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## Key indicators

Single-crystal X-ray study  
 $T = 295\text{ K}$   
Mean  $\sigma(\text{P-O}) = 0.004\text{ \AA}$   
 $R$  factor = 0.026  
 $wR$  factor = 0.064  
Data-to-parameter ratio = 16.3For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>. $\text{Ca}_{10}\text{K}(\text{PO}_4)_7$  from single-crystal data

Crystals of decacalcium potassium heptakis(orthophosphate),  $\text{Ca}_{10}\text{K}(\text{PO}_4)_7$ , were obtained from a melt. The structure of  $\text{Ca}_{10}\text{K}(\text{PO}_4)_7$  is isostructural with  $\beta\text{-Ca}_3(\text{PO}_4)_2$  and has been determined previously [Morozov, Presnyakov, Belik, Khasanov & Lazoryak (2000). *Crystallogr. Rep.* **45**, 19–26]. The present investigation confirms the previous study, but with higher precision and with all displacement parameters refined anisotropically. The structure contains four Ca, one K, three P and ten unique O atoms, of which the K, one Ca, one P and one O atom are located on threefold rotation axes.

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## Comment

The structure determination of phases in the  $\text{CaO-K}_2\text{O-P}_2\text{O}_5$  system is part of an extensive study of the structural and thermodynamic characteristics of these compounds. Crystal structures already determined during this study are  $\text{CaK}_2\text{P}_2\text{O}_7$  (Sandström *et al.*, 2003) and  $\text{CaKP}_3\text{O}_9$  (Sandström & Boström, 2004). We report here the crystal structure of  $\text{Ca}_{10}\text{K}(\text{PO}_4)_7$ , which is isostructural with  $\beta\text{-Ca}_3(\text{PO}_4)_2$  (Dickens *et al.*, 1974). The structure of  $\text{Ca}_{10}\text{K}(\text{PO}_4)_7$  has previously been reported by Morozov *et al.* (2000), who refined the structure from X-ray powder diffraction data using the coordinates of  $\beta\text{-Ca}_3(\text{PO}_4)_2$  as starting parameters for the Rietveld refinement.

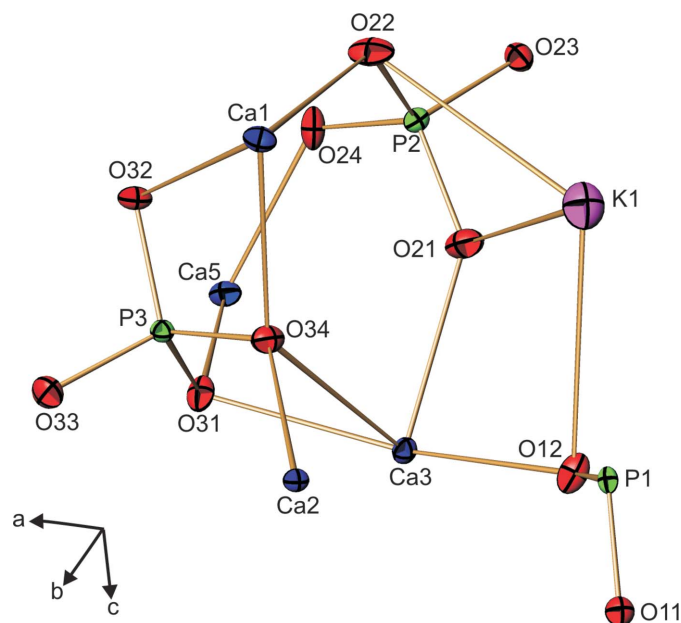
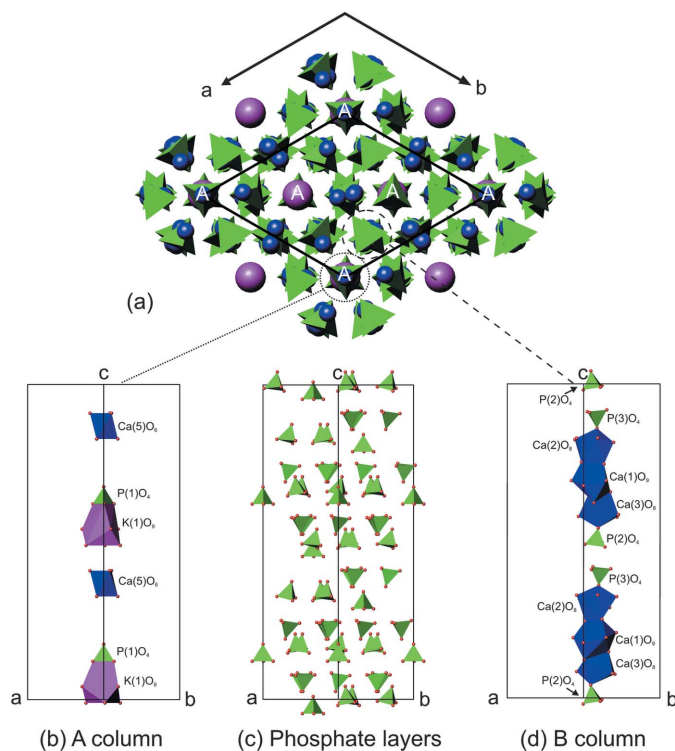


Figure 1

A view of the asymmetric unit of  $\text{Ca}_{10}\text{K}(\text{PO}_4)_7$ , shown with anisotropic displacement ellipsoids drawn at the 50% probability level.


**Figure 2**

(a) A projection of the crystal structure of  $\text{Ca}_{10}\text{K}(\text{PO}_4)_7$  along the  $c$  axis, depicting the  $A$  and  $B$  columns. (b) The polyhedra for  $\text{Ca}_5\text{O}_6$  and  $\text{K}_1\text{O}_9$ , together with  $\text{P}_1\text{O}_4$  in the  $A$  column. (c) The phosphate layers. (d) The polyhedra for  $\text{Ca}_1$ – $\text{Ca}_3$ , together with  $\text{P}_2\text{O}_4$  and  $\text{P}_3\text{O}_4$ .

$\beta\text{-Ca}_3(\text{PO}_4)_2$  allows for iso- and heterovalent substitutions of  $\text{Ca}^{2+}$  by  $M^+$  ( $M = \text{Li}, \text{K}$  and  $\text{Na}$ ) (Morozov *et al.*, 1997, 2000; Belik *et al.*, 1999; Belik, Gutan *et al.*, 2001),  $M^{2+}$  ( $M = \text{Mg}, \text{Mn}, \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}, \text{Ga}, \text{Sr}$  and  $\text{Cd}$ ) (Schroeder *et al.*, 1977; Bigi *et al.*, 1996; Belik *et al.*, 1998; Khan *et al.*, 1997; Belik, Gutan *et al.*, 2001; Jakeman *et al.*, 1989; Nord, 1983; Morozov *et al.*, 1997, 2000; Belik, Yanov & Lazoryak, 2001; Belik *et al.*, 1999; Gopal *et al.*, 1974; Kostiner & Rea, 1976),  $M^{3+}$  ( $M = \text{Sc}, \text{Cr}, \text{Fe}, \text{Ga}, \text{In}$  and rare-earth metals) (Lazoryak *et al.*, 1996; Golubev *et al.*, 1990; Golubev & Lazoryak, 1991) and  $\text{Ce}^{4+}$  cations (Kotov *et al.*, 1997). In the structure of  $\beta\text{-Ca}_3(\text{PO}_4)_3$ , rare-earth cations should occupy the  $M1$ – $M3$  sites (general sites), cations that have a radius smaller than  $0.8 \text{ \AA}$  should occupy the octahedral  $M5$  site, and cations with a radius of  $\sim 1.5 \text{ \AA}$  may occupy the  $M4$  site (Lazoryak, 1996). Thus, the title compound presumably represents one end-member of a solid solution series. Lazoryak (1996) also reported a number of compounds including not only phosphates but also vanadates (Gopal & Calvo, 1973; Evans *et al.*, 2001; Belik *et al.*, 2000), arsenates (Gopal & Calvo, 1971) and a few silicates (Moore & Shen, 1983) as being structurally related to  $\beta\text{-Ca}_3(\text{PO}_4)_2$ .

The asymmetric unit of  $\text{Ca}_{10}\text{K}(\text{PO}_4)_7$  is displayed in Fig. 1. The crystal structure is built up by double layers of orthophosphate groups. Parallel to the  $c$  axis, two different columns can be identified. The  $A$  column runs along the threefold rotation axis (Wyckoff letter 6a), through the  $\text{Ca}1$ ,  $\text{Ca}5$  and  $\text{P}1$  polyhedra. The  $B$  column is parallel to the  $A$  column and runs through the  $\text{P}2$ ,  $\text{P}3$ ,  $\text{Ca}1$  and  $\text{Ca}2$  polyhedra (Fig. 2). The three

$\text{Ca}$  ions,  $\text{Ca}1$ – $\text{Ca}3$ , are situated between the phosphate layers, while  $\text{Ca}5$  and the  $\text{K}^+$  ion are situated within the phosphate layers. The  $\text{K}^+$  ion occupies a position equivalent to the  $\text{Ca}4$  site in the  $\beta\text{-Ca}_3(\text{PO}_4)_2$  structure, slightly above the plane formed by three  $\text{O}21$  atoms.  $\text{K}^+$  is coordinated by nine  $\text{O}$  atoms,  $[\text{KO}12_3\text{O}21_3\text{O}22_3]$ , with distances ranging from  $2.641$  (3) to  $3.250$  (4)  $\text{ \AA}$  (Table 1). The  $\text{Ca}$  ions show different coordination numbers (CN).  $\text{Ca}1$  is nine-coordinate,  $\text{Ca}2$  and  $\text{Ca}3$  have  $\text{CN} = 8$ , whereas  $\text{Ca}5$  has a distorted octahedral coordination ( $\text{CN} = 6$ ). The  $\text{Ca}$ – $\text{O}$  distances of  $\text{Ca}1$ ,  $\text{Ca}2$  and  $\text{Ca}3$  do vary, but are within the range of previously reported  $\text{Ca}$ – $\text{O}$  bond lengths (*International Tables for X-ray Crystallography*, 1962). The octahedrally coordinated  $\text{Ca}$  exhibits  $\text{Ca}$ – $\text{O}$  distances between  $2.239$  (4) and  $2.267$  (4)  $\text{ \AA}$ , the eightfold-coordinate  $\text{Ca}2$  and  $\text{Ca}3$  have  $\text{Ca}$ – $\text{O}$  distances between  $2.329$  (3) and  $2.986$  (4)  $\text{ \AA}$ , and  $\text{Ca}1$  shows  $\text{Ca}$ – $\text{O}$  distances between  $2.393$  (3) and  $2.999$  (4)  $\text{ \AA}$ . The orthophosphate tetrahedra are quite regular, with  $\text{P}$ – $\text{O}$  distances between  $1.524$  (5) and  $1.546$  (3)  $\text{ \AA}$  (Table 1).

## Experimental

Crystals of  $\text{Ca}_{10}\text{K}(\text{PO}_4)_7$  were obtained from a synthesis originally intended to yield a compound with composition  $\text{CaKPO}_4$ . The starting mixture consisted of  $\text{CaCO}_3$  (Riedel-de-Haën, 98%) and  $\text{KH}_2\text{PO}_4$  (Merck, p.a.) in a 2:1 molar ratio. This mixture was placed in an alumina crucible and kept at  $1323 \text{ K}$  for about one month. Probably due to vaporization of potassium and some phosphorus, the composition of the melt shifted in the direction towards the title compound. X-ray powder diffraction data were collected afterwards on the synthesis batch. The material was found to be mainly amorphous. A Rietveld refinement was carried out using the present model as a start, but only cell parameters were refined. No significant shift compared with the single-crystal model was observed.

### Crystal data

$\text{Ca}_{10}\text{K}(\text{PO}_4)_7$   
 $M_r = 1104.69$   
 Trigonal,  $R3c$   
 $a = 10.4630$  (4)  $\text{ \AA}$   
 $c = 37.241$  (1)  $\text{ \AA}$   
 $V = 3530.7$  (2)  $\text{ \AA}^3$   
 $Z = 6$

$D_x = 3.117 \text{ Mg m}^{-3}$   
 Mo  $K\alpha$  radiation  
 $\mu = 3.01 \text{ mm}^{-1}$   
 $T = 295$  (2)  $\text{ K}$   
 Fragment, colourless  
 $0.24 \times 0.13 \times 0.07 \text{ mm}$

### Data collection

Nonius KappaCCD area-detector diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan (SORTAV; Blessing, 1995)  
 $T_{\min} = 0.681$ ,  $T_{\max} = 0.814$

30685 measured reflections  
 2300 independent reflections  
 2257 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.072$   
 $\theta_{\max} = 30.0^\circ$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.026$   
 $wR(F^2) = 0.064$   
 $S = 1.09$   
 2300 reflections  
 141 parameters  
 $w = 1/[\sigma^2(F_o^2) + (0.0247P)^2 + 16.2214P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.70 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -0.72 \text{ e \AA}^{-3}$   
 Extinction correction: SHELXL97 (Sheldrick, 1997)  
 Extinction coefficient:  $0.00067$  (5)  
 Absolute structure: Flack (1983), with 1145 Friedel Pairs  
 Flack parameter:  $0.41$  (4)

Table 1

Selected bond lengths (Å).

|                        |             |                         |           |
|------------------------|-------------|-------------------------|-----------|
| Ca1—O23 <sup>i</sup>   | 2.393 (3)   | Ca3—O21                 | 2.405 (3) |
| Ca1—O34                | 2.396 (3)   | Ca3—O31 <sup>vii</sup>  | 2.435 (3) |
| Ca1—O11 <sup>ii</sup>  | 2.4914 (16) | Ca3—O22 <sup>viii</sup> | 2.440 (3) |
| Ca1—O32 <sup>iii</sup> | 2.535 (3)   | Ca3—O34                 | 2.731 (3) |
| Ca1—O33 <sup>iii</sup> | 2.558 (3)   | Ca3—O33 <sup>vii</sup>  | 2.762 (3) |
| Ca1—O32                | 2.582 (3)   | Ca5—O24                 | 2.239 (4) |
| Ca1—O22                | 2.597 (3)   | Ca5—O31                 | 2.267 (4) |
| Ca1—O21 <sup>i</sup>   | 2.713 (3)   | K1—O21                  | 2.641 (3) |
| Ca1—O12 <sup>iv</sup>  | 2.999 (4)   | K1—O12                  | 3.054 (4) |
| Ca2—O33 <sup>iii</sup> | 2.329 (3)   | K1—O22                  | 3.250 (4) |
| Ca2—O32 <sup>v</sup>   | 2.399 (3)   | P1—O11                  | 1.524 (5) |
| Ca2—O34                | 2.413 (3)   | P1—O12                  | 1.545 (3) |
| Ca2—O24 <sup>v</sup>   | 2.425 (3)   | P2—O21                  | 1.533 (3) |
| Ca2—O24 <sup>vi</sup>  | 2.457 (3)   | P2—O22                  | 1.531 (3) |
| Ca2—O12 <sup>i</sup>   | 2.473 (3)   | P2—O23                  | 1.546 (3) |
| Ca2—O23 <sup>vi</sup>  | 2.522 (3)   | P2—O24                  | 1.545 (3) |
| Ca2—O22 <sup>v</sup>   | 2.986 (4)   | P3—O31                  | 1.538 (3) |
| Ca3—O23 <sup>vi</sup>  | 2.361 (3)   | P3—O32                  | 1.531 (3) |
| Ca3—O12                | 2.390 (3)   | P3—O33                  | 1.530 (3) |
| Ca3—O31                | 2.393 (3)   | P3—O34                  | 1.536 (3) |

Symmetry codes: (i)  $-x + y, -x, z$ ; (ii)  $-x + y + \frac{2}{3}, y + \frac{1}{3}, z - \frac{1}{6}$ ; (iii)  $-y + 1, x - y, z$ ; (iv)  $-y + \frac{2}{3}, -x + \frac{1}{3}, z - \frac{1}{6}$ ; (v)  $-x + y + \frac{1}{3}, y - \frac{1}{3}, z + \frac{1}{6}$ ; (vi)  $x + \frac{1}{3}, x - y + \frac{2}{3}, z + \frac{1}{6}$ ; (vii)  $-x + y, -x + 1, z$ ; (viii)  $-y + \frac{1}{3}, -x + \frac{2}{3}, z + \frac{1}{6}$ .

Attempts to solve the structure in any corresponding centrosymmetric space group failed. The refined Flack (1983) parameter is indicative of inversion twinning of the structure.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *SCALEPACK* and *DENZO* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ATOMS* (Dowty, 2000); software used to prepare material for publication: *SHELXL97* and local procedures.

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