inorganic compounds

A new strontium borophosphate, $Sr_6BP_5O_{20}$, from synchrotron powder data

Namsoo Shin,[a]* Jinyoung Kim,[b] Docheon Ahn[a] and Kee-Sun Sohn[c]

[a]Pohang Accelerator Laboratory, Pohang University of Science and Technology, Pohang 790-784, South Korea, [b]Department of Materials Science and Engineering, Pohang University of Science and Technology, Pohang 790-784, South Korea, and [c]Department of Materials Science and Metallurgical Engineering, Sunchon National University, Chonam 540-742, South Korea
Correspondence e-mail: sns@postech.ac.kr

Strontium borophosphate, $Sr_6BP_5O_{20}$, was prepared by a solution synthesis method. The crystal structure was solved *ab initio* from synchrotron powder data without preliminary knowledge of the chemical formula. The compound crystallizes in space group $I\bar{4}c2$. Sr atoms occupy sites coordinated by eight or nine O atoms, and the anionic layer consists of BO_4 and PO_4 tetrahedra. The eightfold-coordinated Sr atom lies at a site with twofold symmetry, while one P atom and the B atom are located on special positions of site symmetry $\bar{4}$.

Comment

Borophosphates constitute a poorly studied uncommon class of compounds, whose anions contain both boron–oxygen tetrahedra and phosphorus–oxygen tetrahedra forming various combinations. In the present study, the structure of the title compound was determined and refined from synchrotron powder diffraction data, as shown in Fig. 1.

The anion of $Sr_6BP_5O_{20}$ (SBP) is similar to that of $Pb_6BP_5O_{20}$ (PBP), containing two groups, *viz.* the orthophosphate PO_4^{3-} anion of symmetry $\bar{4}$ and the $[B(PO_4)_4]^{9-}$ anion. This propeller-like structure consists of a central $[BO_4]$ tetrahedron of symmetry $\bar{4}$, surrounded by an array of four $[PO_4]$ tetrahedra, as shown in Fig. 2 (Belokoneva *et al.*, 2001). Atom Sr1 is coordinated by eight O atoms at distances of 2.425 (4)–2.990 (4) Å and atom Sr2 is coordinated by nine O atoms at 2.418 (4)–3.169 (4) Å (Table 1). The Sr—O distances of SBP are more regular than those of PBP, which range from 2.04 (6) to 3.35 (4) Å. The B—O and P—O bond lengths are within usual ranges.

The unit cell of SBP can be obtained by multiplication of that of PBP ($a_{SBP} = 2^{1/2}a_{PBP}$ and $c_{SBP} = 2c_{PBP}$). However, intense odd index reflections, such as 211, 213, 215 and 321, indicate that the unit cell of SBP cannot be reduced to that of

PBP. Fig. 3 shows the differences between the structures of SBP and PBP, Figs. 3(a) and 3(b) are the *ab* projections of SBP and PBP, respectively, while Fig. 3(c) shows (100) and (110) projections, in part, of SBP and PBP, respectively. According to the symmetry of the $I\bar{4}c2$ space group of SBP, there is $\bar{4}$ inversion symmetry at the center of the *ab* plane, and there are also *b*-glide planes ($a = \frac{1}{4}$ and $\frac{3}{4}$) and *a*-glide planes ($b = \frac{1}{4}$ and $\frac{3}{4}$) as a result of the centering translation and *c* glide. In Fig. 3(a) we can see that two out of four $[B(PO_4)_4]^{9-}$ anions are mirrored from the others by the glide planes; this configuration is in sharp contrast to the structure of PBP with only $P\bar{4}$ symmetry (Fig. 3b). Belokoneva *et al.* (2001) assumed that general position 4h for atom Pb2 in PBP ($Z = 1$) is randomly occupied (50%). In the present study, however, all the atom sites are fully occupied.

SBP is a new candidate host material for Eu^{2+} activator, an alternative to $BaMgAl_{10}O_{17}$ (BAM), which has been used as a blue component in plasma display panels (PDPs). SBP has superior thermal stability, and the excellent luminescent intensity of Eu^{2+}-doped SBP would make it possible to apply this compound to PDPs in place of BAM. Unlike the BAM
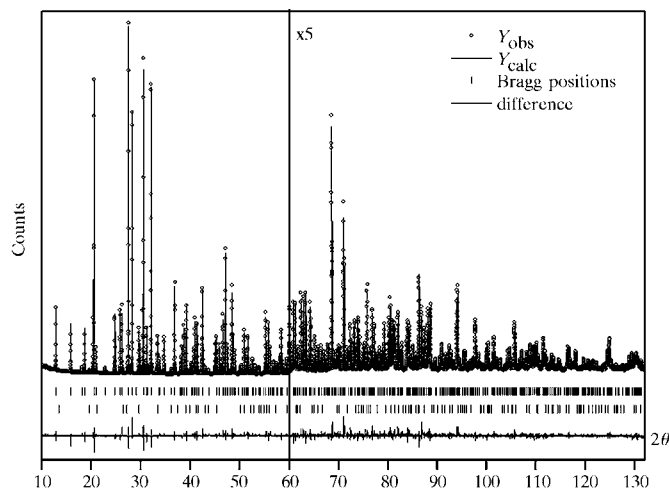

Figure 1
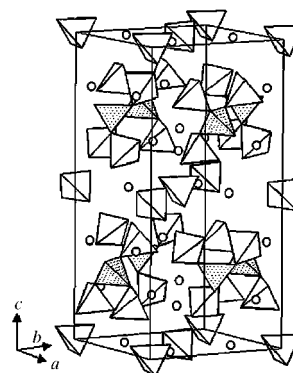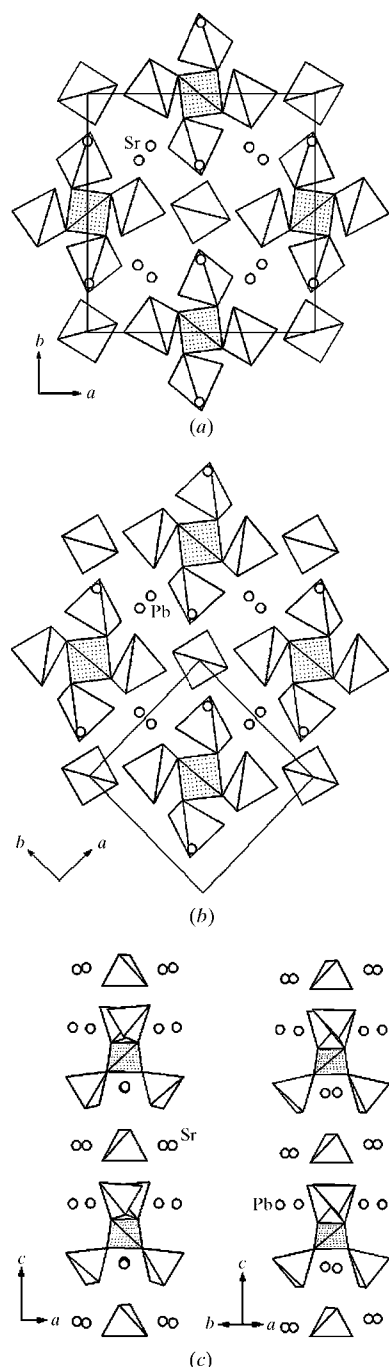Comparison between the observed and calculated patterns and the difference curve for the Rietveld refinement.

Figure 2
The structure of $Sr_6BP_5O_{20}$. Sr atoms (spheres), PO_4 tetrahedra and BO_4 tetrahedra (shaded) are shown.

Figure 3
The crystal structures of $Sr_6BP_5O_{20}$ and $Pb_6BP_5O_{20}$, showing ab projections of (a) $Sr_6BP_5O_{20}$ and (b) $Pb_6BP_5O_{20}$, and (c) selective (100) and (110) projections of $Sr_6BP_5O_{20}$ and $Pb_6BP_5O_{20}$, respectively. Sr and Pb atoms are shown as spheres.

structure, involving open layers on which Eu^{2+} ions can be located, SBP provides tight Eu^{2+} sites. Divalent Eu atoms occupy Sr^{2+} sites in SBP and mostly Ba^{2+} sites in BAM. Two possible Sr^{2+} (or Eu^{2+}) sites are enclosed by eight and nine O atoms at average distances of 2.6729 (4) and 2.7151 (4) Å, respectively. The thermal degradation in BAM is associated with the loose local structure around the Ba^{2+} (or Eu^{2+}) site [nine O atoms are at an average distance of 2.9512 (5) Å from the Ba^{2+} center]. Eu^{2+} ions can easily escape to other trivalent

sites or open spaces by passing through the loosely surrounded O atoms in the case of BAM. On the other hand, both the crystallographic sites for the Sr^{2+} ions in SBP make a relatively tight obstacle against the escape of Eu^{2+} ions. This could be the origin of the excellent thermal stability of SBP.

Experimental

The title compound was produced by a solution-based synthesis method. The raw powders strontium nitrate [$Sr(NO_3)_2$], boric acid (H_3BO_3) and diammonium hydrogen phosphate [($NH_4)_2HPO_4$] were dissolved in deionized water, and then a stoichiometric amount of each solution was collected in a quartz container. The solution in the container was stirred and then dried at 373 K for 48 h, followed by further drying at 873 K for 6 h. The dried samples were pulverized and successively fired at 1473 K under a reducing atmosphere; a white crystalline powder resulted. A small amount of $Sr_3(PO_4)_2$ was detected as an impurity.

Crystal data

$Sr_6BP_5O_{20}$	Synchrotron radiation
$M_r = 1011.43$	$\lambda = 1.5452$ Å
Tetragonal, $I\bar{4}c2$	$T = 298$ K
$a = 9.78392$ (2) Å	Specimen shape: flat sheet
$c = 19.01318$ (3) Å	$20 \times 20 \times 0.5$ mm
$V = 1820.04$ (1) Å³	Specimen prepared at 1473 K
$Z = 4$	Plate-like, white
$D_x = 3.691$ (1) Mg m⁻³	

Data collection

PLS HRPD beamline	Scan method: step
Specimen mounting: packed powder pellet	$2\theta_{min} = 10$, $2\theta_{max} = 132°$
Specimen mounted in reflection mode	Increment in $2\theta = 0.01°$

Refinement

Refinement on I_{net}	Wavelength of incident radiation: 1.54520 Å
$R_p = 0.063$	
$R_{wp} = 0.084$	Profile function: pseudo-Voigt
$R_{exp} = 0.038$	50 parameters
$R_B = 0.037$	Weighting scheme based on measured s.u.'s
$S = 2.21$	$(\Delta/\sigma)_{max} < 0.001$

Table 1
Selected interatomic distances (Å).

Sr1—O2	2.699 (4)	Sr2—O4^{vii}	2.950 (4)
Sr1—O2^i	2.990 (4)	Sr2—O5^{iii}	3.171 (4)
Sr1—O3^{ii}	2.574 (4)	Sr2—O5^{vii}	2.549 (4)
Sr1—O4^{iii}	2.426 (4)	P1—O2	1.574 (4)
Sr2—O1	2.577 (4)	P2—O1	1.583 (4)
Sr2—O1^{iv}	2.538 (4)	P2—O3	1.505 (4)
Sr2—O1^{iii}	2.705 (3)	P2—O4	1.512 (4)
Sr2—O2^v	2.417 (4)	P2—O5	1.589 (4)
Sr2—O3^{vi}	2.597 (4)	B—O5	1.471 (4)
Sr2—O4	2.932 (4)		

Symmetry codes: (i) $-y, x, -z$; (ii) $x, 1-y, z-\frac{1}{2}$; (iii) $y, x, \frac{1}{2}-z$; (iv) $1-x, 1-y, z$; (v) $\frac{1}{2}+y, \frac{1}{2}-x, \frac{1}{2}-z$; (vi) $\frac{1}{2}-x, y-\frac{1}{2}, z$; (vii) $\frac{1}{2}+x, \frac{1}{2}-y, z$.

The diffraction pattern also includes peaks from $Sr_3(PO_4)_2$ ($R\bar{3}m$, $a = 5.3889$ Å and $c = 19.7909$ Å), but the peaks of SBP and $Sr_3(PO_4)_2$ are well separated from each other in the high-resolution synchrotron powder pattern, at least in the low and medium scattering-angle region. We could easily exclude the peaks of $Sr_3(PO_4)_2$ from the rest of the peaks used for unit-cell determination. The SBP powder diffraction pattern was indexed in the tetragonal system

using the *TREOR* program (Werner *et al.*, 1985) with merit $M(30) = 145.0$ ($F30 = 277.0$) and checked with the *DICVOL* program (Boultif & Louer, 1991) with merit $M(30) = 154.3$ ($F30 = 308.3$). The 2θ difference between the positions of observed and calculated peaks was less than $0.002°$. Space group $I\bar{4}c2$ (No. 120) was chosen from the systematic absences and confirmed by the subsequent structure refinement. The positions of the Sr and P atoms were determined by direct methods using the integrated intensities in the *FULLPROF* suite (Rodriguez-Carvajal, 1990). The positions of the O atoms and the B atom were determined by the simulated annealing method with *FULLPROF2K*. The Rietveld refinement was initiated using the atomic positions obtained from the simulated annealing method.

Data collection: PLS HRPD beamline software; cell refinement: *FULLPROF2K* (Rodriguez-Carvajal, 1990); data reduction: *FULL-PROF2K*; program(s) used to solve structure: *FULLPROF2K*; program(s) used to refine structure: *FULLPROF2K*; molecular graphics: *STRUPLO* (Fischer, 1984); software used to prepare material for publication: *FULLPROF2K*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ1203). Services for accessing these data are described at the back of the journal.

References

Belokoneva, E. L., Ruchkina, E. A., Dimitrova, O. V. & Stefanovich, S. Y. (2001). *Russ. J. Inorg. Chem.* **46**, 179–185.
Boultif, A. & Louer, D. (1991). *J. Appl. Cryst.* **24**, 987–993.
Fischer, R. X. (1984). *STRUPLO*. University of Würzburg, Germany.
Rodriguez-Carvajal, J. (1990). Abstracts of the Satellite Meeting on Powder Diffraction of the XVth Congress of the IUCr, p. 127, Toulouse, France.
Werner, P.-E., Eriksson, L. & Westhahl, M. (1985). *J. Appl. Cryst.* **18**, 367–370.