

The H-atom positional and displacement parameters were left unrefined. Final observed, calculated and difference profile plots are shown in Fig. 2.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry for Al₂(HPO₃)₃, and primary powder diffraction data, H-atom coordinates and complete geometry for Ga₂(HPO₃)₃ have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71664 (60 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CR1025]

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X-ray Rietveld Structure Refinement of Ca, Sr and Ba *meta*-Antimonates

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Abstract

The *meta*-antimonates, MSb₂O₆, M = Ca, Sr and Ba, have been prepared, and their crystal structures refined from powder X-ray diffraction data. The interatomic distances have been determined to reasonable accuracy and the preferred space group was found to be *P* $\bar{3}1m$, not the previously identified *P*312 (a subgroup of *P* $\bar{3}1m$). These and other isomorphous AB₂X₆ materials are now identified as belonging to the Li₂ZrF₆ (or better, PbSb₂O₆) structure type. Powder diffraction data in the JCPDS-PDF format are presented.

Comment

These isomorphous *meta*-antimonates have the ideal formula MSb₂O₆, where M = Ca, Sr or Ba. The Ca and Sr forms are thought to occur as intermediates, and sometimes as by-products, in the synthesis of calcium and strontium halophosphate phosphors activated by antimony. Of the three, only the calcium *meta*-antimonate crystal structure appears to have been studied in any detail; however, that was long ago (Magneli, 1941) and therefore not with modern structure-refinement methods. Our interest originated in a need to accurately account for second-phase calcium *meta*-antimonate contributions to the diffraction pattern of a high antimony content fluorapatite (DeBoer, Sakthivel, Cagle & Young, 1991).

In an admirable effort based on visually estimated intensities in powder photographs, Magneli (1941) studied 12 isomorphous antimonate and arsenate compounds, worked out a detailed structure for lead *meta*-antimonate and suggested atomic parameters for calcium *meta*-antimonate, which served well here

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as starting values. He suggested space group $P312$, but his structure fits the higher symmetry of $P\bar{3}1m$. Because of the improved methodology now available, an attempt has been made in this work to test these structures for distortions from $P\bar{3}1m$ that conform to each of the sub-groups, $P312$, $P31m$ and $P\bar{3}$, by performing least-squares refinements.

Space-group determination

Having had our attention drawn to the question of the correct space-group assignment, we attempted to test whether these materials have in fact a lower symmetry. Since one can prove only the absence of symmetry (its presence being demonstrable only to the accuracy of one's measurements), the failure (or equivocation) of tests for lower symmetries forces acceptance of the higher. We considered the higher space group and its three highest-order subgroups:

| | | | |
|---------------------------|----------------|----------------|------------|
| Group: | $P\bar{3}1m$ | | |
| Subgroups: | $P312$ | $P31m$ | $P\bar{3}$ |
| Symmetry elements broken: | $(\bar{1}, m)$ | $(\bar{1}, 2)$ | $(2, m)$ |

The $C2/m$ subgroup was not considered since the superposition of inequivalent diffraction peaks would make its demonstration even more difficult, a difficulty also found, to a lesser degree, in the lower Laue symmetry of $P\bar{3}$.

Rietveld refinements were carried out for all three substances in all four space groups. As expected, refinements in the three subgroups were difficult, as the minimization routine is operating very near to a singularity. Of the nine subgroup refinements, three met the stopping criterion (all shifts less than 0.3 of the corresponding e.s.d.) with the quantity minimized, R_{wp} , greater than or equal to the value obtained at convergence in $P\bar{3}1m$. Of the remainder, three had R_B values, corresponding to the atomic parameter-only variables, larger than in $P\bar{3}1m$, and one more showed a decrease smaller than that expected for the increased number of variables. The final two, despite nominally 'significant' decreases in agreement factors, gave atomic arrangements that were not significantly different from those of $P\bar{3}1m$ symmetry, once the correlation coefficients between atomic coordinates were taken into account. In addition, the deviations that were found could be a reflection of anisotropic thermal motions not modeled for lack of sufficient data to support the additional parameters. In short, none of the subgroup refinements produced creditable evidence for lower symmetry.

Tests for the absence of a center of symmetry by second-harmonic generation in a high-power laser beam, as described by Dougherty & Kurtz (1976), were negative for all three compounds. The sensitivity of this test argues strongly against the two

non-centrosymmetric space groups, $P312$ and $P31m$. Magneli (1941) reports that a Laue photograph of lead *meta*-antimonate showed $\bar{3}m$ symmetry. This argues against $P\bar{3}$, at least to the degree that one believes these materials are isomorphous, and to the extent of photographic accuracy of the intensities.

There are also chemical plausibility arguments against each of the subgroups. $P312$ requires inequivalent Sb^{5+} ions, half of them with (six equivalent) shorter Sb—O bonds and half with longer, but with all six Ba—O (or Ca—O, Sr—O) distances equivalent. $P31m$ requires either (or both of) the Sb^{5+} ions or the alkaline earth ions to be bonded unsymmetrically with respect to the polar direction. $P\bar{3}$ requires that the sheets of (SbO_6) octahedra be puckered, with the Sb^{5+} ions displaced alternately above and below the $z = \frac{1}{2}$ plane. None of these distortions is plausible if we recall that both Ba^{2+} (Ca^{2+} , Sr^{2+}) and Sb^{5+} have spherical filled-shell electronic configurations, s^2p^6 and d^{10} , respectively.

For the above reasons, we conclude that $P\bar{3}1m$ is the correct choice of space group, at least for our data. This is in agreement with recently published studies of the lead and cadmium *meta*-antimonates (Hill, 1987; Castro, Rasines, Sánchez-Martos & Garcia-Castro, 1988). The final refined parameters obtained in this space group are listed in Table 1. Plots of the observed, calculated and difference intensities are presented in Fig. 1.

The structure

Qualitatively, the structure of these materials is that determined by Magneli (1941) and shown in Fig. 2: infinite sheets of edge-sharing $(SbO_6)^{2-}$ octahedra alternating with layers of M^{2+} ions. Hill (1987) gives a good discussion of this structure, while Wells (1984) describes this and related structures containing hexagonally close-packed O-atom layers.

The network of edge-sharing SbO_6 octahedra is stretched in its own plane, relative to perfect octahedra and hexagonal close-packed O^{2-} ions. This can be seen in the deviations of the O-ion coordinates from $\frac{1}{3}, 0, \frac{1}{2} - [a/3(2^{1/2})c]$ and in the unequal O—O distances (Table 2). The weighted average Sb—O distance is 1.959 (3) Å, so the 'expected' octahedron edge (O—O distance) is $2^{1/2}$ times that, *i.e.* 2.770 (4) Å, but we find the shared edge to be from 2.50 (1) to 2.43 (2) Å and the in-plane edges to be 2.86 (1)–2.85 (1) Å. As the octahedra are stretched in the *ab* plane, so they are contracted in the *c* direction. For the interfacial distance parallel to *c*, we find values of 2.11 (1)–2.12 (1) Å, whereas a regular octahedron would give $(2/3^{1/2})$ times the Sb—O distance, *i.e.* 2.262 (4) Å. The triangular faces normal to *c* are also not perfectly staggered at 60° angles, but are found at $2\arctan[2(3^{1/2})(\frac{1}{2} - x)] = 47.5$ (3), 45.2 (5)

and 42.6 (5)° for the Ca, Sr and Ba cases, respectively. This distortion is seen clearly in Fig. 2. Since the additional distortion induced by progressing from Ca to Ba is small, we attribute most of the stretching to Sb—Sb repulsions. If we seek more nearly ideal versions of this structure with the smaller dipositive ions of Mg or Zn, we find that they adopt a different (trirutile) structure (see Wells, 1984) instead.

Isomorphous substances

Magneli (1941) also reported the *meta*-arsenates of Ca, Sr, Cd, Hg, Pb and Co as being isomorphous with the *meta*-antimonates in *P312* and analyzed intensity data for the Ca compound. Stefanidis, Nord & Kierkegaard (1985) reinvestigated CaAs₂O₆, using data to $2\theta = 86^\circ$ photometered from two Guinier photographs taken with Cu *K*α radiation. [The 1991 IUPAC notation is Cu *K* - *L*_{2,3} (see Jenkins, Manne, Robin & Sénémaud, 1991).] They explicitly

considered *P31m*, but rejected it in favor of *P312* on the grounds of implausible Ca—O and As—O distances. Since their reported agreement factors are equal in the two space groups and the only deviation from the higher group, the O-atom coordinate, differs from zero by only one half of its standard deviation, and As⁵⁺ is also a *d*¹⁰ ion, we respectfully disagree with their choice, preferring the hypothesis that some problem in their (limited 2θ range of) intensity data gives an O-atom position that produces the unlikely interatomic distances.

In addition to the *meta*-antimonates and *meta*-arsenates studied by Magneli, several other isomorphous materials have been identified in the Inorganic Crystal Structure Database (from the Fachinformationszentrum Karlsruhe, Germany) (Bergerhoff, Hundt, Sievers & Brown, 1983). These, and the references listed for them in the ICSD (but not inspected by us) are: Li₂ZrF₆ (Brunton, 1973); Li₂NbF₆ (de Bournonville, Bizot, Chassaing & Quarton, 1986); Li₂NbOF₅ (Galy, Andersson & Portier,

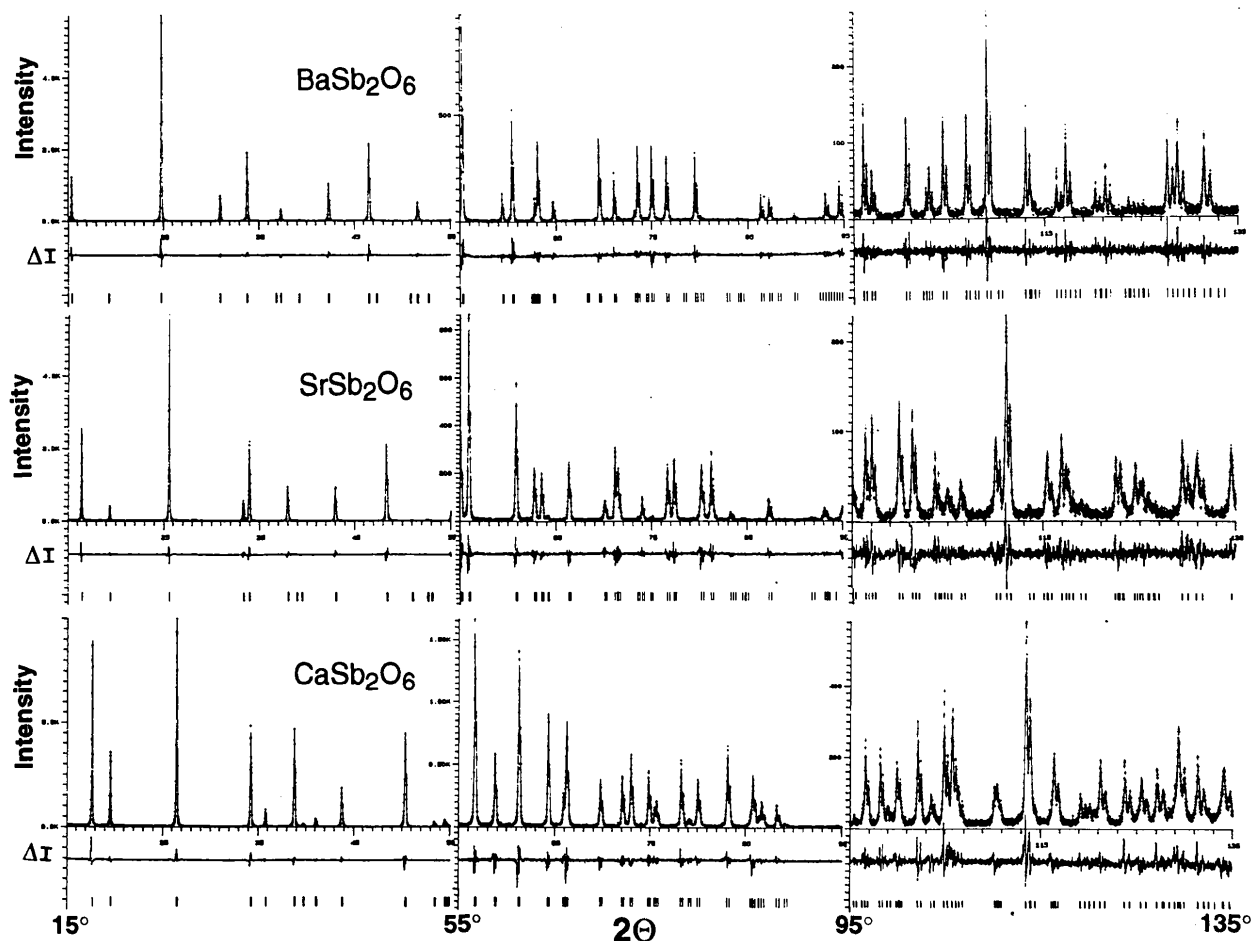


Fig. 1. Plots of the observed (points, marked +), calculated (overlying line) and difference (lower line, labeled ΔI) intensity data for the three compounds, in 40° segments. The short vertical line segments mark the positions of all Bragg peaks. The intensities are scaled to the maximum in each segment, which are: for BaSb₂O₆, 5755, 966 and 270 counts; for SrSb₂O₆, 5671, 861 and 228 counts; and for CaSb₂O₆, 9974, 1660 and 583 counts.

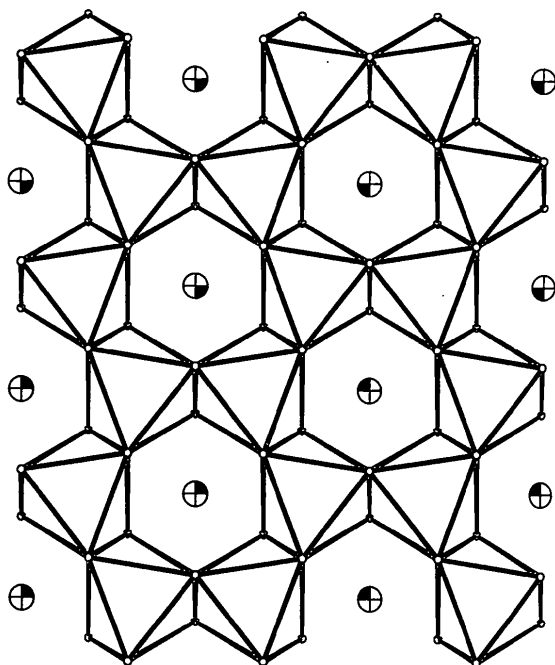


Fig. 2. The structure of BaSb_2O_6 projected down c . The Sb^{5+} atom occupying the center of each octahedron of O ions is not shown. The drawing was produced using ORTEPII (Johnson, 1976), but sphere radii are not related to the atomic displacement factors. Drawings of the Ca and Sr compounds would be virtually indistinguishable.

1969); UCr_2O_6 (Collomb, Gondrand, Lehmann, Capponi & Joubert, 1976); UV_2O_6 (Kovba, 1971); $\text{Li}_2\text{Pt}(\text{OH})_6$ and $\text{Na}_2\text{Pt}(\text{OH})_6$ (Troemel & Lupprich, 1975). [See also Wells (1984); Fig. 4.28 (f), p. 177, and also pp. 173–175 and 905.] That the *meta*-antimonates and *meta*-arsenates belong to the Li_2ZrF_6 structure type (Wells, 1984; Hyde & Andersson, 1989) seems to have been obscured by the previously misidentified space group. However, it would seem more appropriate to name this the PbSb_2O_6 structure type, since Magneli's publication predates Brunton's.

Experimental

The three refractory materials can be synthesized from the oxides or oxide precursors in high-temperature (*e.g.* 1273 K) solid-state reactions similar to those described by Butler, Bergin & Hannaford (1950). A somewhat different method was employed here. Calcium *meta*-antimonate, CaSb_2O_6 , was prepared by dissolving $\text{Ca}(\text{NO}_3)_2$ in a minimum amount of hot water in a $2 \times 2 \times 6$ inch fused silica boat, stirring in a 20–50% excess of Sb_2O_3 and drying this mud at about 378 K for a few hours. The concentrated calcium nitrate solution has also been prepared by treating CaCO_3 with concentrated nitric acid. All materials used were either ACS reagent grade or Sylvania luminescent grade (OSRAM SYLVANIA INC, Towanda, PA). The boat was fired in air in an electric furnace under a chemical fume hood. The temperature was kept at 773 K for the first hour, as the remaining

water and then NO_2 were evolved. [The presumed oxidation of Sb^{3+} to Sb^{5+} at this stage was the motive for choosing $\text{Ca}(\text{NO}_3)_2$ rather than the oxide or carbonate. We have since found that, at least for *ca* 5 g samples, air oxidation is sufficient.] The temperature was raised to 1273 K and held for 1 h, then raised to 1473 K, the furnace door set slightly ajar and the white 'smoke' of Sb_2O_4 watched. When the amount of smoke noticeably decreased (10–45 min), the boat was removed from the furnace. If the boat is removed too early, excess Sb_2O_4 (cervantite) is found in the product, while leaving it too long gives an admixture of the *pyro*-antimonate, $\text{Ca}_2\text{Sb}_2\text{O}_7$. The silica boat almost invariably cracks as it cools, presumably due to the formation of an Sb_2O_3 - SiO_2 glass on its interior surface. An identical method was used for the Sr and Ba compounds, but dry mixing the pulverized hydrated nitrates with Sb_2O_3 was more convenient, as these salts are more difficult to dry before firing.

CaSb_2O_6

Crystal data

$M_r = 379.58$

Trigonal

$P\bar{3}1m$

$a = 5.2405(4) \text{ \AA}$

$c = 5.0221(4) \text{ \AA}$

$V = 119.45(2) \text{ \AA}^3$

$Z = 1$

$D_x = 5.28 \text{ Mg m}^{-3}$

Cu $K\alpha_{1,2}$ radiation

$\lambda = 1.54056, 1.54439 \text{ \AA}$

$\theta = 7.5\text{--}67.5^\circ$

$\mu = 102 \text{ mm}^{-1}$

$T = 294 \text{ K}$

Powder

Colorless

Data collection

Siemens θ - 2θ diffractometer $\theta_{\text{max}} = 67.5^\circ$

Refinement

$R_B = 0.0444$

$R_{\text{wp}} = 0.170$

$S_{\text{wp}} = 1.78$

18 (3 background) parameters

$(\Delta/\sigma)_{\text{max}} = 0.3$

SrSb_2O_6

Crystal data

$M_r = 427.12$

Trigonal

$P\bar{3}1m$

$a = 5.2724(4) \text{ \AA}$

$c = 5.3659(4) \text{ \AA}$

$V = 129.18(2) \text{ \AA}^3$

$Z = 1$

$D_x = 5.49 \text{ Mg m}^{-3}$

Cu $K\alpha_{1,2}$ radiation

$\lambda = 1.54056, 1.54439 \text{ \AA}$

$\theta = 7.5\text{--}67.5^\circ$

$\mu = 100 \text{ mm}^{-1}$

$T = 294 \text{ K}$

Powder

Colorless

Data collection

Siemens θ - 2θ diffractometer $\theta_{\text{max}} = 67.5^\circ$

Refinement

$R_B = 0.0453$

$R_{\text{wp}} = 0.211$

$S_{\text{wp}} = 1.37$

19 (4 background) parameters

$(\Delta/\sigma)_{\text{max}} = 0.3$

BaSb_2O_6

Crystal data

$M_r = 476.84$

Trigonal

$P\bar{3}1m$

Cu $K\alpha_{1,2}$ radiation

$\lambda = 1.54056, 1.54439 \text{ \AA}$

$\theta = 7.5\text{--}67.5^\circ$

$a = 5.3036 (4) \text{ \AA}$
 $c = 5.7602 (4) \text{ \AA}$
 $V = 140.32 (2) \text{ \AA}^3$
 $Z = 1$
 $D_x = 5.64 \text{ Mg m}^{-3}$

$\mu = 133 \text{ mm}^{-1}$
 $T = 294 \text{ K}$
 Powder
 Colorless

Data collection

Siemens θ - 2θ diffractometer $\theta_{\max} = 67.5^\circ$

Refinement

$R_B = 0.0501$ 18 (3 background) parameters
 $R_{wp} = 0.229$ $(\Delta/\sigma)_{\max} = 0.3$
 $S_{wp} = 1.36$

Table 1. Fractional atomic coordinates and isotropic displacement parameters (\AA^2) for CaSb₂O₆, SrSb₂O₆ and BaSb₂O₆

| Ca, Sr and Ba in Wyckoff 1(a) ($\bar{3}m$), Sb in 2(d) (32), O in 6(k) (m). | | | | |
|---|-------------|-----|-------------|------------------|
| | x | y | z | B_{iso} |
| CaSb₂O₆ | | | | |
| Ca | 0 | 0 | 0 | 0.44 (4) |
| Sb | 1/3 | 2/3 | 1/2 | 0.316 (18) |
| O | 0.3730 (9) | 0 | 0.2899 (9) | 1.67 (18) |
| SrSb₂O₆ | | | | |
| Sr | 0 | 0 | 0 | 0.59 (4) |
| Sb | 1/3 | 2/3 | 1/2 | 0.349 (22) |
| O | 0.3798 (14) | 0 | 0.3035 (11) | 1.28 (23) |
| BaSb₂O₆ | | | | |
| Ba | 0 | 0 | 0 | 0.52 (4) |
| Sb | 1/3 | 2/3 | 1/2 | 0.311 (29) |
| O | 0.3875 (19) | 0 | 0.3159 (15) | 0.87 (27) |

Table 2. Selected geometric parameters (\AA) for CaSb₂O₆, SrSb₂O₆ and BaSb₂O₆

| | | | |
|--------------------------------------|------------|-----|------------|
| CaSb₂O₆ | | | |
| Ca—O | 2.437 (5) | O—O | 2.863 (5) |
| Sb—O | 1.961 (5) | O—O | 2.876 (10) |
| O—O | 2.495 (10) | | |
| SrSb₂O₆ | | | |
| Sr—O | 2.581 (7) | O—O | 2.855 (7) |
| Sb—O | 1.957 (7) | O—O | 2.908 (12) |
| O—O | 2.460 (12) | | |
| BaSb₂O₆ | | | |
| Ba—O | 2.745 (10) | O—O | 2.846 (10) |
| Sb—O | 1.956 (10) | O—O | 2.953 (18) |
| O—O | 2.433 (18) | | |

Cell parameters are from the Rietveld refinements. Standard deviations of the unit-cell dimensions resulting from the refinements are unrealistically small (0.00005 \AA) (Hill & Madsen, 1986). Values given above are estimates set equal to one scan step (0.02°) at the highest diffraction angle.

Powder X-ray diffraction data were collected by step scanning on a locally modified horizontal Siemens θ - 2θ diffractometer equipped with a fine-focus copper X-ray tube operated at 50 kV and 20 mA and a curved graphite diffracted-beam monochromator set for the Cu $K\alpha$ (Cu $K-L_{2,3}$) doublet. Soller slits were used in both incident and diffracted beams. Packed samples of the crushed and sieved powders (46 μm mesh) were rotated about an oscillating axis (perpendicular to the sample surface) as the data were taken to average contributions from a larger number of crystallites. Data were taken in steps of 0.02° from 15 to

135° 2θ (6001 values) with counting times of 30 s for the Ca meta-antimonate and 10 s for the Sr and Ba compounds. This scan range encompassed 66, 69 and 74 Bragg peaks for the Ca, Sr and Ba compounds, respectively. For all three, $h_{\max} = 5$ and $l_{\max} = 6$.

Crystal structure refinements were carried out with the Rietveld whole-pattern-fitting structure-refinement method (Rietveld, 1969; Wiles & Young, 1981) using computer programs *DBW3.2S* and *DBWS-9006PC*, both of which are upgraded versions of the program described by Wiles & Young (1981). Individual isotropic displacement factors of all atoms and the site occupancy of O were allowed to vary. Scattering factors, including the real and imaginary parts of anomalous dispersion, were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Observations were weighted by counting statistics only. Backgrounds were modeled as polynomials in $(2\theta - 10)^\circ$. For the final agreement factors, $R_B = \sum_k |I_k(\text{obs}) - I_k(\text{calc})| / \sum_k I_k(\text{obs})$, $R_{wp} = (\sum_i \{ [y_i(\text{obs}) - y_i(\text{calc})] / \sigma [y_i(\text{obs})] \}^2 / \sum_i \{ y_i(\text{obs}) / \sigma [y_i(\text{obs})] \}^2)^{1/2}$, $S_{wp} = R_{wp} / R_{ex}$, where $R_{ex} = ([(\sum_i 1) - p] / \sum_i \{ y_i(\text{obs}) / \sigma [y_i(\text{obs})] \}^2)^{1/2}$ and $DW_{wd} = \sum_i \{ \{ y_i(\text{obs}) / \sigma [y_i(\text{obs})] \}^2 - \{ y_{i-1}(\text{obs}) / \sigma [y_{i-1}(\text{obs})] \}^2 \} / \sum_i \{ y_i(\text{obs}) / \sigma [y_i(\text{obs})] \}^2$ is the weighted Durbin-Watson statistic, values of which were 0.75 (Ca), 1.24 (Sr) and 1.22 (Ba). The symbols $y_i(\text{obs})$ and $y_i(\text{calc})$ are the observed and calculated intensities at the i th 2θ step, p is the number of parameters varied, and $I_k(\text{obs})$ and $I_k(\text{calc})$ are the observed and calculated peak areas under the k th diffraction peak.

PDF-format data: Powder diffraction data imitating the d and I format of the Joint Committee on Powder Diffraction Standards (JCPDS) Powder Diffraction File (PDF) are listed in Tables 3, 4 and 5. The I values given are scaled from the integrated, not peak, observed intensities (I_{obs} values of *DBW3.2*) summed over α_1 and α_2 ($K-L_2$ and $K-L_3$) components, and the lists have been truncated at 90° 2θ . These data differ from the current PDF entries: very substantially for the Sr compound (card No. 11-45), mostly in the relative intensities for the Ca compound (card No. 26-294), and slightly, except for the position of the 213 line, for the Ba compound (card No. 9-26).

Preparation of the tables was assisted by *DISPOW* and *DISANG*, and an interactive version of *ORTEPII* (Johnson, 1976) produced Fig. 2; all three are contained in the *NRCVAX* package (Gabe, Lee & Le Page, 1985; White, Gabe & Le Page, 1991).

Table 3. Powder pattern for CaSb₂O₆

| d space | $I(\text{int})$ | hkl | $2\theta(\text{Cu } K-L_2) (^\circ)$ |
|-----------|-----------------|--------------------|--------------------------------------|
| 5.022 | 77 | 001 | 17.65 |
| 4.538 | 30 | 100 | 19.54 |
| 3.367 | 100 | 101 | 26.45 |
| 2.620 | 50 | 110 | 34.19 |
| 2.511 | 9 | 002 | 35.73 |
| 2.323 | 53 | 111, 2 $\bar{1}$ 1 | 38.73 |
| 2.269 | 1 | 200 | 39.69 |
| 2.197 | 4 | 102 | 41.05 |
| 2.068 | 23 | 201 | 43.74 |
| 1.813 | 64 | 112, 2 $\bar{1}$ 2 | 50.29 |
| 1.715 | 3 | 210 | 53.37 |
| 1.684 | 5 | 202 | 54.46 |
| 1.674 | 2 | 003 | 54.80 |
| 1.623 | 23 | 211, 3 $\bar{1}$ 1 | 56.66 |
| 1.571 | 9 | 103 | 58.74 |
| 1.513 | 20 | 300 | 61.22 |
| 1.449 | 14 | 301 | 64.26 |
| 1.416 | 5 | 212, 3 $\bar{1}$ 2 | 65.89 |
| 1.411 | 13 | 113, 2 $\bar{1}$ 3 | 66.19 |

| | | | | | | | |
|-------|----|----------------------|-------|-------|----|----------------------|-------|
| 1.347 | 7 | 2 0 3 | 69.76 | 1.288 | 10 | 2 1 3, 3 $\bar{1}$ 3 | 73.48 |
| 1.310 | 7 | 2 2 0 | 72.03 | 1.265 | 10 | 1 1 4, 2 $\bar{1}$ 4 | 74.99 |
| 1.296 | 11 | 3 0 2 | 72.95 | 1.244 | 9 | 3 1 1, 4 $\bar{1}$ 1 | 76.53 |
| 1.268 | 8 | 2 2 1, 4 $\bar{2}$ 1 | 74.84 | 1.204 | 8 | 2 2 2, 4 $\bar{2}$ 2 | 79.52 |
| 1.259 | 2 | 3 1 0 | 75.47 | 1.197 | <1 | 3 0 3 | 80.11 |
| 1.256 | 9 | 0 0 4 | 75.69 | 1.126 | 3 | 4 0 1 | 86.32 |
| 1.221 | 9 | 3 1 1, 4 $\bar{1}$ 1 | 78.24 | 1.117 | 3 | 1 0 5 | 87.16 |
| 1.210 | 1 | 1 0 4 | 79.08 | 1.091 | 1 | 2 2 3, 4 $\bar{2}$ 3 | 89.83 |
| 1.198 | 8 | 2 1 3, 3 $\bar{1}$ 3 | 80.03 | | | | |
| 1.162 | 13 | 2 2 2, 4 $\bar{2}$ 2 | 83.09 | | | | |
| 1.135 | 1 | 4 0 0 | 85.52 | | | | |
| 1.132 | 8 | 1 1 4, 2 $\bar{1}$ 4 | 85.74 | | | | |
| 1.125 | 1 | 3 1 2, 4 $\bar{1}$ 2 | 86.40 | | | | |
| 1.122 | 4 | 3 0 3 | 86.68 | | | | |
| 1.107 | 3 | 4 0 1 | 88.22 | | | | |
| 1.099 | <1 | 2 0 4 | 89.05 | | | | |

Table 4. Powder pattern for SrSb₂O₆

| d space | l(int) | h k l | 2θ(Cu K-L ₂) (°) |
|---------|--------|----------------------|------------------------------|
| 5.366 | 39 | 0 0 1 | 16.51 |
| 4.566 | 6 | 1 0 0 | 19.43 |
| 3.477 | 100 | 1 0 1 | 25.60 |
| 2.683 | 12 | 0 0 2 | 33.37 |
| 2.636 | 41 | 1 1 0 | 33.98 |
| 2.366 | 20 | 1 1 1, 2 $\bar{1}$ 1 | 38.00 |
| 2.313 | 1 | 1 0 2 | 38.90 |
| 2.101 | 22 | 2 0 1 | 43.02 |
| 1.880 | 53 | 1 1 2, 2 $\bar{1}$ 2 | 48.37 |
| 1.789 | 1 | 0 0 3 | 51.02 |
| 1.739 | 1 | 2 0 2 | 52.60 |
| 1.726 | 1 | 2 1 0 | 53.02 |
| 1.665 | 11 | 1 0 3 | 55.10 |
| 1.643 | 22 | 2 1 1, 3 $\bar{1}$ 1 | 55.92 |
| 1.522 | 15 | 3 0 0 | 60.81 |
| 1.480 | 7 | 1 1 3, 2 $\bar{1}$ 3 | 62.73 |
| 1.464 | 6 | 3 0 1 | 63.48 |
| 1.451 | 1 | 2 1 2, 3 $\bar{1}$ 2 | 64.11 |
| 1.408 | 8 | 2 0 3 | 66.34 |
| 1.341 | 3 | 0 0 4 | 70.09 |
| 1.324 | 10 | 3 0 2 | 71.17 |
| 1.318 | 6 | 2 2 0 | 71.53 |
| 1.287 | <1 | 1 0 4 | 73.53 |
| 1.280 | 3 | 2 2 1, 4 $\bar{2}$ 1 | 74.00 |
| 1.266 | 1 | 3 1 0 | 74.93 |
| 1.242 | 8 | 2 1 3, 3 $\bar{1}$ 3 | 76.67 |
| 1.233 | 9 | 3 1 1, 4 $\bar{1}$ 1 | 77.36 |
| 1.196 | 9 | 1 1 4, 2 $\bar{1}$ 4 | 80.23 |
| 1.183 | 10 | 2 2 2, 4 $\bar{2}$ 2 | 81.26 |
| 1.159 | 1 | 3 0 3 | 83.30 |
| 1.145 | <1 | 3 1 2, 4 $\bar{1}$ 2 | 84.54 |
| 1.142 | <1 | 4 0 0 | 84.88 |
| 1.117 | 3 | 4 0 1 | 87.25 |

Table 5. Powder pattern for BaSb₂O₆

| d space | l(int) | h k l | 2θ(Cu K-L ₂) (°) |
|---------|--------|----------------------|------------------------------|
| 5.760 | 19 | 0 0 1 | 15.37 |
| 4.593 | <1 | 1 0 0 | 19.31 |
| 3.591 | 100 | 1 0 1 | 24.77 |
| 2.880 | 13 | 0 0 2 | 31.03 |
| 2.652 | 35 | 1 1 0 | 33.77 |
| 2.440 | <1 | 1 0 2 | 36.81 |
| 2.409 | 6 | 1 1 1, 2 $\bar{1}$ 1 | 37.30 |
| 2.296 | <1 | 2 0 0 | 39.20 |
| 2.133 | 21 | 2 0 1 | 42.34 |
| 1.951 | 47 | 1 1 2, 2 $\bar{1}$ 2 | 46.52 |
| 1.795 | <1 | 2 0 2 | 50.82 |
| 1.771 | 12 | 1 0 3 | 51.55 |
| 1.662 | 21 | 2 1 1, 3 $\bar{1}$ 1 | 55.22 |
| 1.555 | 3 | 1 1 3, 2 $\bar{1}$ 3 | 59.38 |
| 1.531 | 11 | 3 0 0 | 60.42 |
| 1.480 | 2 | 3 0 1 | 62.75 |
| 1.473 | 9 | 2 0 3 | 63.06 |
| 1.440 | 3 | 0 0 4 | 64.68 |
| 1.352 | 10 | 3 0 2 | 69.48 |
| 1.326 | 5 | 2 2 0 | 71.04 |
| 1.292 | 1 | 2 2 1, 4 $\bar{2}$ 1 | 73.19 |

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Lists of raw X-ray powder diffraction data have been deposited with the Joint Committee on Powder Diffraction Standards, International Center for Diffraction Data, Swarthmore, USA, as well as with the British Library Document Supply Centre as Supplementary Publication No. SUP 71561 (49pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: ST1071]

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β -Dicobalt Pyrophosphate

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Abstract

A new high-temperature or β form of dicobalt diphosphate, Co₂P₂O₇, has been isolated in space group *A2/m* (non-standard setting of *C2/m*). As in other high-temperature forms of transition-metal pyrophosphates, metal atoms lie on planes in a two-dimensional hexagonal array [Co—Co distances 3.461 (4) and 3.284 (3) Å] with adjacent metal atoms linked by two O-atom bridges. Co atoms are octahedrally coordinated with axial distortions [average Co—O_{eq} 2.14 (1), Co—O_{ax} 2.32 (1) Å]. The pyrophosphate groups lie along planes between metallic layers.

Comment

β -Co₂P₂O₇ is typical of β or high-temperature transition-metal structures [Cu, Ni, Zn; observed in space group *C2/m* (Robertson & Calvo, 1968; Pietraszko & Łukasiewicz, 1968; Calvo, 1968)] showing layers of metal atoms interspersed with layers of P₂O₇ groups; the metal atoms show a hexagonal disposition on the planes. Adjacent metal atoms of the hexagonal array are linked by two single-O-atom bridges and show two different intermetallic separations. Axial distortions of the octahedrally coordinated metal atoms are evident in *M*—O bond lengths. Co atoms bridged by equatorial O atoms are separated by a distance of 3.284 (3) Å, whereas those bridges involving axial O atoms result in a Co··Co separation of 3.461 (4) Å (Fig. 1). Structural rearrangement on transi-

tion from the α or low-temperature form to the β form involves a minor increase in density and is most evident from observation of the hexagonal motif of the metallic plane. α -Co₂P₂O₇ [space group *B2₁/c*, non-standard setting of *P2₁/c*, reported by Krishnamachari & Calvo (1972), or space group *P2₁/c*, from neutron data, reported by Forsyth, Wilkinson, Paster & Wanklyn (1989)] shows a disruption of this regular hexagon with one Co··Co distance of 4.228 (4) Å and no bridging atoms across this distance (Fig. 2a). The unbridged Co atoms are five-coordinate (square-pyramidal geometry) with a distance of 3.409 (4) Å to a sixth (would-be bridging) O atom. The

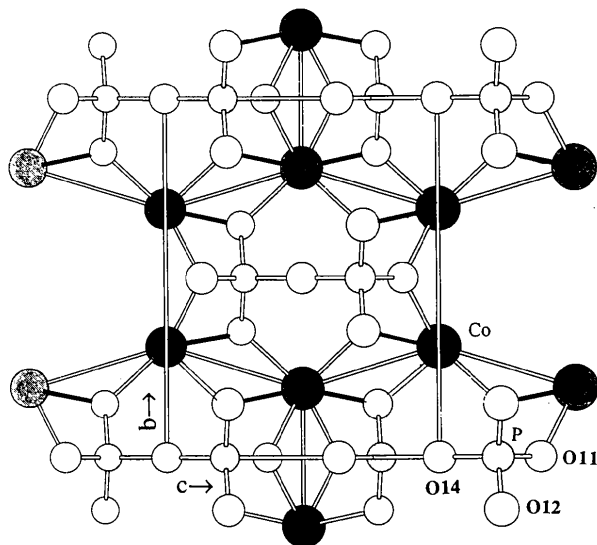


Fig. 1. Projection view of β -Co₂P₂O₇. Elongated axial Co—O distances are shown in black, Co atoms have dark shading, P atoms have light shading and O atoms are unshaded.

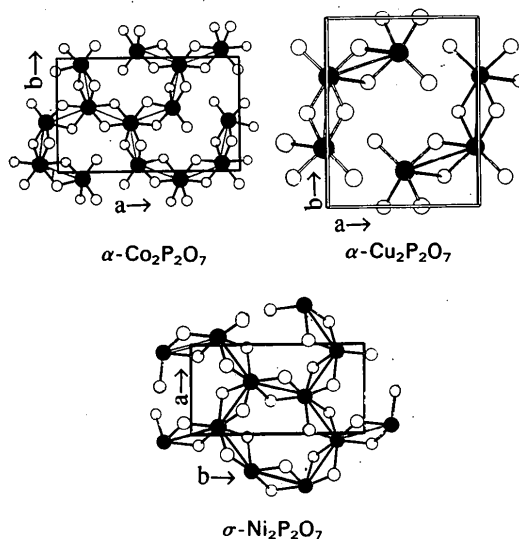


Fig. 2. Projection views of α -Co₂P₂O₇ (α -Ni₂P₂O₇ is isostructural), α -Cu₂P₂O₇ (with elongated axial Cu—O distances shown in black) and σ -Ni₂P₂O₇. In all three projections the P atoms have been omitted for clarity.