

of *S* and relatively minor changes in the positional parameters, displacement ellipsoids, and their standard uncertainties, the original $F > 2\sigma(F)$ cutoff was used in the final structure refinement. The maximum and minimum residual electron-density peaks were located 0.74 Å from Te(2) and 0.89 Å from Te(1), respectively.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1993). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXTL-Plus* (Sheldrick, 1990). Molecular graphics: *SHELXTL-Plus*.

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References

- Akimoto, J. & Takei, H. (1989). *J. Solid State Chem.* **79**, 212–217.
- Bertaut, E. F., Blum, P. & Magnano, G. (1955). *C. R. Acad. Sci. Paris*, **241**, 757–759.
- Brown, I. D. & Altermatt, D. (1985). *Acta Cryst.* **B41**, 244–247.
- Carpenter, J. D. & Hwu, S.-J. (1992). *Acta Cryst.* **C48**, 1164–1167.
- Cromer, D. T. & Waber, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.2A. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- Decker, B. F. & Kasper, J. S. (1957). *Acta Cryst.* **10**, 332–337.
- Hörkner, W. & Müller-Buschbaum, H. (1976). *Z. Naturforsch. Teil B*, **31**, 1710–1711.
- Larson, A. C. (1970). *Crystallographic Computing*, edited by F. R. Ahmed, S. R. Hall & C. P. Huber, pp. 291–294. Copenhagen: Munksgaard.
- Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- Molecular Structure Corporation (1993). *TEXSAN. Single Crystal Structure Analysis Software*. Version 1.6b. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Reid, A. F., Wadsley, A. D. & Sienko, M. J. (1968). *Inorg. Chem.* **7**, 112–118.
- Shannon, R. D. (1976). *Acta Cryst.* **A32**, 751–767.
- Sheldrick, G. M. (1985). *SHELXS86. Crystallographic Computing 3*, edited by G. M. Sheldrick, C. Krüger & R. Goddard, pp. 175–189. Oxford University Press.
- Sheldrick, G. M. (1990). *SHELXTL-Plus*. Version 4.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

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A Neodymium-Substituted Britholite Compound

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Abstract

A single crystal of calcium neodymium fluoride oxide phosphate silicate, $\text{Ca}_9\text{Nd}(\text{PO}_4)_5(\text{SiO}_4)\text{F}_{1.5}\text{O}_{0.25}$, was obtained by a synthesis involving the heating of a $\text{CaF}_2/\text{P}_2\text{O}_5/\text{CaCO}_3/\text{Nd}_2\text{O}_3/\text{SiO}_2$ mixture at 1973 K over a period of 2 h followed by cooling at 50 K min^{-1} . The structure is of the britholite type, a mixed silica-phosphate apatite. The neodymium is distributed over both calcium sites, 17% in calcium site I and 83% in calcium site II. The channel which contains the anions is partially filled with 77% F^- and 13% O^{2-} , the remaining 10% being vacancies.

Comment

The treatment of radioactive wastes and their safe storage are problems of the next few decades and more distant future. One of the solutions considered for the long term involves the storage of the separated radionuclides in a crystalline matrix-like apatite (Carpéna & Lacout, 1993). Studies of this rather abundant natural mineral have shown good resistance of its structure to nuclear radiation damage (Carpéna & Mailhe, 1992; Carpéna, 1996). Replacing calcium with a radionuclide involves balancing the excess charge by substitution of anions or cations. Rare earth elements are good analogues to actinides and are used as model ions in nuclear chemistry. Britholite is one of the minerals with an apatite-type structure which includes rare earth ions. The electro-neutrality is maintained by substituting the phosphate with a silicate ion. The chemical stability makes the title compound, $(\text{Ca}_9\text{Nd})(\text{PO}_4)_5(\text{SiO}_4)\text{F}_2$, a good candidate for its intended use.

Comparison of the cell parameters of the title compound with those of fluorapatite ($a = 9.372$ and $c = 6.885$ Å; Sudarsanan *et al.*, 1972) and those of the rare earth silicate apatite $\text{Nd}_{9.33}(\text{SiO}_4)_6\text{O}_2$ ($a = 9.573$ and

$c = 7.0336 \text{ \AA}$; Nørlund Christensen *et al.*, 1997) shows that the variations of the parameters *versus* SiO_4 contents are about linear (Boyer *et al.*, 1997). The elemental analysis indicates a non-stoichiometric compound with deficiencies in F^- , Nd^{3+} and, most pronounced, SiO_4^{4-} . The structure determination revealed that the lack of charge due to the missing F^- is counterbalanced by O^{2-} ions. In the tunnel, the O^{2-} and F^- ions do not completely fill the site; 10% of the site is empty. The assembling of the PO_4 tetrahedra with the CaIO_9 tri-capped trigonal prisms (Fig. 1) reveals the Ca2 and F sites in the tunnels. The (P,Si)—O distances [average $1.545(2) \text{ \AA}$] are similar to the P—O bond lengths in PO_4^{3-} [$1.548(5) \text{ \AA}$] and shorter than the Si—O bonds in SiO_4^{4-} [$1.62(2) \text{ \AA}$; Bergerhoff, 1992]. As the electronic distribution in the (P,Si)—O bond is the average of the electronic cloud of five P—O bonds of 1.54 \AA and one Si—O bond of 1.62 \AA , an extension of the electronic density and consequently of the displacement parameter in the bond direction must be expected. The displacement ellipsoids do not show any elongation in the bond directions (Fig. 2), which implies that the substitution of P by Si results in negligible perturbations. In the case of the (Ca1,Nd1)—O distances, the average of the nine distances [$2.56(2) \text{ \AA}$] is equal to the average calculated for $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ [$2.56(20) \text{ \AA}$], and is shorter than that for $\text{Nd}_{9.33}(\text{SiO}_4)_6\text{O}_2$ [$2.59(19) \text{ \AA}$]. In the case of the (Ca2,Nd2)—O distances, the average value [$2.44(13) \text{ \AA}$] is closer to that observed for calcium fluorapatite [$2.43(14) \text{ \AA}$] than that of oxy neodymium silica-apatite [$2.47(13) \text{ \AA}$]. Such observations reveal that, from the distances point of view, the substitution of one Ca by an Nd atom does not disturb the structure of the fluorapatite. The variation of the cell

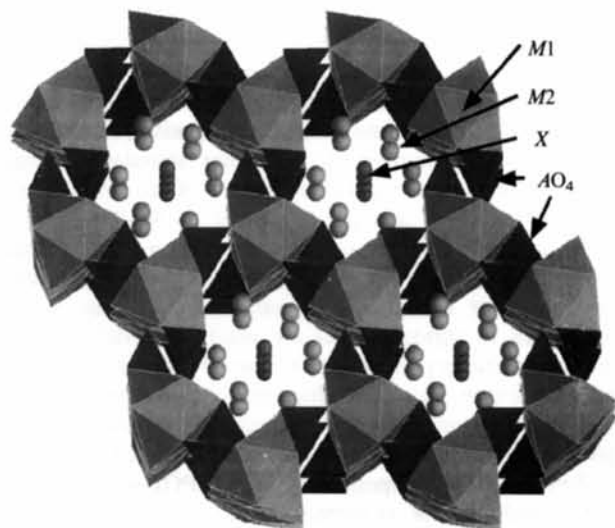


Fig. 1. View of the cell with the apatite tunnels. M1: site I, Nd1 or Ca1 atoms included in an O-atom tricapped trigonal prism. M2: site II, Nd2 or Ca2 atoms. X: F and O4 site. AO₄: PO₄ or SiO₄ tetrahedron.

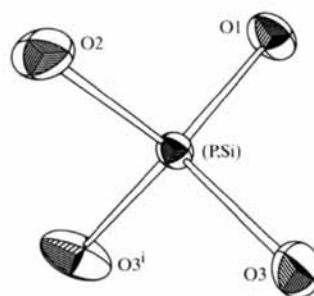


Fig. 2. View of the (Si,P) environment showing 66% probability displacement ellipsoids.

parameters is due to the distortion of the coordination polyhedron around the calcium sites.

Experimental

Crystals of the title compound were obtained from an initial mixture of CaF_2 , P_2O_5 , CaCO_3 , Nd_2O_3 and SiO_2 , with stoichiometry according to the equation $8\text{CaCO}_3 + \frac{5}{2}\text{P}_2\text{O}_5 + \text{CaF}_2 + \frac{1}{2}\text{Nd}_2\text{O}_3 + \text{SiO}_2 \rightarrow \text{Ca}_9\text{Nd}(\text{SiO}_4)(\text{PO}_4)_5\text{F}_2 + 8\text{CO}_2$, after the following thermal treatment. Rapid heating to 1973 K with a ramp rate of 300 K h^{-1} was performed. After a dwelling time of 2 h , the temperature was decreased to ambient temperature at a rate of 50 K min^{-1} . IR spectroscopy and X-ray diffraction studies confirmed that the crystals pertained to the apatite type. The chemical analyses of several crystals were obtained using an SX 50 CAMECA microprobe. From the average experimental values [Ca 33.5 (1), Nd 11.9 (1), P 14.4 (1), Si 2.3 (1) and F 2.6 (1)%], the composition of the crystals was determined as $\text{Ca}_{9.1}\text{Nd}_{0.9}(\text{SiO}_4)_{0.9}(\text{PO}_4)_{5.1}\text{F}_{1.5}\text{O}_{0.25}$, with a calcium-content error of 0.06.

Crystal data

$(\text{Ca}_{0.02}\text{Nd}_{0.98})$ -
 $[(\text{PO}_4)_{5.1}(\text{SiO}_4)_{0.9}]$ -
 $\text{F}_{1.53}\text{O}_{0.27}$
 $M_r = 1104.40$
 Hexagonal
 $P6_3/m$
 $a = 9.3938(8) \text{ \AA}$
 $c = 6.9013(5) \text{ \AA}$
 $V = 527.40(7) \text{ \AA}^3$
 $Z = 1$
 $D_x = 3.47 \text{ Mg m}^{-3}$
 $D_m = 3.4 \text{ Mg m}^{-3}$
 D_m measured by pycnometer
 (water)

Mo $K\alpha$ radiation
 $\lambda = 0.71073 \text{ \AA}$
 Cell parameters from 25
 reflections
 $\theta = 12\text{--}24^\circ$
 $\mu = 5.221 \text{ mm}^{-1}$
 $T = 293(2) \text{ K}$
 Hexagonal slab
 $0.42 \times 0.27 \times 0.14 \text{ mm}$
 Clear light blue (pink if
 illuminated)

Data collection

Enraf–Nonius CAD-4
 diffractometer
 ω - 2θ scans
 Absorption correction:
 Gaussian (Coppens *et al.*,
 1965)
 $T_{\min} = 0.281$, $T_{\max} = 0.434$

1090 reflections with
 $I > 2\sigma(I)$
 $R_{\text{int}} = 0.063$
 $\theta_{\text{max}} = 40.0^\circ$
 $h = 0 \rightarrow 16$
 $k = -16 \rightarrow 0$
 $l = -12 \rightarrow 12$

2848 measured reflections
1101 independent reflections

3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.035$
 $wR(F^2) = 0.093$
 $S = 1.235$
1101 reflections
42 parameters
 $w = 1/[\sigma^2(F_o^2) + (0.0322P)^2 + 0.7559P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.051$
 $\Delta\rho_{\max} = 0.380 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.409 \text{ e } \text{\AA}^{-3}$
Extinction correction: none
Scattering factors from
International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters (\AA , $^\circ$)

P—O1	1.545 (2)	Ca2—F ^{iv}	2.2851 (4)
P—O3	1.5436 (13)	Ca2—O4 ^v	2.309 (4)
P—O3 ⁱ	1.5436 (13)	Ca2—O3 ⁱⁱⁱ	2.3521 (13)
P—O2	1.549 (2)	Ca2—O2 ^{vi}	2.404 (2)
Ca1—O1	2.4007 (13)	Ca2—O3 ^v	2.5067 (14)
Ca1—O2 ⁱⁱⁱ	2.4565 (14)	Ca2—O1 ^{vii}	2.672 (2)
Ca1—O3 ⁱⁱⁱ	2.808 (2)		
O1—P—O3	111.26 (7)	O1—P—O2	111.52 (10)
O3—P—O3 ⁱ	107.12 (11)	O3—P—O2	107.73 (8)

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

The general structure of apatite was used as a starting point (Sudarsanan & Young, 1969). In a first step, the distributions of the Ca and Nd atoms in the 6*h* and 4*f* Ca sites were optimized. Then the P and Si occupancies were refined. Chemical analysis had shown that the stoichiometry of the compound was not strictly $\text{Ca}_9\text{Nd}(\text{PO}_4)_5(\text{SiO}_4)\text{F}_2$; a lack of Si and F atoms was observed. In order to take this observation into account, an electro-neutrality constraint involving these atoms was used. As the resulting $\Delta\rho$ map revealed a residual peak near the F atom and out of the mirror plane, an extra O atom was introduced in a 4*e* site, as in calcium hydroxyapatite (Sudarsanan & Young, 1969). The electro-neutrality constraint was modified accordingly, assuming the added ion to be O^{2-} . The final cycles of refinement revealed that a vacancy still existed in the 4*e* tunnel site.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1993). Cell refinement: *CAD-4 EXPRESS*. Data reduction: *CADAK* (Savariault, 1991). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AB1515). Services for accessing these data are described at the back of the journal.

References

- Bergerhoff, G. (1992). *International Tables for Crystallography*, Vol. C, edited by A. J. C. Wilson, Table 9.4.2.1, pp. 683–684. Dordrecht: Kluwer Academic Publishers.
- Boyer, L., Carpena, J. & Lacout, J.-L. (1997). *Solid State Ion.* **95**, 121–129.
- Carpena, J. (1996). *International Workshop on Fission Track Dating*, Gent, pp. 26–30.
- Carpena, J. & Lacout, J.-L. (1993). French Patent No. 93 08676.

- Carpena, J. & Mailhe, D. (1992). *Méthodes de Datations par les Phénomènes Nucléaires Naturels. Applications. Masson Collect. CEA*, pp. 203–249.
- Coppens, P., Leiserowitz, L. & Rabinovich, D. (1965). *Acta Cryst.* **18**, 1035–1041.
- Enraf–Nonius (1993). *CAD-4 EXPRESS*. Version 5.1. Enraf–Nonius, Delft, The Netherlands.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Nørlund Christensen, A., Hazell, R. G. & Hewat, A. W. (1997). *Acta Chem. Scand.* **51**, 37–43.
- Savariault, J. M. (1991). *CADAK. Programme de Réduction des Données du CAD-4*. CEMES, France.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- Sudarsanan, K., Mackie, P. E. & Young, R. (1972). *Mater. Res. Bull.* **7**, 1331–1336.
- Sudarsanan, K. & Young, R. (1969). *Acta Cryst.* **B25**, 1534–1541.

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A Mixed Zinc–Cobalt Diphosphate, ZnCoP_2O_7

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Abstract

The structure of the mixed zinc cobalt diphosphate ZnCoP_2O_7 presents a low-dimensional system not previously observed in the diphosphates of 3*d* transition elements. The paramagnetic Co^{2+} ions are grouped into dimers linked by $\text{P}_2\text{O}_4^{4-}$ groups, forming tunnels in which the diamagnetic Zn^{2+} ions are located. The metal environments can be described as a distorted octahedron and a distorted square-based pyramid for Co and Zn, respectively, the two coordination polyhedra sharing common edges through the O atoms O1–O2 and O6–O7.

Comment

Until now, the diphosphates of the 3*d* transition elements have rarely shown a restricted cationic order. The structure of the simple diphosphates $M_2\text{P}_2\text{O}_7$ ($M = \text{Cr, Co, Ni, Cu or Zn}$), with two principal allotropic varieties α (low temperature) and β (high temperature), shows a fivefold and/or sixfold metal atom coordination. The