.141	Pb(2)–O(6)	2.511(13)	0.34
Bi–O(2)#4	2.41(4)[a]	0.213	Pb(1)–O(7)#11	2.58(3)[a]	0.141	Pb(2)–O(8)#15	2.81(3)[a]	0.076
Bi–O(2)#5	2.41(4)[a]	0.213	Pb(1)–O(4)#11	2.632(17)	0.245	Pb(2)–O(8)#17	2.81(3)[a]	0.076
Bi–O(3)#6	2.436(12)	0.397	Pb(1)–O(4)	2.632(17)	0.245	Pb(2)–O(7)#15	2.86(3)[a]	0.066
Bi–O(3)#7	2.436(12)	0.397	Pb(1)–O(2)#12	2.87(4)[a]	0.065	Pb(2)–O(7)#17	2.86(3)[a]	0.066
			Pb(1)–O(2)#13	2.87(4)[a]	0.065	Pb(2)–O(3)#15	3.031(12)	0.083
Bond valence sum	2.94		Pb(1)–O(9)#13	2.91(3)[a]	0.058	Pb(2)–O(3)#17	3.031(12)	0.083
			Pb(1)–O(9)#12	2.91(3)[a]	0.058			
			Bond valence sum	1.74		Bond valence sum	1.76	
Pb(3)–O(8)#18	2.24(3)[a]	0.708	P(1)–O(5)	1.503(17)		P(2)–O(9)[a]	1.49(2)	
Pb(3)–O(1)	2.283(5)	0.63	P(1)–O(6)	1.511(14)		P(2)–O(2)[a]	1.51(3)	
Pb(3)–O(9)#19	2.31(3)[a]	0.293	P(1)–O(3)	1.513(13)		P(2)–O(7)#25[a]	1.49(2)	
Pb(3)–O(6)	2.376(13)	0.49	P(1)–O(4)#24	1.531(17)		P(2)–O(8)#25[a]	1.49(3)	
Pb(3)–O(4)	2.412(17)	0.444						
Pb(3)–O(5)#20	2.476(17)	0.374	O(5)–P(1)–O(6)	110.1(8)		O(9)–P(2)–O(8)#25	109.5(14)	
Pb(3)–O(2)#21	2.68(4)[a]	0.108	O(5)–P(1)–O(3)	111.7(8)		O(7)#25–P(2)–O(8)#25	107.6(13)	
Pb(3)–O(7)	2.72(3)[a]	0.097	O(6)–P(1)–O(3)	112.7(7)		O(7)#25–P(2)–O(2)	110.4(14)	
Pb(3)–O(8)#11	3.01(3)[a]	0.044	O(5)–P(1)–O(4)#24	106.6(9)		O(8)#25–P(2)–O(2)	108.0(15)	
Pb(3)–O(9)#22	3.03(3)[a]	0.042	O(6)–P(1)–O(4)#24	109.4(8)		O(9)–P(2)–O(2)	109.5(14)	
Bond valence sum	3.23		O(3)–P(1)–O(4)#24	105.9(8)		O(9)–P(2)–O(7)#25	111.7(14)	
Mn(3) in same site								
P(2)–O(9)#11[a]	1.49(2)		O(9)#11–P(2)–O(8)#20	109.5(14)				
P(2)–O(7)#20[a]	1.49(2)		O(7)#20–P(2)–O(8)#20	107.6(13)				
P(2)–O(8)#20[a]	1.49(3)		O(9)#11–P(2)–O(2)#11	109.5(14)				
P(2)–O(2)#11[a]	1.51(3)		O(7)#20–P(2)–O(2)#11	110.4(14)				
			O(8)#20–P(2)–O(2)#11	108.0(15)				
			O(9)#11–P(2)–O(7)#20	111.7(14)				

#1: $x+1/2,y,-z+3/2$ #2: $x+1,y,z+1$ #3: $x+1,-y+1/2,z+1$ #4: $-x+2,y-1/2,-z+1$, #5: $-x+2,-y+1,-z+1$, #6: $-x+1,y-1/2,-z+1$, #7: $-x+1,-y+1,-z+1$, #8: $-x+3/2,-y+1,z+1/2$, #9: $-x+3/2,y-1/2,z+1/2$, #10: $x+1/2,-y+1/2,-z+3/2$, #11: $x,-y+3/2,z$, #:12 $x-1,y,z$, #13: $x-1,-y+3/2,z$, #:14 $-x+1/2,y+1/2,z+1/2$, #15: $-x+1/2,-y+1,z+1/2$, #16: $x,-y+1/2,z$, #17: $-x+1/2,y-1/2,z+1/2$, #18: $-x+1,y-1/2,-z$, #19: $-x+3/2,y-1/2,z-1/2$, #20: $x+1/2,y,-z+1/2$, #21: $x-1/2,y,-z+1/2$, #22: $x-1/2,-y+3/2,-z+1/2$, #23: $x-1/2,y,-z+3/2$, #24: $-x+1/2,-y+1,z-1/2$, #25: $x+1/2,-y+3/2,-z+1/2$, #26: $x+1/2,-y+1/2,-z+1/2$, #27: $x+1,y,z$, #28: $-x+3/2,-y+1,z-1/2$, #29: $x-1,y,z-1$, #30: $-x,-y+1,-z$, #31: $-x+1,y+1/2,-z$, #32: $-x+3/2,y+1/2,z+1/2$.

[a] Disordered oxygen atoms; valence bond values are multiplied by 0.5. Symmetry transformations used to generate equivalent atoms.

structure. Moore, et al. [6] report similar large displacement parameters and tetrahedral distortions. Difference electron density maps indicated that the oxygen ions bonded to P2 could be split into two positions giving rise to two disordered tetrahedra. These two disordered tetrahedra were restrained in the least-squares refinement resulting in bond lengths and angles as shown in Table 3. Analogous disordered phosphate groups were also observed in the crystal structures of $Pb_5Bi_{18}P_4O_{42}$ [10,11] and $Bi_2PbMnO_4(PO_4)_2$ [3]. The final parameters are shown in Table 2, bond distances and angles in Table 3 and anisotropic displacement parameters in Table 4. The stoichiometry based on these parameters is $Bi_{2.93}(Pb_{14.58}Mn_{1.42})P_{12}O_{50.64}$ or $Bi_{1.5}(Pb_{7.3}Mn_{0.7})(PO_4)_6O_{1.3}$ in keeping with the previously published formulation [6]. The two disordered $P2O_4$ moieties are present about 50% of the time within each domain. Moore et al. state that their solution of the structure of $Pb_8Bi_2(PO_4)_6O_2$ showed "…no evidence of partial occupancy." [6]. The presence of a Bi vacancy indicates that a different solid solution is possible in addition to that reported previously.

Table 4
Anisotropic displacement parameters ($Å^2 \times 10^3$) for $Bi_{1.5}(Pb_{7.3}Mn_{0.7})(PO_4)_6O_{1.3}$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + \cdots + 2hka^*b^*U_{12}]$

	U11	U22	U33	U23	U13	U12
Bi	22(1)	26(1)	29(1)	0	−1(1)	0
Pb(1)	19(1)	23(1)	23(1)	0	−1(1)	0
Pb(2)	17(1)	57(1)	32(1)	0	4(1)	0
Pb(3)	24(1)	19(1)	40(1)	−2(1)	1(1)	2(1)
Mn	24	19	40	−2	1	2
P(1)	28(2)	13(1)	32(2)	1(1)	−7(1)	1(1)
P(2)	30(2)	26(2)	34(2)	0	9(2)	0

The atomic structure shown in Fig. 2 is almost parallel to the a-b plane. As in [6] O1 is bonded to Bi, Pb2 and two Pb3 in tetrahedral coordination,

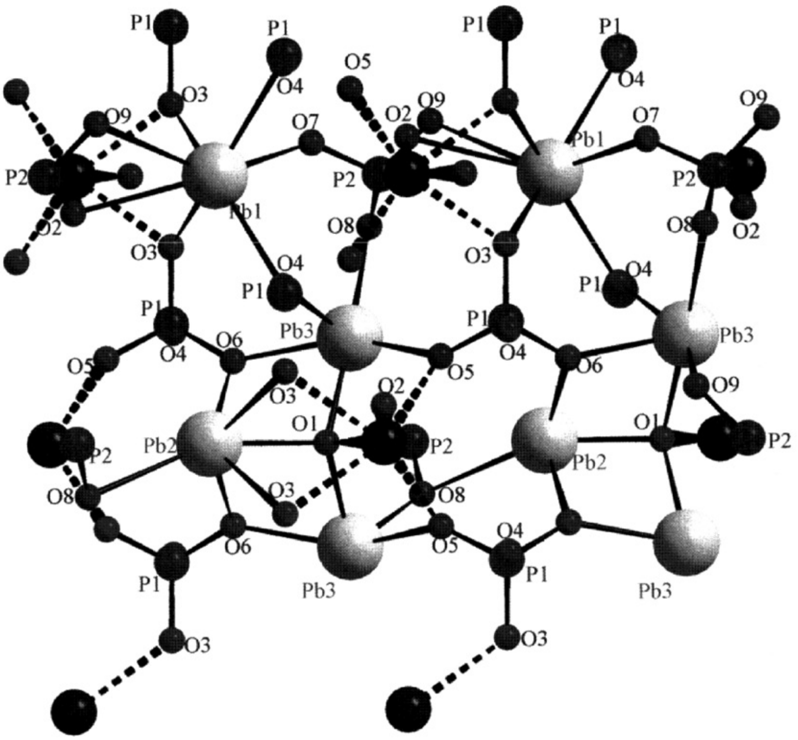

Fig. 2. The crystal structure of $Bi_{1.5}(Pb_{7.3}Mn_{0.7})(PO_4)_6O_{1.3}$ viewed along the *c*-axis. One periodicity is shown for the horizontal *a*-axis and one for the vertical *b*-axis. Only the section between $c = 0$ and 0.55 is drawn to minimize overlap. Only one of the disordered P2 tetrahedra is shown.

O1–(Bi, Pb2, 2Pb3), and this is reflected in its low value of the displacement parameter. The interatomic bond lengths shown in Table 3 and coordination polyhedra for Bi, Pb1, Pb2, and Pb3, Fig. 1, are consistent with previously reported values, [6,10,11]. A comparison with those reported in [6] shows significant differences for the $P2O_4$ tetrahedron. Further, the previous large values of the oxygen displacement parameters bonded to P2 have now reasonable values. The closest O–O contact for ordered oxygen ions is 2.42(2) Å. Moore et al. [6] show the existence of a solid solution $Pb_{8-x}Bi_2(PO_4)_6O_{2-x}$ and report syntheses for $x = 0$, 0.5, 1.0, and 1.5. The results of this investigation support the existence of a second type of solid solution, $Pb_8Bi_{2-x}(PO_4)_6O_{2-1.5x}$, in which vacancies occur in the Bi positions, while the Pb sites are fully occupied either by Pb or an isovalent ion.

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