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Neodymium-Doped Sr-5(Po4)(3)F And Sr-5(Vo4)(3)F

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Table 2. Selected geometric parameters (Å, °)

Cs(1)—O(2^i)	2.975 (7)	Ga(1)—O(3^{iv})	1.824 (7)
Cs(1)—O(2^{ii})	3.456 (8)	Ga(1)—O(4^{ix})	1.842 (7)
Cs(1)—O(4)	3.316 (8)	Ga(1)—O(6)	1.830 (8)
Cs(1)—O(4^{iii})	3.337 (8)	Ga(1)—O(7^{viii})	1.822 (7)
Cs(1)—O(4^{iv})	3.210 (8)	Ga(2)—O(1)	1.827 (7)
Cs(1)—O(5)	3.410 (7)	Ga(2)—O(2^{viii})	1.847 (8)
Cs(1)—O(7^{iv})	3.063 (8)	Ga(2)—O(5^{vii})	1.836 (8)
Cs(1)—O(7^v)	3.204 (8)	Ga(2)—O(7)	1.794 (7)
Cs(2)—O(1)	3.173 (7)	B(1)—O(1)	1.39 (1)
Cs(2)—O(1^{vi})	3.178 (8)	B(1)—O(2^x)	1.37 (1)
Cs(2)—O(2^{vii})	3.439 (8)	B(1)—O(3)	1.35 (1)
Cs(2)—O(3)	2.885 (7)	B(2)—O(4)	1.38 (1)
Cs(2)—O(5)	3.102 (7)	B(2)—O(5)	1.37 (1)
Cs(2)—O(5^{viii})	3.221 (8)	B(2)—O(6^{viii})	1.36 (1)
Cs(2)—O(6)	3.241 (8)		
Cs(2)—O(6^{viii})	3.321 (8)		
O(3^{iv})—Ga(1)—O(4^{ix})	106.2 (4)	O(2^{viii})—Ga(2)—O(5^{vii})	109.6 (3)
O(3^{iv})—Ga(1)—O(6)	104.4 (4)	O(2^{viii})—Ga(2)—O(7)	110.4 (3)
O(3^{iv})—Ga(1)—O(7^{viii})	108.4 (3)	O(5^{vii})—Ga(2)—O(7)	108.6 (3)
O(4^{ix})—Ga(1)—O(6)	114.4 (3)	O(1)—B(1)—O(2^x)	121 (1)
O(4^{ix})—Ga(1)—O(7^{viii})	110.5 (3)	O(2^x)—B(1)—O(3)	121 (1)
O(6)—Ga(1)—O(7^{viii})	112.4 (4)	O(3)—B(1)—O(1)	118 (1)
O(1)—Ga(2)—O(2^{viii})	104.9 (3)	O(4)—B(2)—O(5)	119 (1)
O(1)—Ga(2)—O(5^{vii})	109.4 (3)	O(5)—B(2)—O(6^{viii})	118 (1)
O(1)—Ga(2)—O(7)	113.8 (3)	O(6^{viii})—B(2)—O(4)	123 (1)

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

A clear, colorless, plate-shaped crystal was mounted on a glass fiber with epoxy for X-ray structure analysis. Data were collected with a scan speed of 16.0° min^{-1} in ω and a scan width of $(1.5 + 0.3\tan\theta)°$.

The *TEXSAN* crystallographic software package (Molecular Structure Corporation, 1989) was used to solve the crystal structure. The Laue symmetry 2/m and the systematic absences $h0l$ ($l = 2n + 1$) and $0k0$ ($k = 2n + 1$) unambiguously indicated space group $P2_1/c$. The positions of the Cs atoms were determined by a Patterson vector map and the remaining atoms were found by examination of the difference electron density maps. After isotropic refinement, the data were averaged and corrected for absorption.

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Neodymium-Doped Sr5(PO4)3F and Sr5(VO4)3F

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Abstract

Neodymium-doped Sr5(PO4)3F [neodymium strontium fluoride phosphate, (Nd,Sr)5(PO4)3F] and neodymium-doped Sr5(VO4)3F [neodymium strontium fluoride vanadate, (Nd,Sr)5(VO4)3F] crystallize in space group $P6_3/m$ and are isostructural with calcium fluorophosphate, Ca5(PO4)3F. There are two different Sr sites in Sr5(XO4)3F, denoted Sr(1) and Sr(2). Using single-crystal X-ray diffraction the two structures were refined to R factors of 2.3 and 2.2%, respectively, showing that Nd is present at both Sr sites in (Sr,Nd)5(VO4)3F but only at the Sr(2) site in (Sr,Nd)5(PO4)3F.

Comment

Calcium fluorophosphate (FAP) crystals have been investigated previously as laser hosts, and lasing characteristics of rare-earth-doped FAP were reported as early as 1968 (Ohlmann, Steinbruegge & Mazelsky, 1968). Recent developments have reopened investigations into FAP and the whole calcium–strontium fluorophosphate system for use as laser hosts. This paper presents the detailed crystal structure refinements that followed the recent successful crystal growth of neodymium-doped Sr5(PO4)3F (SFAP) and neodymium-doped Sr5(VO4)3F (SVAP).

Both crystals were grown by the Czochralski method. SVAP and SFAP are isostructural and belong to the hexagonal space group $P6_3/m$. The structure contains layers of XO4 tetrahedra (X = P, V) centred at two levels along [001] and F$^-$ ions lying along the c axis, as can be seen in Fig. 1. V—O and P—O bond lengths are given in Tables 2 and 4, respectively, and show that the VO4 tetrahedra are distorted [average/(deviation) for P—O and V—O bond distances are 1.541 Å/(0.004 Å) and 1.711 Å/(0.01 Å), respectively].

There are two independent Sr sites in the structures, the first of which, Sr(1), contains 40% of the Sr^{2+}

ions when fully occupied and has threefold symmetry. The remaining 60% of the Sr^{2+} ions are found at the Sr(2) sites, which have reflection symmetry in the plane perpendicular to the c axis. Each Sr(2) site has an F^- ion as its nearest neighbour. Nd substitutes for Sr in both SVAP and SFAP, but the location of the dopant in the two compounds is different to within the precision of the X-ray structure refinement. Nd^{3+} was found to be present on the Sr(2) site in both SVAP and SFAP, but only in SVAP was Nd^{3+} present on the Sr(1) site as well.

A charge-compensation mechanism is required for the 1:1 substitution of Nd^{3+} for Sr^{2+}. This has been discussed previously by Mackie & Young (1973) for the similar structure of neodymium-doped FAP, where the substitution of O^{2-} for F^- and the creation of Ca^{2+} (in this case Sr^{2+}) vacancies were considered. For this reason, all site occupancies in the present work were refined. In both SVAP and SFAP all the O-site occupancies converged to a value slightly greater than unity, and so were fixed at unity for the final cycles of refinement. Likewise, the occupancy of the F sites refined to a value greater than or within experimental error of unity. However, a reduction in the site occupancy factors for the V and P sites in SVAP and SFAP, respectively, was observed, which could be the mechanism for charge balance in these compounds.

Further evidence supporting the location of the Nd dopant was obtained by investigation of the absorption and fluorescence spectra of Nd in SVAP and SFAP. This work, carried out at CREOL, suggested that essentially all the Nd in SFAP is on the Sr(2) site, while Nd was

seen on both Sr sites in SVAP. However, the results indicated a preference for the Sr(2) site which could not be seen from the X-ray analysis. The preference for substitution at the Sr(2) site, which is smaller than the Sr(1) site, can be explained by the fact that the ionic radius of Nd^{3+} is much smaller than that of Sr^{2+}.

Experimental
SVAP
Crystal data

$(Sr_{0.982}Nd_{0.012})_5(VO_4)_3F$	Mo $K\alpha$ radiation
$M_r = 798.02$	$\lambda = 0.71069$ Å
Hexagonal	Cell parameters from 36
$P6_3/m$	reflections
$a = 10.0077$ (6) Å	$\theta = 18–20°$
$c = 7.4342$ (8) Å	$\mu = 23.66$ mm^{-1}
$V = 644.82$ Å^3	Room temperature
$Z = 2$	Irregular
$D_x = 4.11$ Mg m^{-3}	$0.15 \times 0.11 \times 0.07$ mm
	Blue

Data collection

Stoe Stadi-4 diffractometer	$R_{int} = 0.078$
ω–2θ scans	$\theta_{max} = 32.5°$
Absorption correction:	$h = -13 \rightarrow 13$
ψ scans of five reflections	$k = -15 \rightarrow 15$
$T_{min} = 0.0825$, $T_{max} =$	$l = -11 \rightarrow 11$
0.1860	3 standard reflections
3146 measured reflections	frequency: 60 min
831 independent reflections	intensity decay: 1.5%
421 observed reflections	
$[I > 3\sigma(I)]$	

Refinement

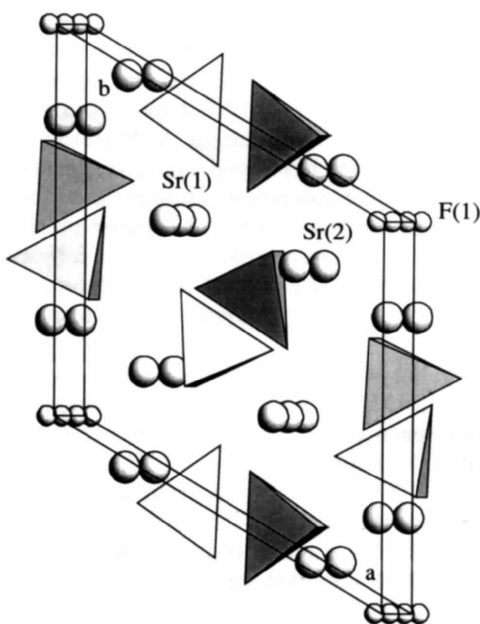|	
Refinement on F	$(\Delta/\sigma)_{max} = 0.002$
$R = 0.022$	$\Delta\rho_{max} = 0.620$ e Å^{-3}
$wR = 0.027$	$\Delta\rho_{min} = -0.677$ e Å^{-3}
$S = 0.87$	Extinction correction:
421 reflections	secondary (Larson, 1970)
51 parameters	Extinction coefficient: 99 (4)
Weighting scheme:	Atomic scattering factors
Chebychev polynomial	from *International Tables*
with parameters 16.3,	*for X-ray Crystallography*
20.5, 7.19	(1974, Vol. IV)

Fig. 1. The structure of $Sr_5(PO_4)_3F$ projected along [001] and then rotated 6° around the y axis, showing the two Sr sites and the PO_4 tetrahedra.

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for SVAP*

$$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	Occupancy	x	y	z	U_{eq}
Sr(1)	0.980 (3)	1/3	2/3	0.0004 (1)	0.0123 (3)
Nd(1)	0.014 (3)	1/3	2/3	0.0004 (1)	0.0123 (3)
Sr(2)	0.983 (3)	0.23884 (7)	−0.01060 (8)	1/4	0.0114 (3)
Nd(2)	0.011 (2)	0.23884 (7)	−0.01060 (8)	1/4	0.0114 (3)
O(1)	1.0	0.3159 (7)	0.4835 (6)	1/4	0.014 (3)
O(2)	1.0	0.5962 (6)	0.4705 (6)	1/4	0.016 (3)
O(3)	1.0	0.3405 (5)	0.2498 (4)	0.0671 (6)	0.018 (2)
V(1)	0.972 (4)	0.3982 (1)	0.3682 (1)	1/4	0.0080 (5)
F(1)	0.98 (2)	0	0	1/4	0.023 (6)

Table 2. *Selected geometric parameters* (Å) *for* SVAP

Sr(1)—O(1^i)	2.552 (3)	Sr(2)—O(3^{vii})	2.510 (4)
Sr(1)—O(1^{ii})	2.552 (3)	Sr(2)—O(2^{viii})	2.521 (5)
Sr(1)—O(1)	2.552 (3)	Sr(2)—O(3^{ix})	2.651 (4)
Sr(1)—O(2^{iii})	2.611 (4)	Sr(2)—O(3)	2.651 (4)
Sr(1)—O(2^{iv})	2.611 (4)	Sr(2)—O(1^x)	2.768 (6)
Sr(1)—O(2^v)	2.611 (4)	Sr(2)—O(3^x)	3.569 (4)
Sr(1)—O(3^{iv})	2.980 (4)	Sr(2)—O(3^{xi})	3.569 (4)
Sr(1)—O(3^{iii})	2.980 (4)	V(1)—O(1)	1.721 (5)
Sr(1)—O(3^v)	2.980 (4)	V(1)—O(2)	1.716 (5)
Sr(2)—F(1)	2.445 (1)	V(1)—O(3)	1.703 (4)
Sr(2)—O(3^{vi})	2.510 (4)	V(1)—O(3^{ix})	1.703 (4)

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

SFAP

Crystal data

(Sr$_{0.992}$Nd$_{0.005}$)$_5$(PO$_4$)$_3$F
$M_r = 739.79$
Hexagonal
$P6_3/m$
$a = 9.7156$ (4) Å
$c = 7.2810$ (3) Å
$V = 595.19$ Å^3
$Z = 2$
$D_x = 4.13$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 46 reflections
$\theta = 17-19°$
$\mu = 23.73$ mm^{-1}
Room temperature
Irregular
$0.14 \times 0.10 \times 0.06$ mm
Blue–purple

Data collection

Stoe Stadi-4 diffractometer
$\omega-2\theta$ scans
Absorption correction:
  ψ scans of five reflections
  $T_{min} = 0.0817$, $T_{max} = 0.2043$
3682 measured reflections
942 independent reflections
460 observed reflections
  $[I > 3\sigma(I)]$

$R_{int} = 0.075$
$\theta_{max} = 35°$
$h = -13 \rightarrow 13$
$k = -15 \rightarrow 15$
$l = -11 \rightarrow 11$
3 standard reflections
  frequency: 60 min
  intensity decay: 1%

Refinement

Refinement on F
$R = 0.023$
$wR = 0.029$
$S = 0.84$
460 reflections
51 parameters
Weighting scheme:
  Chebychev polynomial
  with parameters 7.0, 8.44, 3.09

$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.881$ e Å^{-3}
$\Delta\rho_{min} = -0.741$ e Å^{-3}
Extinction correction:
  secondary (Larson, 1970)
Extinction coefficient: 67 (3)
Atomic scattering factors
  from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* SFAP

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

	Occupancy	x	y	z	U_{eq}
Sr(1)	0.996 (3)	1/3	2/3	-0.0002 (1)	0.0098 (3)
Sr(2)	0.989 (3)	0.23910 (7)	-0.01445 (7)	1/4	0.0092 (3)
Nd(2)	0.009 (2)	0.23910 (7)	-0.01445 (7)	1/4	0.0092 (3)
O(1)	1.0	0.3306 (6)	0.4810 (6)	1/4	0.011 (2)
O(2)	1.0	0.5827 (5)	0.4644 (6)	1/4	0.010 (3)
O(3)	1.0	0.3441 (4)	0.2612 (4)	0.0788 (5)	0.013 (2)
P(1)	0.975 (5)	0.3992 (2)	0.3685 (2)	1/4	0.0066 (6)
F(1)	1.0	0	0	1/4	0.021 (6)

Table 4. *Selected geometric parameters* (Å) *for* SFAP

Sr(1)—O(1^i)	2.554 (3)	Sr(2)—O(3^{vii})	2.522 (3)
Sr(1)—O(1^{ii})	2.554 (3)	Sr(2)—O(1^{viii})	2.744 (5)
Sr(1)—O(1)	2.554 (3)	Sr(2)—O(3)	2.652 (3)
Sr(1)—O(2^{iii})	2.576 (3)	Sr(2)—O(3^{ix})	2.652 (3)
Sr(1)—O(2^{iv})	2.576 (3)	Sr(2)—O(2^x)	2.499 (4)
Sr(1)—O(2^v)	2.576 (3)	Sr(2)—O(3^{viii})	3.403 (4)
Sr(1)—O(3^{iv})	2.906 (4)	Sr(2)—O(3^{xi})	3.403 (4)
Sr(1)—O(3^{iii})	2.906 (4)	P(1)—O(1)	1.539 (4)
Sr(1)—O(3^v)	2.906 (4)	P(1)—O(2)	1.545 (5)
Sr(2)—F(1)	2.396 (1)	P(1)—O(3)	1.539 (3)
Sr(2)—O(3^{vi})	2.522 (3)	P(1)—O(3^{ix})	1.539 (3)

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

Data were collected using a learnt-profile method (Clegg, 1981). Data collection and reduction were performed using *DIF4* (Stoe & Cie, 1988*a*) and *REDU4* (Stoe & Cie, 1988*b*). Cell constants were refined using high 2θ reflections extracted from the data collection and measured with double stepscans. Refinement of both structures was carried out using *CRYSTALS* (Watkin, Carruthers & Betteridge, 1985). The atomic coordinates for Ca$_5$(PO$_4$)$_3$F (Mackie & Young, 1973) were used as an initial model for both refinements. The positional and displacement parameters for Nd rode with the corresponding Sr parameters. Their occupancies were refined separately so that a vacancy on an Sr site would not give rise to an increase in Nd occupancy.

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