Temperature dependent structural, vibrational and magnetic properties of $K_3Gd_5(PO_4)_6$

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ESI-X. Field dependent magnetization of $K_3Gd_5(PO_4)_6$ at different temperatures. Solid lines indicate fitting with calculated magnetization for free ions $K_3Gd_5(PO_4)_6$. Magnetizations were calculated by Brillouin function, $M\ (emu/gm) = N_Z g\ J\ \mu_B \left[\frac{2J+1}{2J}\left[coth\frac{2J+1}{2J}\frac{g\ J\ \mu_B\ B}{k_B T}\right] - \frac{1}{2J}\left[coth\frac{1}{2J}\frac{g\ J\ \mu_B\ B}{k_B T}\right]\right]$. At 3 K, the magnetization reaches to maximum moment for free Gd^{3+} ions (with g = 2.00 and J = S= 7/2).

ESI-I. Refined position coordinates of $K_3Gd_5(PO_4)_6$ at 300 K.

Atom	*Wyc.*	x	y	z	U(eq) (Å)^2
Gd1	*4e*	0	0.3660(5)	1/4	0.0042(2)
Gd2	*8f*	0.14295(14)	-0.4145(2)	0.48045(14)	0.0042(2)
Gd3	*8f*	0.21939(13)	0.1249(3)	0.29181(12)	0.0042(2)
K1	*8f*	0.0759(2)	0.9029(5)	0.0756(2)	0.014(2)
K2	*4e*	0	0.8236(7)	1/4	0.014(2)
P1	*8f*	0.1382(2)	0.0897(6)	0.4133(2)	0.0011(9)
P2	*8f*	0.2098(3)	0.6253(6)	0.3403(2)	0.0011(9)
P3	*8f*	-0.0759(3)	0.4044(6)	0.3788(3)	0.0011(9)
O1	*8f*	0.2022(4)	0.7813(8)	0.2752(4)	0.0234(15)
O2	*8f*	-0.0970(4)	0.2445(8)	0.3115(3)	0.0234(15)
O3	*8f*	0.2348(4)	0.072(2)	0.4250(5)	0.0234(15)
O4	*8f*	0.1238(7)	0.2349(9)	0.4689(6)	0.0234(15)
O5	*8f*	0.2477(4)	0.6719(13)	0.4326(3)	0.0234(15)
O6	*8f*	-0.1468(4)	0.5309(9)	0.3862(4)	0.0234(15)
O7	*8f*	0.0021(3)	0.5201(8)	0.3799(4)	0.0234(15)
O8	*8f*	0.1004(4)	-0.1001(7)	0.4328(4)	0.0234(15)
O9	*8f*	-0.0455(5)	0.3160(10)	0.4658(3)	0.0234(15)
O10	*8f*	0.2725(4)	0.4652(8)	0.3432(4)	0.0234(15)
O11	*8f*	0.1183(3)	0.5463(11)	0.3288(4)	0.0234(15)
O12	*8f*	0.0871(4)	0.1312(10)	0.3226(3)	0.0234(15)

Monoclinic, (Space Group: *C2/c*, No. 15)
a = 17.4717(4) Å, b = 6.9345(2) Å, c = 18.1088(4) Å, V = 114.409(2)°
V = 1997.92(8) Å^3, Z = 4, $\rho_{x\text{-}ray}$ = 4.898 g/cc
R_p = 3.25 %, R_{wp} = 4.50, $\chi 2$ = 3.50
R_B = 2.57 %, R_F = 1.90 %

ESI-II. Typical inter-atomic distances in structure of $K_3Gd_5(PO_4)_6$ at selected temperatures

ESI-IIa. Typical inter-atomic distances in structure of $K_3Gd_5(PO_4)_6$ at selected temperatures

20K		300K		1073K	
Bonds	Bond lengths (Å)	Bonds	Bond lengths (Å)	Bonds	Bond lengths (Å)
Gd1-O2	2.5198(62) × 2	Gd1-O2	2.5263(75) × 2	Gd1-O2	2.5353(76) × 2
Gd1-O7	2.5703(59) × 2	Gd1-O7	2.5701(74) × 2	Gd1-O7	2.6188(78) × 2
Gd1-O11	2.3176(54) × 2	Gd1-O11	2.3311(59) × 2	Gd1-O11	2.3563(65) × 2
Gd1-O12	2.2342(53) × 2	Gd1-O12	2.2454(66) × 2	Gd1-O12	2.3086(71)
CN	8		8		8
Av.BL	2.4105(20)		2.4182(24)		2.4548(26)
Distt (× 10^4)	33.209		30.87		26.736
Gd2-O3	2.3914(75)	Gd2-O3	2.3799(85)	Gd2-O3	2.4337(117)
Gd2-O4	2.4379(52)	Gd2-O4	2.4513(65)	Gd2-O4	2.4925(76)
Gd2-O5	2.3953(67)	Gd2-O5	2.4021(82)	Gd2-O5	2.4217(88)
Gd2-O5	2.5447(61)	Gd2-O5	2.5443(73)	Gd2-O5	2.5979(81)
Gd2-O6	2.5183(62)	Gd2-O6	2.5205(80)	Gd2-O6	2.6663(87)
Gd2-O7	2.4141(45)	Gd2-O7	2.4236(49)	Gd2-O7	2.5187(63)
Gd2-O8	2.3379(45)	Gd2-O8	2.3495(52)	Gd2-O8	2.3856(57)
Gd2-O9	2.3799(78)	Gd2-O9	2.3838(93)	Gd2-O9	2.4217(98)
Gd2-O11	2.6098(59)	Gd2-O11	2.6122(77)	Gd2-O11	2.7025(82)
CN	9		9		9
Av.BL	2.4477(21)		2.4519(25)		2.5156(28)
Distt (× 10^4)	11.953		11.552		18.644
Gd3-O1	2.4062(47)	Gd3-O1	2.4048(59)	Gd3-O1	2.4077(66)
Gd3-O1	2.4305(73)	Gd3-O1	2.4289(84)	Gd3-O1	2.4580(89)
Gd3-O2	2.3521(45)	Gd3-O2	2.3354(54)	Gd3-O2	2.3806(59)
Gd3-O3	2.3554(79)	Gd3-O3	2.3426(97)	Gd3-O3	2.3682(123)
Gd3-O6	2.3729(47)	Gd3-O6	2.3472(59)	Gd3-O6	2.4338(64)
Gd3-O10	2.5739(46)	Gd3-O10	2.5656(59)	Gd3-O10	2.5818(66)
Gd3-O10	2.7451(61)	Gd3-O10	2.7405(79)	Gd3-O10	2.7608(99)
Gd3-O12	2.5988(64)	Gd3-O12	2.5923(80)	Gd3-O12	2.5997(86)
CN	8		8		8
Av.BL	2.4794(21)		2.4697(26)		2.4988(30)
Distt (× 10^4)	29.375		31.276		26.208

CN=coordination number; Av. BL = Average bond length; Distt. = distortion

ESI IIb. Typical inter-atomic distances in structure of $K_3Gd_5(PO_4)_6$ at selected temperatures.

20K		300K		1073K	
Bonds	Bond lengths (Å)	Bonds	Bond lengths (Å)	Bonds	Bond lengths (Å)
K1-O2	3.0251(62)	K1-O2	3.0503(66)	K1-O2	3.0574(71)
K1-O4	2.5719(130)	K1-O4	2.5852(132)	K1-O4	2.6152(147)
K1-O6	2.8080(69)	K1-O6	2.8212(71)	K1-O6	2.7786(71)
K1-O7	3.2081(69)	K1-O7	3.2343(72)	K1-O7	3.2176(78)
K1-O8	2.9868(81)	K1-O8	3.0206(84)	K1-O8	3.0063(86)
K1-O8	3.0907(73)	K1-O8	3.1073(85)	K1-O8	3.1239(94)
K1-O9	2.9609(70)	K1-O9	2.9532(76)	K1-O9	2.9121(77)
K1-O9	2.6599(61)	K1-O9	2.6965(68)	K1-O9	2.6722(71)
K1-O10	2.4643(54)	K1-O10	2.4790(66)	K1-O10	2.5309(68)
CN	9		9		9
Av.BL	2.8640(26)		2.8831(27)		2.8794(29)
Distt ($\times 10^4$)	69.101		68.983		62.641
K2-O7	3.1216(65) × 2	K2-O7	3.1453(75) × 2	K2-O7	3.1784(79) × 2
K2-O8	3.0739(48) × 2	K2-O8	3.0848(62) × 2	K2-O8	3.1177(64) × 2
K2-O11	2.7388(67) × 2	K2-O11	2.7511(71) × 2	K2-O11	2.7577(77) × 2
K2-O12	2.6193(64) × 2	K2-O12	2.6345(75) × 2	K2-O12	2.6151(77) × 2
CN	8		8		8
Av.BL	2.8884(22)		2.9039(25)		2.9172(26)
Distt ($\times 10^4$)	55.01		55.417		66.143

CN=coordination number; Av. BL = Average bond length; Distt. = distortion

ESI IIc. Typical inter-atomic distances in structure of $K_3Gd_5(PO_4)_6$ at selected temperatures.

20K		300K		1073K	
Bonds	Bond lengths (Å)	Bonds	Bond lengths (Å)	Bonds	Bond lengths (Å)
P1-O3	1.6217(68)	P1-O3	1.6165(83)	P1-O3	1.5854(110)
P1-O4	1.5086(108)	P1-O4	1.5167(112)	P1-O4	1.5275(120)
P1-O8	1.5656(68)	P1-O8	1.5767(74)	P1-O8	1.5678(80)
P1-O12	1.5299(57)	P1-O12	1.5381(57)	P1-O12	1.5495(59)
CN	4		4		4
Av.BL	1.5564(39)		1.5620(42)		1.5576(48)
Distt ($\times 10^4$)	7.57		5.954		1.903
P2-O1	1.5628(65)	P2-O1	1.5647(78)	P2-O1	1.5846(80)
P2-O5	1.5515(61)	P2-O5	1.5562(62)	P2-O5	1.5585(62)
P2-O10	1.5437(63)	P2-O10	1.5453(81)	P2-O10	1.5485(85)
P2-O11	1.6173(67)	P2-O11	1.6199(79)	P2-O11	1.5868(80)
CN	4		4		4
Av.BL	1.5688(32)		1.5715(38)		1.5696(39)
Distt ($\times 10^4$)	3.37		3.349		1.108
P3-O2	1.5685(63)	P3-O2	1.5746(72)	P3-O2	1.5660(72)
P3-O6	1.5615(78)	P3-O6	1.5682(91)	P3-O6	1.5666(89)
P3-O7	1.5517(76)	P3-O7	1.5744(79)	P3-O7	1.5402(88)
P3-O9	1.5485(64)	P3-O9	1.5647(74)	P3-O9	1.5747(76)
CN	4		4		4
Av.BL	1.5575(35)		1.5705(40)		1.5619(41)
Distt ($\times 10^4$)	0.259		0.073		0.687

CN=coordination number; Av. BL = Average bond length; Distt. = distortion

ESI-III. Refined positional parameters of $K_3Gd_5(PO_4)_6$ at 20 K.

Atom	*Wyc.*	x	y	z	U(eq) (Å)^2
Gd1	*4e*	0	0.3656(4)	1/4	0.0028(2)
Gd2	*8f*	0.14206(12)	-0.4151(2)	0.48074(11)	0.0028(2)
Gd3	*8f*	0.21910(11)	0.1247(3)	0.29200(11)	0.0028(2)
K1	*8f*	0.0761(2)	0.9044(5)	0.0763(2)	0.0003
K2	*4e*	0	0.8249(7)	1/4	0.0003
P1	*8f*	0.1354(2)	0.0888(6)	0.4138(2)	0.0007(9)
P2	*8f*	0.2094(2)	0.6252(6)	0.3415(2)	0.0007(9)
P3	*8f*	-0.0726(3)	0.4031(6)	0.3816(2)	0.0007(9)
O1	*8f*	0.2027(4)	0.7801(6)	0.2761(3)	0.0156(15)
O2	*8f*	-0.0962(3)	0.2465(7)	0.3129(3)	0.0156(15)
O3	*8f*	0.2325(3)	0.069(2)	0.4256(4)	0.0156(15)
O4	*8f*	0.1216(7)	0.2361(7)	0.4687(6)	0.0156(15)
O5	*8f*	0.2476(3)	0.6712(11)	0.4339(3)	0.0156(15)
O6	*8f*	-0.1443(3)	0.5312(9)	0.3861(3)	0.0156(15)
O7	*8f*	0.0014(3)	0.5240(8)	0.3794(3)	0.0156(15)
O8	*8f*	0.0991(4)	-0.1020(6)	0.4332(3)	0.0156(15)
O9	*8f*	-0.0421(4)	0.3170(9)	0.4683(3)	0.0156(15)
O10	*8f*	0.2726(3)	0.4664(6)	0.3440(3)	0.0156(15)
O11	*8f*	0.1173(3)	0.5469(10)	0.3286(3)	0.0156(15)
O12	*8f*	0.0862(3)	0.1313(8)	0.3231(3)	0.0156(15)

Monoclinic, (Space Group: C2/c, No. 15)
a = 17.4267(4) Å, b = 6.9243(2) Å, c = 18.0410(3) Å, = 114.388(2)°
V = 1982.70(7) Å^3, Z = 4, $\rho_{x\text{-}ray}$ = 4.936 g/cc
R_p = 3.50 %, R_{wp} = 4.86, $\chi 2$ = 4.68
R_B = 2.64 %, R_F = 1.78 %

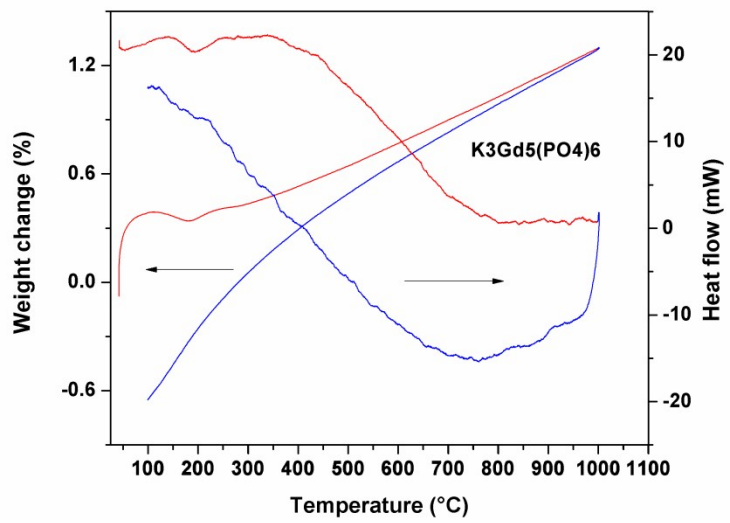
ESI-IV. Crystallographic information files for the structural data for all temperature

SI-IV-KGDPO.cif

ESI-V. Typical inter-atomic distances in $K_3Gd_5(PO_4)_6$ at different temperature.

SI-V-KGDPO-Bond-lengths.xlsx

ESI-VI. TG-DTA plots of $K_3Gd_5(PO_4)_6$ in heating and cooling cycles.



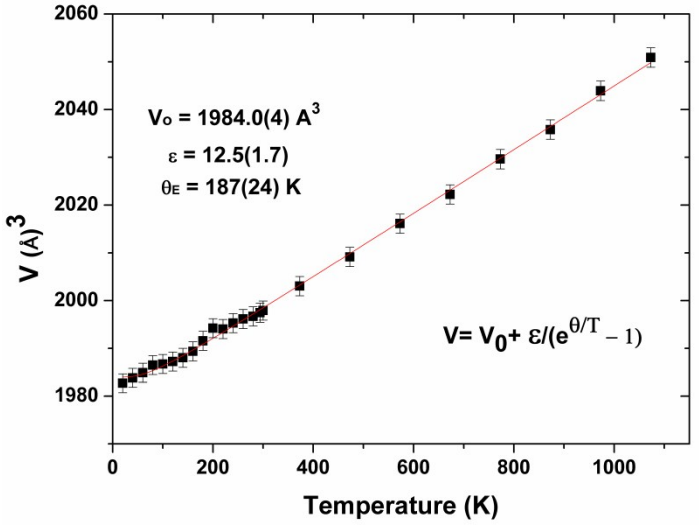
The TG and DTA curves were recorded while heating and cooling of the sample of about 100 mg up to 1273 K in a thermobalance (SETARAM Instrumentation, France) with heating/cooling rate of 10 K/min.

ESI-VII. Refined positional parameters of $K_3Gd_5(PO_4)_6$ at 1073 K.

Atom	Wyc.	x	y	z	U(eq) (Å)^2
Gd1	*4e*	0	0.3669(7)	1/4	0.0268(10)
Gd2	*8f*	0.1446(2)	-0.4132(4)	0.48124(19)	0.0268(10)
Gd3	*8f*	0.2206(2)	0.1245(5)	0.29128(18)	0.0268(10)
K1	*8f*	0.0739(2)	0.9071(5)	0.0748(3)	0.060(5)
K2	*4e*	0	0.8269(8)	1/4	0.060(5)
P1	*8f*	0.1376(3)	0.0897(7)	0.4132(2)	0.022(2)
P2	*8f*	0.2086(3)	0.6238(7)	0.3387(2)	0.022(2)
P3	*8f*	-0.0717(3)	0.3952(6)	0.3808(3)	0.022(2)
O1	*8f*	0.1993(4)	0.7831(8)	0.2739(4)	0.075(4)
O2	*8f*	-0.0957(4)	0.2443(8)	0.3116(3)	0.075(4)
O3	*8f*	0.2307(5)	0.069(3)	0.4223(6)	0.075(4)
O4	*8f*	0.1277(8)	0.2311(10)	0.4723(6)	0.075(4)
O5	*8f*	0.2483(4)	0.6605(14)	0.4307(3)	0.075(4)
O6	*8f*	-0.1385(4)	0.5392(9)	0.3841(4)	0.075(4)
O7	*8f*	-0.0015(4)	0.5242(8)	0.3790(4)	0.075(4)
O8	*8f*	0.0997(4)	-0.0970(7)	0.4325(4)	0.075(4)
O9	*8f*	-0.0444(5)	0.3116(10)	0.4677(3)	0.075(4)
O10	*8f*	0.2722(4)	0.4655(8)	0.3435(5)	0.075(4)
O11	*8f*	0.1187(3)	0.5509(12)	0.3261(4)	0.075(4)
O12	*8f*	0.0893(4)	0.1257(10)	0.3222(3)	0.075(4)

Monoclinic, (Space Group: *C2/c*, No. 15)
a = 17.6214(3) Å, b = 6.9648(1) Å, c = 18.3532(3) Å, = 114.425(1)°
V = 2050.90(7) Å^3, Z = 4, $\rho_{x\text{-}ray}$ = 4.772 g/cc
Rp = 12.58 %, Rwp = 16.91, $\chi 2$ = 2.13
R_B = 7.30 %, R_F = 4.77 %

ESI-VIII. Variation of unit cell volume with temperature. Solid lines indicate fitted line.



ESI-IX. Observed Raman mode frequencies at 80 K and their temperature coefficients in $K_3Gd_5(PO_4)_6$.

Mode frequency (cm^{-1})		$\left(\frac{d\omega}{dT}\right)$ ($cm^{-1}K^{-1}$)	$\frac{1}{\omega}\left(\frac{d\omega}{dT}\right)$ (10^{-5} K^{-1})	$\gamma_{iP}{}^{a}$	Assign.	Mode frequency (cm^{-1})	$\left(\frac{d\omega}{dT}\right)$ ($cm^{-1}K^{-1}$)	$\frac{1}{\omega}\left(\frac{d\omega}{dT}\right)$ (10^{-5} K^{-1})	$\gamma_{iP}{}^{a}$	Assign.
1143.65		-0.02346(3)	-2.05	0.631		387.75	+0.00253(2)	+0.65	-0.2	
1121.79		+0.00169(1)	+0.15	-0.046		303.26	-0.01983(1)	-6.53	2.009	
1116.2		-0.01495(3)	-1.33	0.409		286.37	-0.02111(5)	-7.37	2.267	
1107.79		-0.01663(5)	-1.5	0.461		275.38	-	-	-	
1098.27		-0.02422(8)	-2.2	0.676		267.85	-0.02149(2)	-8.02	2.467	
1089.87	ν3	-0.02137(6)	-1.96	0.603	ν_{as} (PO_4)	258.01	-0.02077(1)	-8.05	2.476	
1081.25		-0.01865(7)	-1.72	0.529		236.26	-0.02712(1)	-11.47	3.529	
1060.38		-0.01777(3)	-1.67	0.513		229.7	-0.01404(8)	-6.11	1.88	
1036.57		-0.01435(5)	-1.38	0.424		219.11	-0.01130(7)	-5.16	1.587	
1027.88		-0.01577(1)	-1.53	0.471		211.52	-0.01517(4)	-7.17	2.206	
1006.08		-0.00840(7)	-0.83	0.255		196.87	-0.00952(4)	-4.83	1.486	
						180.67	-	-	-	
997.5		-0.01444(9)	-1.45	0.446		177.13	-0.01291(4)	-7.28	2.240	
984.59		-0.01057(4)	-1.07	0.329		167.67	-0.00534(1)	-3.18	0.978	
968.57	ν1	-0.00662(2)	-0.68	0.209	ν_{s} (PO_4)	156.05	-0.01070(1)	-6.85	2.107	Lattice modes
940.85		-0.00939(6)	-0.99	0.304		140.51	-0.00526(5)	-3.74	1.151	
						129.79	-0.00824(3)	-6.35	1.954	
						123.15	-0.01286(1)	-10.44	3.212	
641.45		-0.01133(9)	-1.8	0.554		119.92	-	-	-	
630.83		-0.01717(7)	-2.72	0.837		112.04	-0.00983(6)	-8.77	2.698	
624.65		-0.00820(1)	-1.31	0.403	δ_{as}(O-P-O)	103.79	-0.01037(3)	-9.99	3.074	
595.64	ν2	-0.00875(9)	-1.46	0.449		93.15	-	-	-	
587.18		-0.00461(3)	-0.78	0.24		84.13	-	-	-	
540.67		+0.01204(8)	+2.22	-0.683		80.6	-0.00649(5)	-8.05	2.477	
490.08		-	-	-		73.46	-0.00321(3)	-4.36	1.341	
						66.94	-	-	-	
485.13		-0.00303(3)	-0.62	0.191		61.08	-0.00697(1)	-11.41	3.511	
471.5		-	-	-		57.48	-0.00766(4)	-13.32	4.098	
454.72		-0.00025(6)	-0.054	0.017		54.02	-	-		
442.76		-0.00364(2)	-0.82	0.252	δ_{s}(O-P-O)					

434.31	ν4	-0.00359(1)	-0.83	0.255
410.87		-0.00221(3)	-0.54	0.166
398.49		-0.00280(6)	-0.7	0.215

[a] The thermal (dimensionless) Grüneisen parameter is calculated using the volume thermal expansion coefficient α_V as: $= -1/\omega_0(d\omega/dT)/\alpha_V = -(dln\omega/dlnV)_{P = constant}$

ESI-X. Field dependent magnetization of $K_3Gd_5(PO_4)_6$ at different temperatures. Solid lines indicate fitting with calculated magnetization for free ions $K_3Gd_5(PO_4)_6$. Magnetizations were calculated by Brillouin function, $M\ (emu/gm) = N_Z g\ J\ \mu_B \left[\frac{2\,J+1}{2\,J}\left[coth\frac{2J+1}{2J}\frac{g\,J\,\mu_B\ B}{k_B T}\right] - \frac{1}{2J}\left[coth\frac{1}{2J}\frac{g\,J\,\mu_B\ B}{k_B T}\right]\right]$. At 3 K, the magnetization reaches to maximum moment for free Gd3+ ions (with g = 2.00 and J = S= 7/2).