Crystal structure of praseodymium pentaphosphide, PrP_5 and of samarium pentaphosphide, SmP_5

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1. Praseodymium pentaphosphide, PrP_5

Source of material: The compound was synthesized by reaction of the elements in sealed Pyrex-glass or quartz ampoules in the presence of molten alkaline metal halides and small amounts of iodine (see refs. 1, 2). PrP_5 forms bright black crystals of prismatic or columnar shape and is stable against dilute bases and non-oxidizing acids. PrP_5 is paramagnetic with $\mu_{\text{eff}} = 3.54 \mu_B$ (see ref. 3). PrP_5 crystallizes in the space group $P2_1/m$ and is isotypic to NdP_5 . The P–P distances vary between 2.166 Å and 2.212 Å, the Pr–P distances vary between 3.004 Å and 3.065 Å.

P_5Pr , monoclinic, $P12_1/m1$ (No. 11), $a = 4.938(1)$ Å, $b = 9.595(2)$ Å, $c = 5.482(2)$ Å, $\beta = 103.64(2)^\circ$, $V = 252.4$ Å³, $Z = 2$, $R(F) = 0.042$, $R_w(F) = 0.048$.

Table 1. Parameters used for the X-ray data collection

Crystal:	black, spherical, metallic luster, size 0.1 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ :	110.5 cm ⁻¹
Diffractometer:	SYNTEX P1
Scan mode:	ω
$T_{\text{measurement}}$:	293 K
$2\theta_{\text{max}}$:	55°
$N(hkl)_{\text{unique}}$:	673
Criterion for I_o :	$I_o > 2 \sigma(I_o)$
$N(\text{param})_{\text{refined}}$:	31
Program:	SHELXTL-plus

Table 2. Final atomic coordinates and displacement parameters (in Å²)

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pr	2e	0.0241(1)	1/4	0.3606(1)	0.0149(4)	0.0022(3)	0.0060(4)	0	0.0049(3)	0
P(1)	4f	0.3810(4)	0.5901(2)	0.0414(4)	0.0118(9)	0.0017(9)	0.0067(8)	0.0014(8)	0.0033(6)	−0.0003(6)
P(2)	4f	0.2910(4)	0.5354(2)	0.3975(4)	0.016(1)	0.0044(9)	0.0110(9)	0.0000(8)	0.0092(8)	0.0001(6)
P(3)	2e	0.2884(6)	1/4	0.9135(5)	0.013(1)	0.004(1)	0.008(1)	0	0.005(1)	0

2. Samarium pentaphosphide, SmP₅

Source of material: The compound was synthesized by reaction of the elements in sealed Pyrex-glass or quartz ampoules in the presence of molten alkaline metal halides and small amounts of iodine (see refs. 1-3). SmP₅ forms bright black crystals of prismatic, needle or irregular shape and is stable against non-oxidizing acids and bases. SmP₅ is semiconducting with $E_g = 0.48$ eV (see ref. 4). Temperature independent van Vleck paramagnetism overlap the temperature dependent paramagnetism with $\mu_{\text{eff}} = 1.6 \mu_B$ (see ref. 4).

SmP₅ crystallizes in the space group $P2_1/m$ and is isotypic to NdP₅ (see ref. 1). The P-P distances vary between 2.161 Å and 2.215 Å, the Sm-P distances vary between 2.976 Å and 3.025 Å.

P₅Sm, monoclinic, $P12_1/m1$ (No. 11), $a = 4.936(3)$ Å, $b = 9.508(2)$ Å, $c = 5.411(1)$ Å, $\beta = 102.90(2)^\circ$, $V = 247.5$ Å³, $Z = 2$, $R(F) = 0.071$, $R_w(F) = 0.079$.

Table 3. Parameters used for the X-ray data collection

Crystal:	black needle, metallic luster.
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	134.6 cm ⁻¹
Diffractometer:	SYNTEX P1
Scan mode:	ω
$T_{\text{measurement}}$:	293 K
$2\theta_{\text{max}}$:	55°
$N(hkl)_{\text{unique}}$:	677
Criterion for I_0 :	$I_0 > 2 \sigma(I_0)$
$N(\text{param})_{\text{refined}}$:	31
Program:	SHELXTL-plus

Table 4. Final atomic coordinates and displacement parameters (in Å²)

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sm	2e	0.0136(2)	1/4	0.3540(2)	0.0215(6)	0.0096(6)	0.0162(6)	0	0.0060(4)	0
P(1)	4f	0.3820(7)	0.5907(4)	0.0433(7)	0.023(1)	0.008(1)	0.017(1)	0.005(1)	0.000(1)	0.000(1)
P(2)	4f	0.2879(8)	0.5321(5)	0.4008(7)	0.024(1)	0.012(1)	0.023(2)	0.000(1)	0.010(1)	0.001(1)
P(3)	2e	0.285(1)	1/4	0.905(1)	0.023(2)	0.011(2)	0.020(2)	0	0.007(1)	0

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