Persistence of the stereochemical activity of the Bi^{3+} lone electron pair in $Bi_2Ga_4O_9$ up to 50 GPa and crystal structure of the high-pressure phase

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Table 1. *Atom positions and equivalent (ambient pressure) or isotropic displacement parameters (Å^2) of the $Bi_2Ga_4O_9$ low-pressure phase up to 15 GPa.*

p / GPa	0.0001	3.3(2)	6.2(3)	8.9(1)	14.9(3)
Bi, x	0.32564(4)	0.3318(1)	0.3368(1)	0.3416(1)	0.3514(2)
Bi, y	0.17119(3)	0.16775(7)	0.1646(5)	0.1633(5)	0.1620(2)
Bi, z	0	0	0	0	0
Bi, $U_{eq/iso}$	0.0047(1)	0.0063(2)	0.0066(4)	0.0064(3)	0.0046(4)
Ga(1), x / y	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0
Ga(1), z	0.2583(1)	0.2571(3)	0.2568(4)	0.2555(4)	0.258(2)
Ga(1), $U_{eq/iso}$	0.0031(2)	0.0046(3)	0.0048(5)	0.0043(5)	0.0050(9)
Ga(2), x	0.1487(1)	0.1476(3)	0.1472(3)	0.1462(3)	0.1437(5)
Ga(2), y	0.33727(8)	0.3354(2)	0.335(1)	0.332(1)	0.3282(5)
Ga(2), z	0.5	0.5	0.5	0.5	0.5
Ga(2), $U_{eq/iso}$	0.0034(2)	0.0054(3)	0.0043(5)	0.0042(5)	0.0061(9)
O(1), x	0.3528(8)	0.347(2)	0.350(2)	0.348(2)	0.342(3)
O(1), y	0.4312(6)	0.428(2)	0.423(8)	0.427(9)	0.427(3)
O(1), z	0	0	0	0	0
O(1), $U_{eq/iso}$	0.005(1)	0.009(2)	0.008(3)	0.011(4)	0.003(5)
O(2), x	0.3700(8)	0.371(2)	0.374(2)	0.373(2)	0.374(3)
O(2), y	0.4070(6)	0.405(2)	0.392(7)	0.390(6)	0.391(3)
O(2), z	0.5	0.5	0.5	0.5	0.5
O(2), $U_{eq/iso}$	0.006(1)	0.011(3)	0.009(3)	0.007(3)	0.008(7)
O(3), x	0.1301(5)	0.135(2)	0.135(2)	0.136(2)	0.140(2)
O(3), y	0.2072(4)	0.205(1)	0.209(5)	0.207(5)	0.200(2)
O(3), z	0.2422(7)	0.242(2)	0.240(2)	0.239(2)	0.246(8)
O(3), $U_{eq/iso}$	0.006(1)	0.008(2)	0.009(2)	0.008(2)	0.006(4)
O(4), x / y / z	0 / 0.5 / 0.5	0 / 0.5 / 0.5	0 / 0.5 / 0.5	0 / 0.5 / 0.5	0 / 0.5 / 0.5
O(4), $U_{eq/iso}$	0.028(2)	0.047(9)	0.04(1)	0.06(2)	0.02(1)

Table 2. *Refinement results of atomic displacement parameters (Å^2) for $Bi_2Ga_4O_9$ at ambient conditions.*

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Bi	0.0032(2)	0.0053(2)	0.0057(2)	0.0000(0)	0.0000(0)	-0.00041(8)
Ga(1)	0.0025(4)	0.0053(3)	0.0014(3)	0.0000(0)	0.0000(0)	0.0002(2)
Ga(2)	0.0026(4)	0.0051(3)	0.0025(3)	0.0000(0)	0.0000(0)	-0.0002(2)
O(1)	0.006(3)	0.005(2)	0.003(2)	0.0000(0)	0.0000(0)	-0.002(2)
O(2)	0.004(3)	0.011(2)	0.002(2)	0.0000(0)	0.0000(0)	-0.005(2)
O(3)	0.004(2)	0.008(1)	0.004(1)	-0.002(1)	0.000(1)	-0.003(1)
O(4)	0.025(4)	0.017(3)	0.044(4)	0.0000(0)	0.0000(0)	0.012(3)

Table 3. *Atom positions and isotropic displacement parameters ($Å^2$) of the $Bi_2Ga_4O_9$ high-pressure phase at 21.4(5) and 30.5(5) GPa.*

Atom	x	y	z	U_{iso}
		21.4(5) GPa		
Bi(1)	0.3689(2)	0.16752(1)	0.02244(2)	0.0048(3)
Ga(1)	-0.0244(5)	0.0082(5)	0.1251(6)	0.0042(8)
Ga(2A)	0.1413(8)	0.3410(6)	0.25	0.004(1)
Ga(2B)	0.6225(8)	0.2020(5)	0.25	0.004(1)
O(1)	0.335(3)	0.426(2)	0.011(3)	0.003(2)
O(2A)	0.397(5)	0.377(3)	0.25	0.003(2)
O(2B)	0.841(4)	0.080(4)	0.25	0.003(2)
O(3A)	0.102(3)	0.217(4)	0.121(3)	0.003(2)
O(3B)	0.672(3)	0.308(2)	0.114(3)	0.003(2)
O(4)	0.069(5)	0.552(4)	0.25	0.003(2)
		30.5(5) GPa		
Bi(1)	0.38052(7)	0.16686(6)	0.02679(7)	0.0042(2)
Ga(1)	-0.0282(2)	0.0105(2)	0.1241(2)	0.0036(4)
Ga(2A)	0.1331(3)	0.3431(3)	0.25	0.0042(5)
Ga(2B)	0.6218(3)	0.2104(3)	0.25	0.0041(5)
O(1)	0.327(1)	0.425(1)	0.017(1)	0.003(2)
O(2A)	0.403(2)	0.381(2)	0.25	0.005(3)
O(2B)	0.827(2)	0.073(2)	0.25	0.015(4)
O(3A)	0.097(1)	0.220(1)	0.120(1)	0.005(2)
O(3B)	0.680(1)	0.312(1)	0.113(2)	0.010(2)
O(4)	0.076(2)	0.559(2)	0.25	0.012(4)

Table 4. *Pressure dependence of Raman band positions (cm^{-1}) of $Bi_2Ga_4O_9$ and mode-Grüneisen-parameters γ for the modes of the low-pressure structure. Abbreviations: vw = very weak, w = weak, s = strong, vs = very strong, sh = shoulder.*

Band assignment† - p / GPa	0.0001*	0.0001	0.9(1)	2.0(1)	3.5(1)	4.6(1)	6.0(1)	7.0(1)	7.8(1)	9.2(1)	10.0(1)	11.1(1)	12.3(3)	15.4(1)	17.3(1)	18.4(2)	19.4(1)	20.8(1)	21.8(1)	24.0(1)	25.3(2)	26.5(1)	27.6(1)	$d\nu/dP$	γ
Bi−O−Bi bend	102 w															118 vw	120	122	122	125	126	128			
Bi−O−Bi bend	122 w						128	129	130	131	132	134	135	138.5	137	136	134.5	136	137	140	141	143	144	1.12	0.94
															154	156	157	159	160	162					
	173.5 vw	172.5		175.5											169	168 vs	167	166	164	165	164	165	165		
	183 vw	183	184	185	187	187.5	188	189	190.5	191	192	192.5	193	195										0.81	0.45
Bi−O stretch	201.5 s	201	202	203	204	204	204	204	204.5	205	205	205	206	204.5	203.5	203.5 s	203.5	204	204	204	204	205	205	0.24	0.12
	208.5 vw	208.5	209	210	211	212	211.5	212	212	212.5	213.5	214												0.45	0.22
	215.5 w	215.5	217	217.5	219	219.5	220.5	221	222	222.5	222.5	223	223.5	226									0.64	0.30	
Bi−O stretch	239	239.5	239	238.5	238	238	237.5	237	238	238	238	238	238 s	240.5	240	243	244	241	245	246	246	247	0.02	0.01	
																			255 sh	256	258	259	262		
															266.5	270 s	273	276	278	284	287	290	294		
																298 vw	301.5	304	307	310	312	315	316		
ν_2 O−Ga−O bend (GaO_4)	294 w	293	294.5	297.5	302	302.5	305.5	308	311	315	314	316	322	331.5	327.5	329 w	332.5	335	337	341	344	345	348	2.40	0.84
ν_5 O−Ga−O bend (GaO_6)	321.5 s	321.5	323.5	325.5	328	329.5	331.5	333	334	335.5	337.5	339	339.5	343	353	357	358.5	361						1.42	0.45
	349.5 sh		350.5	351.5	353		370.5	372	373	375	377	379	379	384.5	395.5	401 vw	404	409						2.63	0.77
ν_2 Ga−O stretch (GaO_6)	357.5 vs	357.5	362	367.5	373	377.5	382.5	387	389.5	394	398.5	402	405.5	416	422	425 s	427	430	433	438	440	443	446	3.82	1.09
ν_1 Ga−O stretch (GaO_6)	442	442	445.5	450.5	455	459	465	468	471	475	479	481	485	492										3.42	0.79
ν_3 Ga−O stretch (GaO_6)	477.5 w	475.5	481	481	487	492	498	502	505	510	514	517	520	530.5	540.5	542 w	543	547	549	555	557	561	563	3.68	0.79
				491.5 w	502	508.5	517.5	524	528	536	539	546	550		586.5	588 w	589	592	594	599	604	606	607	5.83	1.25
															644.5	645	643.5	644.5	646	650	651	654	656		
Ga−O−Ga bend (GaO_4)	591.5 s	591	595.5	600.5	608	612	619	622	625	630	635	638	642	653	657	661.5	656.5	658.5		659	664	665	669	4.08	0.70
ν_1,ν_3 Ga−O stretch (GaO_4)	698.5 s	698.5	704.5	711	719	724.5	731.5	736	740	746	753	757	762	775.5	775.5	780	779.5	782	784	788.5	791	794	798	5.05	0.74
Ga−O stretch (GaO_4) ∥ [001]	781 w		792.5	797	807	812	820.5	825	829	836	841	843	848	858.5		871.5 vw	870.5	870.5	872	875	877.5	876	879	4.79	0.63
																886.5 vw	886.5	890							

† Band positions and assignments at ambient conditions from Beran *et al.* (2008).