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**Key indicators**

Single-crystal X-ray study  
 $T = 293\text{ K}$   
 Mean  $\sigma(\text{Pr}-\text{F}) = 0.002\text{ \AA}$   
 $R$  factor = 0.018  
 $wR$  factor = 0.048  
 Data-to-parameter ratio = 16.2

For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.

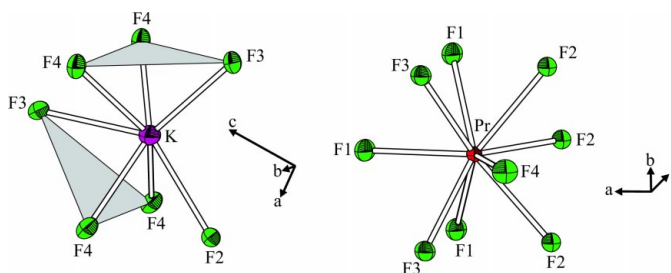
**KPrF<sub>4</sub>**

KPrF<sub>4</sub>, potassium praseodymium tetrafluoride, is isotypic with  $\beta$ -KCeF<sub>4</sub> and KSmF<sub>4</sub>. The structure is composed of a three-dimensional framework of [PrF<sub>9</sub>] and [KF<sub>7</sub>] polyhedra whose corresponding coordination geometries might be described as a tricapped and a monocapped trigonal prism, respectively. The [KF<sub>7</sub>] polyhedra form buckled  ${}_{\infty}[\text{KF}_{1/1}\text{F}_{2/2}\text{F}_{4/4}]$  layers parallel to (001), which are connected perpendicularly by the intermediate Pr atoms along [001].

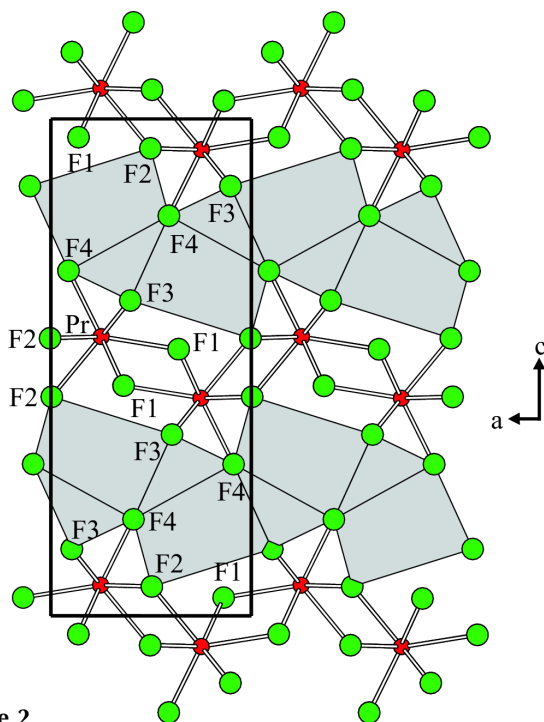
**Comment**

Host lattices based on complex alkaline earth fluorides are promising materials for luminescence applications when they are doped or substituted with rare earth elements (Nakajima *et al.*, 2000). The previously described phase KMgPr<sub>3</sub>F<sub>12</sub> (Labeau *et al.*, 1972) seems to be an appropriate candidate for that purpose. Since no structural or crystallographic data have been published for this compound, crystal growth experiments were started. During these investigations the only crystals suitable for subsequent structure analyses were those of KPrF<sub>4</sub>. This phase was examined for the first time as a result of melting diagram determinations (Dergunov, 1952). Later, the magnetic properties were also investigated (Bukhalova *et al.*, 1968) and the crystal symmetry reported 'to be lower than cubic' (Bukhalova *et al.*, 1969). The correct orthorhombic symmetry was found independently by Metin *et al.* (1981) and Samiev *et al.* (1980), who showed that the title compound is isotypic with  $\beta$ -KCeF<sub>4</sub> (Brunton, 1969) and KSmF<sub>4</sub> (Saf'yanov *et al.*, 1973). Although, during a more detailed investigation of hydrothermal synthesis and thermal behavior, lattice parameters were determined (Khaidukov *et al.*, 1991), no structural details of KPrF<sub>4</sub> were given. Results of a single-crystal structure refinement are reported in this article.

The unit-cell volume of the title compound (370 Å<sup>3</sup>) lies between the corresponding Ce (373 Å<sup>3</sup>) and Sm (362 Å<sup>3</sup>) phases; this is caused by the contraction of the lanthanide's


**Figure 1**

The coordination around potassium (left) and praseodymium (right), both with displacement ellipsoids drawn at the 75% probability level. The congruent faces which connect the polyhedra along [100] are outlined for the left figure.



**Figure 2**  
View of  $\text{KPrF}_4$  along  $[010]$ ; the unit cell and the  $[\text{KF}_7]$  polyhedra are outlined

radius. The structure is made up of nine-coordinated Pr atoms and seven-coordinated K atoms. The polyhedron around the lanthanide atom might be described as a slightly distorted tricapped triangular prism, with an average Pr–F distance of 2.444 Å (Fig. 1, right). The alkali metal atom is surrounded by seven F atoms, which form a monocapped trigonal prism with a mean K–F distance of 2.690 Å (Fig. 1, left). Two F1 atoms with a considerably longer bond length of 3.310 (2) Å augment this coordination polyhedron, but show only very weak interaction. This is supported by bond-valence calculations (Brown, 2002). Using the parameters provided by Brese & O’Keeffe (1991) leads to a bond-valence contribution of only 0.028 bvu (bond valence units), which indicates that this contribution can be disregarded.

The  $[\text{KF}_7]$  polyhedra share common faces and edges to form buckled  ${}_{\infty}[\text{KF}_{1/1}\text{F}_{2/2}\text{F}_{4/4}]$  layers parallel to (001) and a repeating unit of  $c/2$ , as emphasized in Fig. 2. The Pr atoms are located in the voids between the layers and connect the K–F sheets in a perpendicular manner along the  $[001]$  direction.

The coordination numbers (CN) of the F atoms are in the range 3–5, showing the following coordination geometries with slight distortions for each polyhedron: F1 (CN = 3), vertex of a trigonal pyramid; F2 and F3 (CN = 4), tetrahedron; F5 (CN = 5), square pyramid.

## Experimental

59 mg KF (Merck, p. A.), 16 mg  $\text{MgF}_2$  (Merck, Patinal) and 150 mg  $\text{PrF}_3$  [obtained by reacting  $\text{Pr}_2\text{O}_3$  (Fluka, puriss.) with  $\text{NH}_4\text{F}\cdot\text{HF}$  (Fluka, p. A.)], corresponding to a molar ratio of 4:1:3, were heated in a graphite crucible under a static atmosphere of a (98/2)% mixture of  $\text{N}_2/\text{H}_2$  up to 1273 K over the course of 5 h. This temperature was held

for 2 h and then decreased to 773 K within 50 h. After cooling to room temperature, the solidified melt was leached with demineralized water. From the remaining residue, light-green plates of  $\text{KPrF}_4$  could be isolated. Besides  $\text{KPrF}_4$  as the main phase, perovskite-type  $\text{KMgF}_3$  (de Vries & Roy, 1953) could be identified by qualitative phase analysis of the bulk sample.

## Crystal data

$\text{KPrF}_4$   
 $M_r = 256.01$   
Orthorhombic,  $Pnma$   
 $a = 6.2727$  (8) Å  
 $b = 3.7821$  (5) Å  
 $c = 15.578$  (3) Å  
 $V = 369.58$  (9) Å<sup>3</sup>  
 $Z = 4$   
 $D_x = 4.601$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation  
Cell parameters from 25 reflections  
 $\theta = 12.7\text{--}19.0^\circ$   
 $\mu = 14.24$  mm<sup>-1</sup>  
 $T = 293$  (2) K  
Plate, light green  
 $0.11 \times 0.11 \times 0.03$  mm

## Data collection

Enraf–Nonius CAD-4 diffractometer  
 $\omega/2\theta$  scans  
Absorption correction: numerical (*HABITUS*; Herrendorf, 1993–1997)  
 $T_{\min} = 0.187$ ,  $T_{\max} = 0.755$   
4028 measured reflections  
617 independent reflections

519 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.048$   
 $\theta_{\text{max}} = 30.0^\circ$   
 $h = -8 \rightarrow 8$   
 $k = -5 \rightarrow 5$   
 $l = -20 \rightarrow 21$   
3 standard reflections  
frequency: 500 min  
intensity decay: none

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.018$   
 $wR(F^2) = 0.048$   
 $S = 1.13$   
617 reflections  
38 parameters

$w = 1/[\sigma^2(F_o^2) + (0.0265P)^2 + 0.0964P]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.001$   
 $\Delta\rho_{\text{max}} = 0.96$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -1.49$  e Å<sup>-3</sup>  
Extinction correction: *SHELXL97*  
Extinction coefficient: 0.0074 (6)

**Table 1**

Selected geometric parameters (Å).

K–F3 <sup>i</sup>	2.607 (2)	Pr–F3 <sup>v</sup>	2.3857 (14)
K–F2 <sup>ii</sup>	2.616 (2)	Pr–F3	2.3857 (14)
K–F3	2.652 (3)	Pr–F2 <sup>vi</sup>	2.436 (2)
K–F4 <sup>iii</sup>	2.7231 (15)	Pr–F1 <sup>ii</sup>	2.4541 (19)
K–F4 <sup>ii</sup>	2.7231 (15)	Pr–F2 <sup>v</sup>	2.4795 (14)
K–F4	2.7534 (17)	Pr–F2	2.4795 (14)
K–F4 <sup>iv</sup>	2.7534 (17)	Pr–F1 <sup>viii</sup>	2.5336 (15)
Pr–F4	2.305 (2)	Pr–F1 <sup>viii</sup>	2.5336 (15)

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

The highest difference peak is located at a distance of 1.21 Å from Pr and the deepest hole 0.72 Å from the same atom.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *HELENA* implemented in *PLATON* (Spek, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ATOMS* (Dowty, 2000); software used to prepare material for publication: *SHELXL97*.

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