

Substitutional and positional disorder
in $\text{Sr}_{2.88}\text{Cu}_{3.12}(\text{PO}_4)_4$ Ljiljana Karanović,^{a*} Sabina Šutović,^a Dejan Poleti,^b
Tamara Đorđević^c and Aleksandar Pačevski^a^aFaculty of Mining and Geology, University of Belgrade, Đušina 7, 11000 Belgrade, Serbia, ^bFaculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11000 Belgrade, Serbia, and ^cInstitut für Mineralogie und Kristallographie, Universität Wien-Geozentrum, Althanstrasse 14, A-1090 Vienna, Austria
Correspondence e-mail: ljika2002@yahoo.com

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The title compound, a hydrothermally synthesized strontium copper(II) phosphate(V) (2.88/3.12/4), is isotypic with $\text{Sr}_3\text{Cu}_3(\text{PO}_4)_4$, obtained previously by solid-state reaction, but not with $\text{Sr}_3\text{Cu}_3(\text{PO}_4)_4$, obtained previously by the hydrothermal method. A surplus of copper was observed by both structural and chemical analysis, and the formula obtained by the structural analysis is in full agreement with results of the EDX (energy-dispersive X-ray diffraction) analysis. The structure consists of layers of Cu_3O_{12} groups which are linked *via* the PO_4 tetrahedra. The Cu_3O_{12} groups are formed by one Cu_1O_4 and two Cu_2O_5 coordination polyhedra sharing corners. The central Cu1 atom of the Cu_3O_{12} group is located at an inversion centre (special position 2a). The unique structural feature of the title compound is the presence of 12% Cu in the Sr1 site (special position 2b, site symmetry $\bar{1}$). Moreover, disordered Sr2 atoms were observed: a main site (Sr2a, 90%) and a less occupied site (Sr2b, 10%) are displaced by 0.48 (3) Å along the *b* axis. Such substitutional and positional disorder was not observed previously in similar compounds.

Comment

Natural and synthetic metal phosphates often form tetrahedral–octahedral framework structures with potentially interesting physical and chemical properties (*e.g.* ionic conductivity, ion exchange and catalytic activity). An ongoing extensive study on the low-temperature hydrothermal synthesis, crystallography and properties of compounds in the insufficiently known $\text{AO–CuO–X}_2\text{O}_5\text{–H}_2\text{O}$ ($A = \text{Cd}^{2+}$ or Sr^{2+} ; $X = \text{As}^{5+}$ or P^{5+}) system has already yielded a couple of interesting structures (Šutović *et al.*, 2009; Đorđević *et al.*, 2008; Stojanović *et al.*, 2008). This contribution reports on the hydrothermal synthesis and crystal structure of the title compound, (I), and its relationship to similar structures. Selected bond lengths and angles for (I) are listed in Table 1.

The title compound, (I), belongs to the group of compounds adopting the general formula $A_3B_3(\text{XO}_4)_4$, where $A = \text{Ca}^{2+}$, Pb^{2+} or Sr^{2+} , $B = \text{Cu}^{2+}$ and $X = \text{As}^{5+}$ or P^{5+} (Belik *et al.*, 2002; Effenberger, 1999; Osterloh & Müller-Buschbaum, 1994). Some examples with mixed *B* cations, *viz.* $\text{Ca}_3\text{Cu}_2\text{Ni}(\text{PO}_4)_4$ and $\text{Ca}_3\text{CuNi}_2(\text{PO}_4)_4$, are also known (Pomjakushin *et al.*, 2007). In all these crystal structures, $B_3\text{O}_{12}$ groups are linked to XO_4 tetrahedra (Fig. 1), forming layers with *A* cations between them. In (I), these layers are approximately parallel to the (101) planes (Fig. 2a).

The title compound is isotypic with $\text{Sr}_3\text{Cu}_3(\text{PO}_4)_4$ (Belik *et al.*, 2002) obtained as a polycrystalline material by solid-state reaction, as well as with $\text{Ca}_3\text{Cu}_3(\text{PO}_4)_4$ (Anderson *et al.*, 1981), $\text{Ca}_3\text{Cu}_3(\text{AsO}_4)_4$ (Osterloh & Müller-Buschbaum, 1994) and $\text{Sr}_3\text{Cu}_2\text{Ni}(\text{PO}_4)_4$ (Pomjakushin *et al.*, 2007). All these compounds crystallize in the space group $P2_1/c$ (No. 14) with $Z = 2$, but they are described in different settings: $P2_1/c$ for $\text{Sr}_3\text{Cu}_3(\text{PO}_4)_4$, $P2_1/a$ for $\text{Ca}_3\text{Cu}_3(\text{PO}_4)_4$, $\text{Ca}_3\text{Cu}_3(\text{AsO}_4)_4$ and $\text{Sr}_3\text{Cu}_2\text{Ni}(\text{PO}_4)_4$, and $P2_1/n$ for (I).

On the other hand, (I) differs from $\text{Sr}_3\text{Cu}_3(\text{PO}_4)_4$ which was synthesized previously by the hydrothermal method and reported in the space group $C2/c$ (No. 15) with $Z = 4$ (Effenberger, 1999). Although the unit-cell parameters and volumes of (I), $\text{Sr}_3\text{Cu}_3(\text{PO}_4)_4$ (Belik *et al.*, 2002) and the transformed unit cell of $\text{Sr}_3\text{Cu}_3(\text{PO}_4)_4$ (Effenberger, 1999) are almost identical (Table 2), there is a noticeable difference in the stacking sequences of the layers. In the isotypic structures that crystallize in the space group $P2_1/c$, the succeeding layers are identical and the Cu_3O_{12} groups are arranged in a herringbone-like pattern (Fig. 2a). However, in the non-

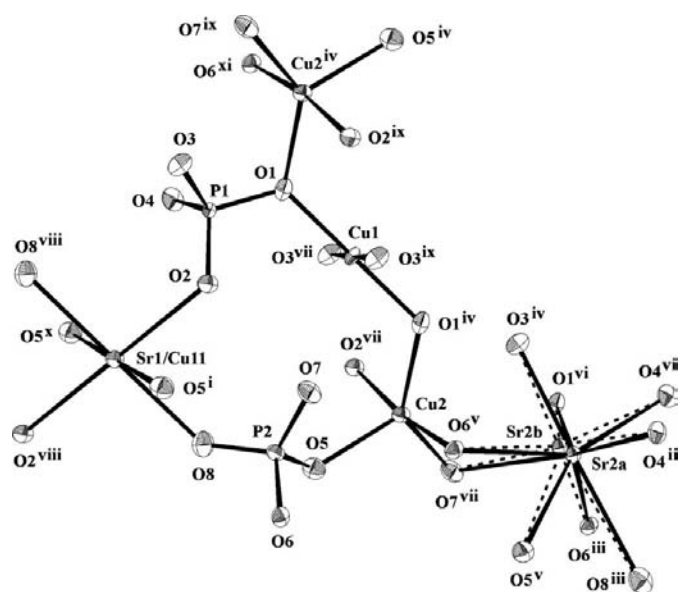


Figure 1

Part of the $\text{Sr}_{2.88}\text{Cu}_{3.12}(\text{PO}_4)_4$ structure and the atom-labelling scheme. Displacement ellipsoids are plotted at the 50% probability level. The $\text{Sr}2b\text{–O}$ bonds in the minor disorder component are represented by dashed lines. [Symmetry codes: (i) $x, y + 1, z$; (ii) $x - \frac{1}{2}, -y - \frac{1}{2}, z - \frac{1}{2}$; (iii) $-x + \frac{1}{2}, y - \frac{3}{2}, -z - \frac{1}{2}$; (iv) $-x, -y, -z$; (v) $-x + \frac{1}{2}, y - \frac{1}{2}, -z - \frac{1}{2}$; (vi) $-x, -y - 1, -z$; (vii) $x, y - 1, z$; (viii) $-x + 1, -y + 1, -z$; (ix) $-x, -y + 1, -z$; (x) $-x + 1, -y, -z$; (xi) $x - \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$.]

isotypic $\text{Sr}_3\text{Cu}_3(\text{PO}_4)_4$ (Effenberger, 1999), the succeeding layers form an *ABABAB* stacking sequence and the Cu_3O_{12} groups are oriented parallel to each other due to the translation symmetry (Fig. 2*b*).

During the crystal structure refinement of (I) it was observed that the average $M1\text{—O}$ distance of 2.49 (2) Å is significantly shorter than the distance of 2.58 Å calculated from the ionic radii (Shannon, 1976), suggesting possible incorporation of the Cu atom in the Sr1 site. As a consequence, the sum of bond valences (Wills, 2009) for the Sr1 atom showed an oversaturation [$\sum v_{ij}(\text{Sr1}) = 2.21$ v.u.]. In order to check this result, the chemical composition of the title compound was determined by EDX (energy-dispersive X-ray diffraction) analysis. It confirmed a copper enrichment in the investigated crystal compared to the Sr:Cu = 1:1 atomic ratio expected for $\text{Sr}_3\text{Cu}_3(\text{PO}_4)_4$. A new refinement showed that the special *M1* position is occupied by 0.88 (3) Sr1 and 0.12 Cu11. At the same time, considering 12% of Cu in the *M1* site resulted in an ideal bond valence sum of 2.02 v.u. In this way, the formula calculated from the structure refinement and the formula obtained by chemical analysis are in full agreement.

The *M1* site is surrounded by six O atoms forming a 4+2 coordination polyhedron, which can be described as a

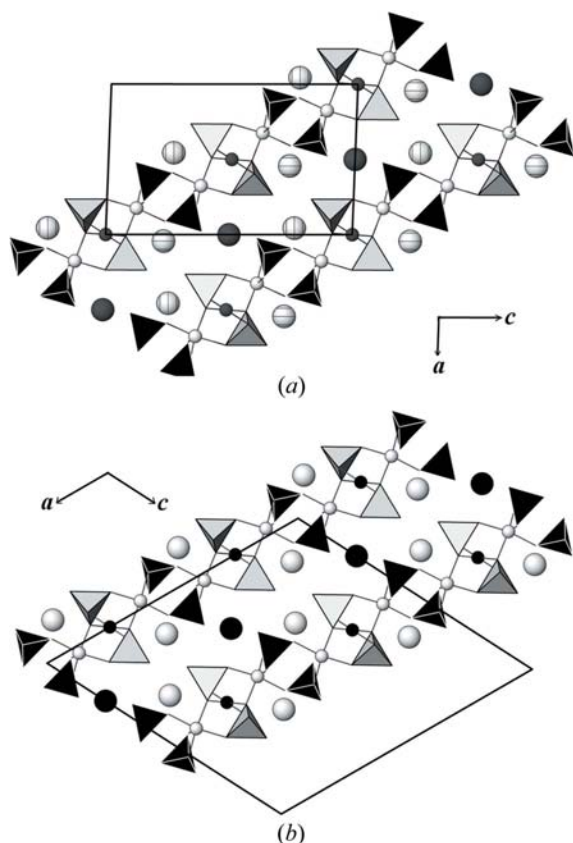


Figure 2

The stacking sequence of layers in (a) $\text{Sr}_{2.88}\text{Cu}_{3.12}(\text{PO}_4)_4$ and (b) non-isotypic $\text{Sr}_3\text{Cu}_3(\text{PO}_4)_4$ (Effenberger, 1999), as viewed along the *b* axis. The large black and grey spheres represent *M1* and *M2* atoms, while the small black and grey spheres represent Cu1 and Cu2 atoms, respectively. In (a), Sr2*a* and Sr2*b* atoms are hatched horizontally and vertically, respectively. P1O_4 (grey) and P2O_4 (black) coordination tetrahedra are shaded.

deformed slightly elongated octahedron (Fig. 1 and Table 1). The ratio of average short to long bond distances is 2.464/2.544 Å. It is worth noticing that the corresponding ratios for isotypic and non-isotypic $\text{Sr}_3\text{Cu}_3(\text{PO}_4)_4$ are very similar (2.446/2.519 and 2.465/2.570, respectively). This implies that similar substitution of Cu for Sr could also be expected, but it has not been reported.

Additionally, the structure refinements showed that the Sr2 cations in the general *M2* site are split into two positions: a main Sr2*a* site [site-occupancy factor (SOF) = 0.90 (1)] and a less occupied Sr2*b* site [SOF = 0.10 (1)]. Sr2*a* is coordinated by nine O atoms and the coordination polyhedron has the form of a slightly distorted tricapped trigonal prism with Sr2*a*—O distances in the range 2.487 (5)–2.989 (6) Å. The Sr2*b* cation is displaced by 0.48 (3) Å along the *b* axis, so that O4^{vi} and O8^{iii} [symmetry codes: (vi) $-x, -y - 1, -z$; (iii) $-x + \frac{1}{2}, y - \frac{3}{2}, -z - \frac{1}{2}$] are moved to longer distances of 3.14 (2) and 3.24 (2) Å, respectively, from Sr2*b*. Therefore, Sr2*b* cations are coordinated by 5+2+2 O atoms which form highly distorted coordination polyhedra with distances ranging from 2.351 (14) to 3.24 (2) Å. The $\langle \text{Sr2a—O} \rangle$ and $\langle \text{Sr2b—O} \rangle$ distances of 2.70 (6) and 2.75 (11) Å, respectively, are close to the sum of the ionic radii of 2.71 Å for nine-coordinated Sr (Shannon, 1976). The valence requirements of Sr2*a* are well satisfied by nine oxygens with a bond valence sum of 2.04, but the valence sum for the Sr2*b* atom [$\sum v_{ij}(\text{Sr2b}) = 2.19$ v.u.] suggests an oversaturation if all nine ligands are considered. Neglecting the longest two distances gives an improved bond valence sum of 2.08 v.u. for Sr2*b*. For coordination number (CN) = 7, the $\langle \text{Sr2b—O} \rangle$ distance is 2.63 (9) Å, while that calculated from the ionic radii (Shannon, 1976) is 2.61 Å.

Experimental

During efforts to synthesize single crystals in the system $\text{SrO—CuO—P}_2\text{O}_5\text{—H}_2\text{O}$, the title compound was obtained hydrothermally from a mixture of $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ (Merck, >97%), $\text{Cu}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ (Merck, >99%) and $(\text{NH}_4)_2\text{HPO}_4$ (LobaChemie, >99%) in a 1:3:2 molar ratio. The mixture was transferred into a Teflon vessel and filled to approximately 70% of its volume with distilled water. The initial pH of the mixture was 8. Finally the vessel was enclosed in a stainless steel autoclave. The autoclave containing the reactant solution was sealed tightly, placed in a furnace and kept at 473 K for 9 d; it was then spontaneously cooled to room temperature. The resulting product was filtered off, washed thoroughly with distilled water and dried in air at room temperature. The title compound crystallized as transparent blue needles (yield ca 30%) of up to 0.4 mm in length together with crystals of the starting material and a light-blue powder. The X-ray diffraction pattern of the polycrystalline powder revealed that the strong peaks predominantly correspond to the title compound. $\text{Cu}_2(\text{PO}_4)(\text{OH})$ (libethenite) and $\text{Cu}_5(\text{PO}_4)_2(\text{OH})_4$ (reichenbachite) were present in smaller quantities. Additional weak peaks indicated the existence of crystalline compound(s) that were not identified.

Quantitative chemical analysis, which was performed using a JEOL JSM-6610 LV SEM connected with an Oxford INCA Energy 350 EDX analysis unit, confirmed the presence of Cu and Sr in the average atomic ratio Cu/Sr = 1.08.

Crystal data

Sr_{2.88}Cu_{3.12}(PO₄)₄ V = 684.8 (2) Å³
 M_r = 830.50 Z = 2
 Monoclinic, P2₁/n Mo Kα radiation
 a = 9.2077 (18) Å μ = 16.46 mm⁻¹
 b = 4.9369 (10) Å T = 295 K
 c = 15.074 (3) Å 0.10 × 0.01 × 0.01 mm
 β = 92.15 (3)°

Data collection

Nonius KappaCCD diffractometer 5148 measured reflections
 Absorption correction: multi-scan 1400 independent reflections
 (Otwinowski & Minor, 1997) 1178 reflections with I > 2σ(I)
 T_{min} = 0.829, T_{max} = 0.853 R_{int} = 0.039

Refinement

R[F² > 2σ(F²)] = 0.038 126 parameters
 wR(F²) = 0.083 Δρ_{max} = 1.53 e Å⁻³
 S = 1.12 Δρ_{min} = -0.93 e Å⁻³
 1400 reflections

The M1 site was refined as a mixed Sr1/Cu11 site constrained to full occupancy. Attempts to refine the positional and displacement parameters for Cu11²⁺ and Sr1²⁺ at M1 independently failed because the refinement became unstable. Therefore, identical fractional coordinates and displacement parameters for both atoms were applied. Site occupancies of 0.88 (3) and 0.12 (3) were obtained for Sr1 and Cu11, respectively.

The positional disorder with split positions and the same anisotropic displacement parameters for Sr2a and Sr2b were included in the structure model and their sum was fixed at four atoms per unit cell. Site-occupancy refinements of the Sr2a and Sr2b sites gave values of 0.90 (1) and 0.10 (1), respectively.

Data collection: COLLECT (Nonius, 2002); cell refinement: SCALEPACK (Otwinowski *et al.*, 2003); data reduction: DENZO-SMN (Otwinowski & Minor, 1997; Otwinowski *et al.*, 2003); program(s) used to solve structure: SIR97 (Altomare *et al.*, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008) and WinGX (Farrugia, 1999); molecular graphics: ATOMS (Dowty, 2000); software used to prepare material for publication: publCIF (Westrip, 2010).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LG3029). Services for accessing these data are described at the back of the journal.

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Table 1

Selected geometric parameters (Å, °).

Sr1—O2	2.457 (5)	Sr2b—O6 ⁱⁱⁱ	2.95 (2)
Sr1—O8	2.471 (6)	Sr2b—O1 ^{vi}	2.958 (19)
Sr1—O5 ⁱ	2.542 (5)	Sr2b—O4 ^{vi}	3.14 (2)
Sr2a—O4 ⁱⁱ	2.487 (5)	Sr2b—O8 ⁱⁱⁱ	3.24 (2)
Sr2a—O6 ⁱⁱⁱ	2.525 (6)	Cu2—O6 ^v	1.920 (5)
Sr2a—O3 ^{iv}	2.555 (6)	Cu2—O2 ^{vii}	1.948 (5)
Sr2a—O5 ^v	2.618 (6)	Cu2—O7 ^{vii}	2.083 (6)
Sr2a—O1 ^{vi}	2.697 (5)	Cu2—O5	2.120 (5)
Sr2a—O7 ^{vii}	2.724 (5)	Cu2—O1 ^{iv}	2.124 (5)
Sr2a—O4 ^{vi}	2.791 (6)	P1—O4	1.509 (5)
Sr2a—O8 ⁱⁱⁱ	2.935 (7)	P1—O2	1.532 (5)
Sr2a—O6 ^v	2.989 (6)	P1—O3	1.540 (5)
Sr2b—O3 ^{iv}	2.351 (14)	P1—O1	1.566 (5)
Sr2b—O4 ⁱⁱ	2.429 (12)	P2—O8	1.502 (6)
Sr2b—O5 ^v	2.477 (13)	P2—O7	1.520 (5)
Sr2b—O6 ^v	2.56 (2)	P2—O6	1.561 (5)
Sr2b—O7 ^{vii}	2.665 (12)	P2—O5	1.565 (6)
O2 ^{viii} —Sr1—O8	95.63 (18)	O7 ^{vii} —Cu2—O1 ^{iv}	133.4 (2)
O2—Sr1—O8	84.37 (18)	O5—Cu2—O1 ^{iv}	122.4 (2)
O2 ^{viii} —Sr1—O5 ⁱ	110.86 (16)	O2 ^{viii} —Cu2—O3 ^{iv}	92.24 (18)
O2—Sr1—O5 ⁱ	69.14 (16)	O4—P1—O2	121.1 (3)
O8—Sr1—O5 ⁱ	70.29 (18)	O4—P1—O3	110.1 (3)
O8 ^{viii} —Sr1—O5 ⁱ	109.71 (18)	O2—P1—O3	110.6 (3)
O3 ^{ix} —Cu1—O1 ^{iv}	87.7 (2)	O4—P1—O1	108.7 (3)
O3 ^{vii} —Cu1—O1 ^{iv}	92.3 (2)	O2—P1—O1	108.4 (3)
O6 ^v —Cu2—O2 ^{vii}	171.3 (2)	O3—P1—O1	106.8 (3)
O6 ^v —Cu2—O7 ^{vii}	89.2 (2)	O8—P2—O7	115.0 (3)
O2 ^{vii} —Cu2—O7 ^{vii}	94.8 (2)	O8—P2—O6	105.6 (3)
O6 ^v —Cu2—O5	98.2 (2)	O7—P2—O6	111.9 (3)
O2 ^{vii} —Cu2—O5	88.3 (2)	O8—P2—O5	110.3 (3)
O7 ^{vii} —Cu2—O5	104.2 (2)	O7—P2—O5	107.2 (3)
O6 ^v —Cu2—O1 ^{iv}	83.88 (19)	O6—P2—O5	106.5 (3)
O2 ^{vii} —Cu2—O1 ^{iv}	87.8 (2)		

Symmetry codes: (i) x, y + 1, z; (ii) x - ½, -y - ½, z - ½; (iii) -x + ½, y - ¾, -z - ½; (iv) -x, -y, -z; (v) -x + ½, y - ½, -z - ½; (vi) -x, -y - 1, -z; (vii) x, y - 1, z; (viii) -x + 1, -y + 1, -z; (ix) -x, -y + 1, -z.

Table 2

Unit-cell parameters of (I) (Å, °) and related compounds.

Compound	a	b	c	β	V (Å ³)
Sr ₃ Cu ₃ (PO ₄) ₄ †	9.2010 (1)	4.94104 (4)	17.8998 (3)	122.8952 (9)	683.3
Transformed cell‡	9.2010	4.94104	15.0380	91.98	683.3
Sr ₃ Cu ₃ (PO ₄) ₄ §	18.035 (4)	4.921 (2)	17.337 (4)	117.20 (1)	1368.5
Transformed cell¶	9.219	4.921	15.097	92.54	684.3
Sr _{2.88} Cu _{3.12} (PO ₄) ₄ ††	9.2077 (18)	4.9369 (10)	15.074 (3)	92.15 (3)	684.8 (2)

† Belik *et al.* (2002). ‡ Transformed unit cell 1: 100/010/101. § Effenberger (1999). ¶ Transformed unit cell 2: ½0½010/½0½. †† This work.

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