

Synthesis and structure of $M_{0.5}Bi_3P_2O_{10}$ ($M = Ca, Sr, Ba, Pb$) series

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A series of $M_{0.5}Bi_3P_2O_{10}$ compounds with $M = Ca, Sr, Ba$ and Pb have been synthesized in $MO-Bi_2O_3-P_2O_5$ ternary systems by the ceramic method and the crystal structures were then solved using single-crystal X-ray diffraction data. These compounds are isostructural with $Bi_{6.67}P_4O_{20}$ (triclinic, space group $P\bar{1}$, $Z = 2$). The structures consist of infinite chains of Bi_2O_2 units along the c axis formed by linking BiO_8 and BiO_6 polyhedra. These chains are interconnected by MO_8 polyhedra forming two-dimensional layers in the ac plane. The phosphate tetrahedra are sandwiched between these layers.

1. Introduction

Studies of the $Bi_2O_3-V_2O_5$ binary system and metal-doped $Bi_4V_2O_{11}$, generally known as BIMEVOX, have been intensive because of the high ionic conductivity found in these compounds (Kendall *et al.*, 1996). Many $MO-Bi_2O_3-X_2O_5$ ($M =$ divalent cation and $X = P, V, As$) ternary systems have been studied to synthesize novel materials with a high ionic conductivity (Ketatni *et al.*, 1998; Giraud *et al.*, 2000). During the study of the $Na_2O-Bi_2O_3-V_2O_5$ system, Sinclair *et al.* (1998, 1999) isolated the new compound $NaBi_3V_2O_{10}$ in the $M_2O-Bi_2O_3-V_2O_5$ ternary system. The structure was solved by *ab initio* powder X-ray diffraction (Porob & Guru Row, 2000). The structure was later confirmed by combined single-crystal and neutron diffraction studies (Bliesner *et al.*, 2001). $Bi_4V_2O_{11}$ has a layered structure with Bi_2O_2 sheets alternating with perovskite-like layers. The substitution of one bismuth ion by a monovalent ion such as sodium breaks the Bi_2O_2 sheets into Bi_2O_2 chains. We have continued our studies on the systems involving $M_2O-Bi_2O_3-X_2O_5$ and $MO-Bi_2O_3-X_2O_5$, where M' and M are univalent and divalent cations, and $X = P$ and V , in search of new and intricate motifs using chemical crystallographic concepts. Abraham *et al.* (2002) have conducted extensive studies on several bismuth-based oxyphosphates and oxyvanadates. During the detailed phase diagram study of $2Bi_2O_3-7BiPO_4$, a phase which was stable above 1183 K was identified. Later, during the investigation of the $Bi_2O_3-P_2O_5-CoO$ system, single crystals of this phase were obtained and the subsequent structural analysis gave the composition $Bi_{6.67}P_4O_{20} \cdot Bi_{3.33}P_2O_{10}$ (Ketatni *et al.*, 1998). It was reported that the substitution of 0.67Bi by a divalent cations such as Ca, Sr, Pb or Cd, or of 0.16Bi by a monovalent cation such as Li, Na or K would lead to stabilization of this phase at room temperature. Studies by Giraud *et al.* (2000) on

Table 1

Experimental table.

	CBPO	SBPO	BBPO	PBPO
Crystal data				
Chemical formula	$\text{Bi}_3\text{Ca}_{0.5}\text{O}_{10}\text{P}_2$	$\text{Bi}_3\text{O}_{10}\text{P}_2\text{Sr}_{0.5}$	$\text{Ba}_{0.5}\text{Bi}_3\text{O}_{10}\text{P}_2$	$\text{Bi}_3\text{O}_{10}\text{P}_2\text{Pb}_{0.5}$
M_r	868.92	892.7	917.55	952.47
Cell setting, space group	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$
a, b, c (Å)	6.9100 (9), 7.5426 (10), 9.2027 (12)	6.964 (2), 7.568 (2), 9.207 (3)	7.0141 (9), 7.6084 (10), 9.2525 (12)	7.029 (4), 7.627 (4), 9.268 (5)
α, β, γ (°)	107.053 (2), 93.812 (2), 112.278 (2)	107.196 (4), 93.527 (4), 112.106 (4)	107.339 (2), 93.086 (2), 112.294 (2)	107.295 (7), 93.400 (7), 112.067 (7)
V (Å ³)	415.68 (9)	421.2 (2)	428.24 (10)	431.4 (4)
Z	2	2	2	2
D_x (Mg m ⁻³)	6.942	7.039	7.116	7.333
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
No. of reflections for cell parameters	4853	4394	4758	4345
θ range (°)	2.4–28.0	2.4–27.7	3.1–28.0	2.4–27.6
μ (mm ⁻¹)	64.08	66.07	64.16	71.16
Temperature (K)	293 (2)	293 (2)	293 (2)	293 (2)
Crystal form, color	Block, colorless	Block, colorless	Block, colorless	Block, colorless
Crystal size (mm)	0.10 × 0.09 × 0.08	0.14 × 0.12 × 0.10	0.09 × 0.08 × 0.07	0.08 × 0.07 × 0.06
Data collection				
Diffractometer	Bruker APEX SMART CCD area detector	Bruker APEX SMART CCD area detector	Bruker APEX SMART CCD area detector	Bruker APEX SMART CCD area detector
Data collection method	ω scans	ω scans	ω scans	ω scans
Absorption correction	Numerical	Numerical	Numerical	Numerical
T_{\min}	0.004	0.003	0.005	0.002
T_{\max}	0.017	0.014	0.018	0.013
No. of measured, independent and observed reflections	4853, 1921, 1651	4394, 1881, 1685	4758, 1968, 1740	4345, 1905, 1707
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.068	0.049	0.049	0.043
θ_{\max} (°)	28.0	27.7	28.0	27.6
Range of h, k, l	$-8 \Rightarrow h \Rightarrow 9$ $-9 \Rightarrow k \Rightarrow 9$ $-12 \Rightarrow l \Rightarrow 12$	$-9 \Rightarrow h \Rightarrow 9$ $-9 \Rightarrow k \Rightarrow 9$ $-11 \Rightarrow l \Rightarrow 11$	$-9 \Rightarrow h \Rightarrow 9$ $-9 \Rightarrow k \Rightarrow 9$ $-12 \Rightarrow l \Rightarrow 11$	$-9 \Rightarrow h \Rightarrow 9$ $-10 \Rightarrow k \Rightarrow 10$ $-12 \Rightarrow l \Rightarrow 12$
Refinement				
Refinement on	F^2	F^2	F^2	F^2
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.057, 0.155, 1.05	0.069, 0.184, 1.02	0.069, 0.182, 1.06	0.062, 0.176, 1.07
No. of reflections	1921	1881	1968	1905
No. of parameters	142	142	142	142
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.1072P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.128P)^2 + 18.6788P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0871P)^2 + 67.3458P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.1309P)^2 + 1.2985P]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$	<0.0001	0.003	0.001	0.002
$\Delta\rho_{\max}, \Delta\rho_{\min}$ (e Å ⁻³)	3.82, -7.94	4.18, -10.81	8.86, -9.43	6.07, -5.95

Computer programs: SMART and SAINT (Bruker, 1998), SHELXS97 and SHELXL97 (Sheldrick, 1997), ORTEP3 for Windows (Farrugia, 1997), PLATON (Spek, 1990).

$\text{PbBi}_6\text{X}_4\text{O}_{20}$ ($X = \text{P, V}$ and As) using the Rietveld method on X-ray powder data proved that stabilization could indeed occur. In order to systematically investigate the nature and extent of substitution in this compound we have studied the divalent cation-doped series $M_{0.5}\text{Bi}_3\text{P}_2\text{O}_{10}$ with $M = \text{Ca, Sr, Ba}$ and Pb . The formula $M_{0.5}\text{Bi}_3\text{P}_2\text{O}_{10}$ will be used for this series of compounds rather than $M\text{Bi}_6\text{P}_4\text{O}_{20}$ in order to preserve the analogy with the $\text{NaBi}_3\text{V}_2\text{O}_{10}$ system we have previously studied. Here we report the synthesis and detailed single-crystal structure analysis of four compounds in the $\text{MO}-\text{Bi}_2\text{O}_3-\text{P}_2\text{O}_5$ system, namely $\text{Ca}_{0.5}\text{Bi}_3\text{P}_2\text{O}_{10}$ (CBPO), $\text{Sr}_{0.5}\text{Bi}_3\text{P}_2\text{O}_{10}$ (SBPO), $\text{Ba}_{0.5}\text{Bi}_3\text{P}_2\text{O}_{10}$ (BBPO) and $\text{Pb}_{0.5}\text{Bi}_3\text{P}_2\text{O}_{10}$ (PBPO).

2. Experimental

2.1. Synthesis

$M_{0.5}\text{Bi}_3\text{P}_2\text{O}_{10}$ ($M = \text{Ca, Sr, Ba, Pb}$) were prepared by the conventional solid-state reaction of Bi_2O_3 , CaCO_3 , SrCO_3 , BaCO_3 , PbO and $(\text{NH})_2\text{HPO}_4$ (all AR grade) reagents. The reaction mixtures of the respective stoichiometries were weighed from the starting reagents, ground together in an agate pestle and mortar, and fired in a platinum crucible initially at 573 K for 2 h to decompose $(\text{NH})_2\text{HPO}_4$ and later ground and reheated to 1173 for 2 d with intermediate grinding. Powder X-ray diffraction patterns were recorded to

Table 2

Bond lengths (Å) and bond-valence sum (Hormillosa, 1993) in CBPO, SBPO, BBPO and PBPO.

O and O' are symmetry-related O atoms.

	CBPO	SBPO	BBPO	PBPO
Bi1—O1	2.174 (10)	2.155 (13)	2.177 (16)	2.177 (11)
Bi1—O1'	2.272 (11)	2.290 (13)	2.266 (18)	2.284 (12)
Bi1—O3	2.445 (10)	2.477 (14)	2.485 (19)	2.513 (14)
Bi1—O7	2.339 (12)	2.308 (13)	2.321 (19)	2.346 (14)
Bi1—O8	2.387 (12)	2.409 (15)	2.405 (19)	2.443 (13)
Bi1—O9	2.719 (11)	2.720 (14)	2.731 (16)	2.741 (13)
BVS	2.965	2.964	2.926	2.788
Bi2—O1	2.573 (10)	2.574 (13)	2.596 (17)	2.603 (12)
Bi2—O3	2.573 (11)	2.626 (13)	2.662 (19)	2.645 (11)
Bi2—O4	2.226 (12)	2.252 (14)	2.295 (19)	2.279 (12)
Bi2—O4'	2.372 (11)	2.398 (14)	2.441 (19)	2.422 (13)
Bi2—O5	2.449 (11)	2.423 (14)	2.470 (24)	2.449 (13)
Bi2—O6	2.397 (11)	2.422 (16)	2.499 (22)	2.453 (14)
Bi2—O7	2.756 (12)	2.772 (14)	2.804 (21)	2.786 (15)
Bi2—O10	2.626 (13)	2.663 (17)	2.347 (19)	2.735 (14)
BVS	3.254	2.800	2.475	2.591
Bi3—O1	2.301 (11)	2.289 (13)	2.290 (17)	2.315 (12)
Bi3—O2	2.424 (10)	2.441 (14)	2.463 (19)	2.471 (12)
Bi3—O4	2.093 (12)	2.099 (13)	2.100 (19)	2.112 (13)
Bi3—O8	2.946 (12)	2.913 (14)	2.957 (19)	2.995 (12)
Bi3—O9	2.269 (11)	2.279 (13)	2.255 (17)	2.284 (12)
Bi3—O10	2.320 (12)	2.331 (14)	2.347 (19)	2.368 (12)
BVS	3.248	3.212	3.192	3.027
M—O2 × 2	2.484 (13)	2.587 (15)	2.633 (19)	2.616 (14)
M—O4 × 2	2.704 (11)	2.707 (15)	2.722 (23)	2.768 (14)
M—O5 × 2	2.384 (13)	2.490 (14)	2.494 (22)	2.530 (14)
M—O6 × 2	2.537 (12)	2.616 (14)	2.612 (21)	2.650 (14)
BVS	1.842	2.224	3.356	1.966
P1—O3	1.558 (11)	1.542 (14)	1.549 (21)	1.549 (11)
P1—O5	1.535 (12)	1.552 (14)	1.544 (19)	1.549 (14)
P1—O8	1.556 (12)	1.556 (14)	1.535 (19)	1.537 (12)
P1—O10	1.578 (12)	1.565 (15)	1.547 (21)	1.525 (13)
BVS	4.711	4.747	4.864	4.927
P2—O2	1.536 (12)	1.553 (15)	1.548 (18)	1.578 (13)
P2—O6	1.535 (11)	1.538 (16)	1.517 (19)	1.534 (15)
P2—O7	1.533 (12)	1.523 (14)	1.514 (20)	1.525 (13)
P2—O9	1.549 (12)	1.539 (13)	1.547 (18)	1.550 (12)
BVS	4.950	4.951	5.065	4.843

confirm the formation of a single phase. The single crystals in each case were grown by melting the product in a platinum crucible at 1373 K (1448 K for CBPO) and slowly cooling to room temperature at a rate of 6 K h⁻¹. EDAX (energy-dispersive analysis by X-rays) analysis on the crystallites confirms the formation of the compound in the desired ratio and that there is no trace of the starting reagents. X-ray powder diffraction data of the polycrystalline samples were recorded on a Stoe/Stadi-P X-ray powder diffractometer with germanium-monochromated Cu Kα₁ (λ = 1.54056 Å) radiation from a sealed-tube X-ray generator (30 kV, 25 mA) in the transmission mode using a linear PSD (position-sensitive detector).

2.2. Crystal structure

The data sets were collected on a Bruker APEX SMART CCD system (Mo Kα, λ = 0.7107 Å). The initial unit cell was

Table 3

Comparative ionic radius and cell volume in M_{0.5}Bi₃P₂O₁₀ compounds.

Formula	M cation	Ionic radius (Shannon, 1976)	Cell volume
Bi _{0.33} Bi ₃ P ₂ O ₁₀	Bi ³⁺	1.17	417.90 ^(a)
Ca _{0.5} Bi ₃ P ₂ O ₁₀	Ca ²⁺	1.12	415.68
Sr _{0.5} Bi ₃ P ₂ O ₁₀	Sr ²⁺	1.26	421.20
Ba _{0.5} Bi ₃ P ₂ O ₁₀	Ba ²⁺	1.42	428.24
Pb _{0.5} Bi ₃ P ₂ O ₁₀	Pb ²⁺	1.29	431.40

Reference: (a) Ketatni *et al.* (1998).

determined using a least-squares analysis of a random set of reflections collected from three sets of 0.3° wide ω scans (50 frames per set) that were well distributed in reciprocal space. Data frames were collected with 0.3° wide ω scans, 10 s per frame, 606 frames per set. Four complete sets were collected, using a crystal-to-detector distance of 6.03 cm, thus providing a complete sphere of data. The final unit-cell parameters were obtained and refined using all the reflections. SMART (Bruker, 1998) software was used for data acquisition and SAINT software (Bruker, 1998) for data integration. The structure determination was satisfactorily achieved in space group *P*1̄. The structure was solved by direct methods using the SHELXS97 module in the WinGX suite of software (Farrugia, 1999). The positions of three Bi atoms and one M atom were obtained from the Fourier map. Two P and ten O atoms were subsequently located by difference-Fourier synthesis. The positional parameters and anisotropic displacement parameters of all the atoms were refined using SHELXL97 (Sheldrick, 1997). Experimental details are given in Table 1.¹

3. Results and discussion

The atomic fractional coordinates and displacement parameters for CBPO, SBPO, BBPO and PBPO are given in the supplementary data. Selected bond lengths and the bond-valence sum are given in Table 2. The crystal structures of CBPO, SBPO, BBPO and PBPO are isostructural to Bi_{6.67}P₄O₂₀. The bismuth ion with 0.67 occupancy in Bi_{6.67}P₄O₂₀ is replaced by one divalent cation M (M = Ca, Sr, Ba, Pb). The structures of CBPO, SBPO, BBPO and PBPO have similar bond lengths and polyhedral distortions. The oxygen environment around Bi1, Bi2, Bi3 and Ca in CBPO are shown in Fig. 1, which serves as a representative for all four compounds. The Bi1 and Bi3 atoms are coordinated to six O atoms forming BiO₆ polyhedra. The effect of the 6s² lone pair on these Bi atoms is clearly evidenced by the distorted geometry of these polyhedra. The Bi1 atom has five relatively short bonds (2.155–2.485 Å) with O1, O1', O3, O7 and O8 on one side, while O9 forms a long bond (2.719–2.731 Å) on the other side which would host the lone pair. A similar coordination is observed in the case of Bi3. The five O atoms O1, O2, O4, O9 and O10 form five relatively short bonds (2.093–

¹Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK5000). Services for accessing these data are described at the back of the journal.

2.463 Å) on one side, while O8 forms a long bond (2.911–2.958 Å) on the other side. The Bi2 and *M* cations are bonded to eight O atoms. The BiO₈ coordination is highly distorted with two distinct types of bond length as observed in other Bi atoms, a clear signature of the lone-pair effect. The *M* atom occupies a special position and is coordinated to eight O atoms, two each of O2, O4, O5 and O6 forming a distorted MO₈ polyhedron. It is noteworthy that the *M* cation has a high anisotropy in thermal parameters compared with the Bi atoms. A similar situation existed in the structure of Bi_{6.67}P₄O₂₀ (Ketatni *et al.*, 1998). The bond-valence sum calculation for the *M* site (Table 2) suggests a possible split on either side of the center of symmetry where the *M* atom resides. Such a split would allow for a larger thermal parameter if the *M* atom were

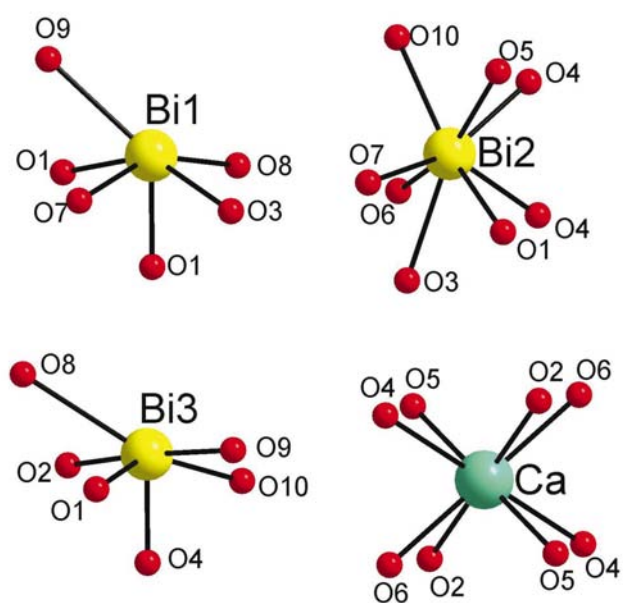


Figure 1
Oxygen environment of Ca and Bi atoms in CBPO.

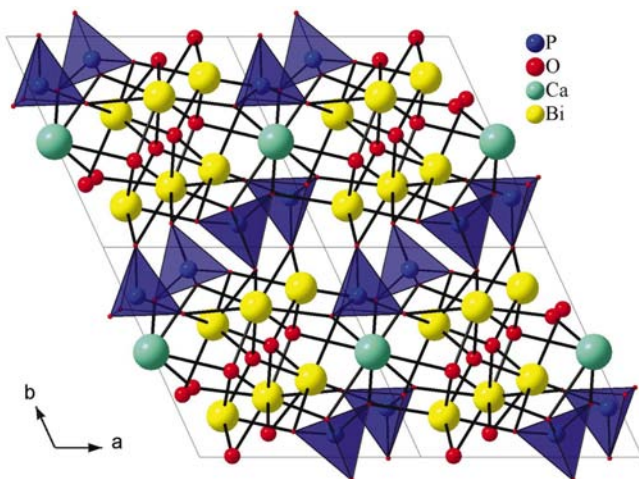


Figure 2
Structure of CBPO viewed down the *c* axis.

restrained to the $\bar{1}$ site. However, refinement based on a 'split-atom model' resulted in oscillations and convergence could be attained only by fixing the atom at the center of symmetry, as was also found in the structure of Bi_{6.67}P₄O₂₀ (Ketatni *et al.*, 1998). The P1 and P2 atoms occupy the central interstitial of regular phosphate tetrahedra. The P–O bond lengths are listed in Table 2. The crystal structure can be described as built

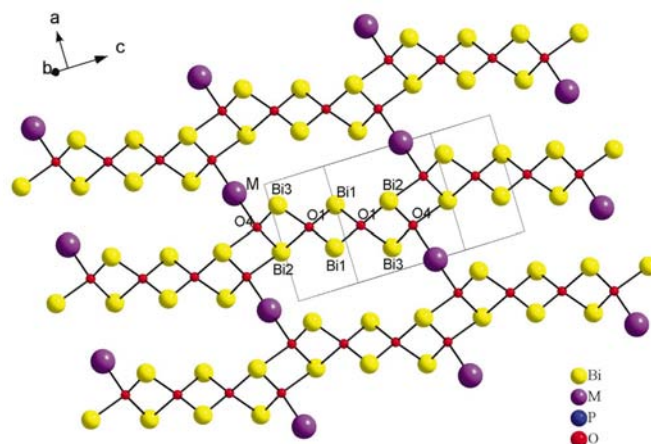


Figure 3
A perspective view of Bi₂O₂ chains formed by (Bi₆O₄) blocks (shown in the box).

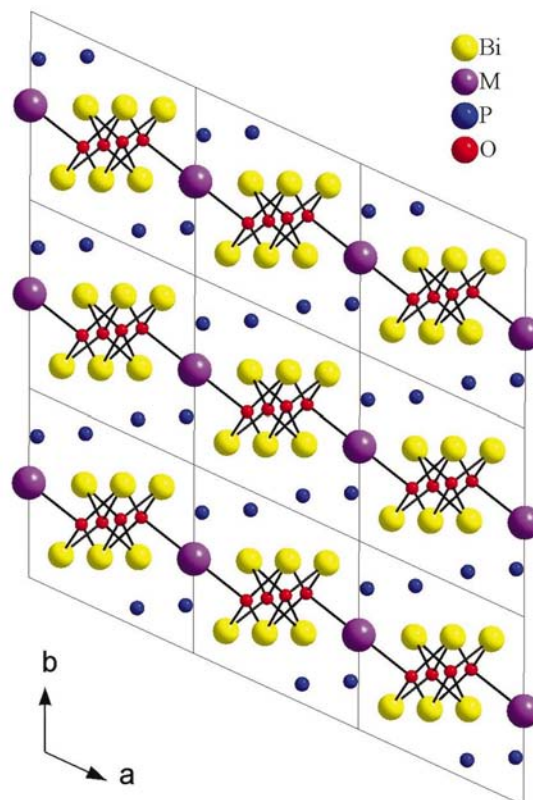


Figure 4
View of Bi₂O₂ chains linked *via* the *M* cation forming a 'step-like arrangement' with P atoms sitting on the step.

from Bi_2O_2 chains interlinked *via* M cations forming a slab with PO_4 tetrahedra residing between these slabs (Fig. 2). The packing diagram of CBPO viewed down the c axis (representative example for the entire series) is shown in Fig. 2. The Bi_6O_4 block forms a basic repeat unit of the chain formed by

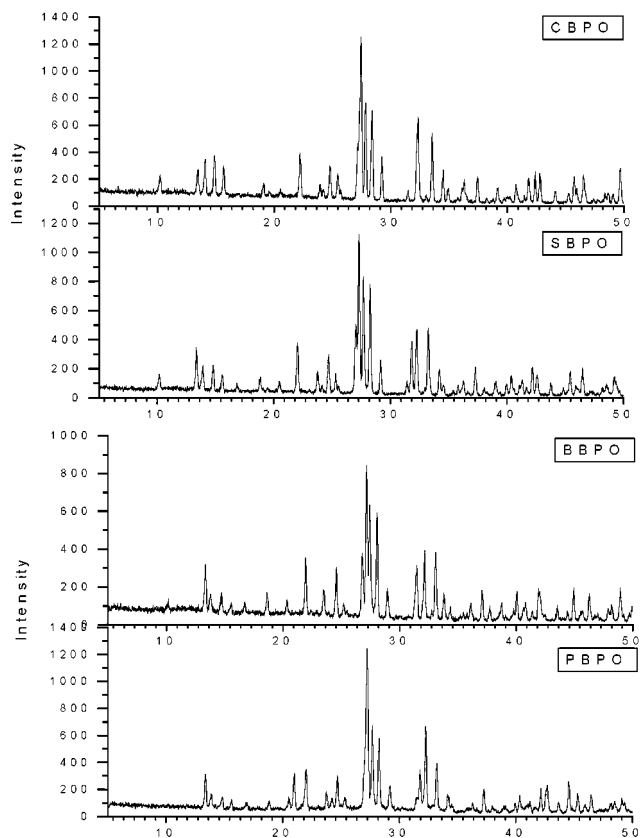


Figure 5 X-ray powder pattern of CBPO, SBPO, BBPO and PBPO.

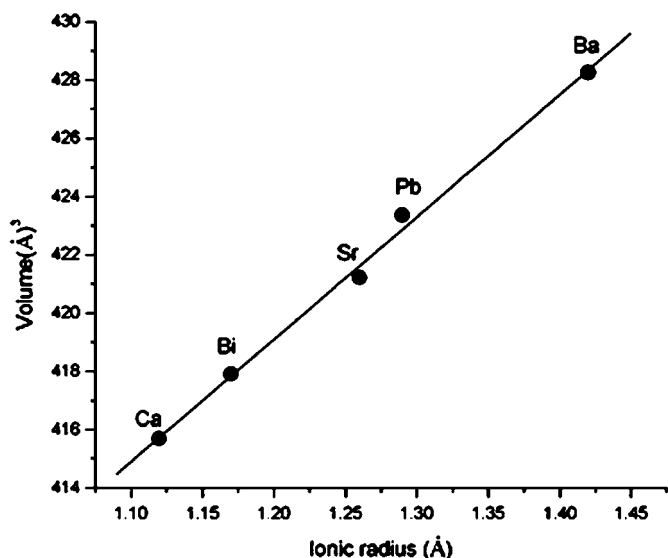


Figure 6 Plot of the ionic radius of M cations versus unit-cell volume of $\text{M}_{0.5}\text{Bi}_3\text{P}_2\text{O}_{10}$.

O1 , O4 and Bi atoms. The Bi_6O_4 blocks are interconnected through two symmetry-related O atoms, O4 and $\text{O4}'$, resulting in the formation of an infinite (Bi_2O_2) chain (Fig. 3) which extends along the c axis. The M cation then links the Bi_2O_2 chains in the ac plane to form a slab by bonding to the O4 atom of each chain. A perpendicular view of the chains indicates Bi_6O_4 and the M cation forming a 'step-like structure' with P atoms sitting on each step (Fig. 4).

The powder patterns of these compounds show a clear change from that of $\text{Bi}_{6.67}\text{P}_4\text{O}_{20}$ as the M cation changes from Bi to Ca , Sr , Ba and Pb (Fig. 5). The effect of a change in cation is also reflected in the unit-cell parameters and volume. The volume is the least for CBPO (the smallest M ion) and the greatest for BBPO (the largest M ion) and there is a linear dependence of the ionic radius with the volume of the unit cell (Table 3, Fig. 6). The bond-valence sum (BVS) values calculated for all the cations indicate regular bonding features. However, the BVS for Ba in BBPO is rather high (3.38), which is a result of short bonds. This could be due to the size effect of the Ba ion in this lattice, a limiting factor to the retention of this structural type. The structural analyses prove unequivocally that the substitution of 0.67Bi in $\text{Bi}_{6.67}\text{P}_4\text{O}_{20}$ by a divalent cation such as Ca , Sr , Ba or Pb leads to the stabilization of this phase at room temperature.

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