

**Persistence of the stereochemical activity of the Bi³⁺
lone electron pair in Bi₂Ga₄O₉ up to 50 GPa and crystal
structure of the high-pressure phase**

ALEXANDRA FRIEDRICH,^{a*} ERICK A. JUAREZ-ARELLANO,^{a1} EIKEN HAUSSÜHL,^a
REINHARD BOEHLER,^{b2} BJÖRN WINKLER,^a LEONORE WIEHL,^a
WOLFGANG MORGENROTH,^{a,c} MANFRED BURIANEK^d AND MANFRED MÜHLBERG^d

^a*Institut für Geowissenschaften, Goethe Universität Frankfurt, Altenhöferallee 1,
D-60438 Frankfurt a.M., Germany, ^bMax-Planck Institut für Chemie, D-55020
Mainz, Germany, ^cc/o DESY/HASYLAB, D-22603 Hamburg, Germany, and
^dInstitut für Kristallographie, Universität zu Köln, D-50674 Cologne, Germany.*

E-mail: friedrich@kristall.uni-frankfurt.de

(Received 0 XXXXXXXX 0000; accepted 0 XXXXXXXX 0000)

¹ Present address: Universidad del Papaloapan, Circuito Central 200, Parque Industrial, Tuxtpec 68301, México.

² Present address: Geophysical Laboratory, Carnegie Institution of Washington, Washington, DC 20015, USA.

Table 1. *Atom positions and equivalent (ambient pressure) or isotropic displacement parameters (\AA^2) of the $\text{Bi}_2\text{Ga}_4\text{O}_9$ 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 (\AA^2) for $\text{Bi}_2\text{Ga}_4\text{O}_9$ 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 (\AA^2) of the $\text{Bi}_2\text{Ga}_4\text{O}_9$ 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 $\text{Bi}_2\text{Ga}_4\text{O}_9$ 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† - <i>p</i> / 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						128	129	130	131	132	134	135	138.5	137	118 vw	120	122	122	125	126	128	144	1.12	0.94	
Bi-O-Bi bend	122 w														154	136	134.5	136	137	140	141	143	144			
Bi-O stretch	173.5 vw	172.5	175.5												169	156	157	159	160	162	164	165	165		0.81	0.45
	183 vw	183	185	187	187.5	188	189	190.5	191	192	192.5	192.5	193	195	203.5 s	168 vs	203.5 s	203.5	204	204	204	205	205		0.24	0.22
	201.5 s	201	202	203	204	204	204	204.5	205	205	205	205	206	204.5											0.30	0.01
	208.5 vw	208.5	209	210	211	211.5	212	212	212.5	212.5	213.5	214	223.5	226											0.64	0.45
	215.5 w	215.5	217	217.5	219	219.5	220.5	221	222	222.5	222.5	223	223.5	226	240.5										0.30	0.01
	239	239.5	239	238.5	238	238	237.5	237	238	238	238	238	238 s	240.5		243	244	241	241	245	246	247	247		0.30	0.01
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	266.5	270 s	273	276	278	284	287	290	294		2.40	0.84
ν_3 O-Ga-O bend (GaO_6)	321.5 s	321.5	323.5	325.5	328	320.5	331.5	333	334	335.5	337.5	339	339.5	343	327.5	298 vw	301.5	304	307	310	312	315	316		1.42	0.45
	349.5 sh	350.5	351.5	353	353	370.5	372	373	373	375	377	379	379	384.5	353	329 w	332.5	335	337	341	344	345	348		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	401 vw	404	409	409	433	440	443	446		3.82	1.09
ν_1 Ga-O stretch (GaO_6)	442	442	445.5	450.5	455	439	465	468	471	475	479	481	485	492	425 s	427	430	430	433	438	440	443	446		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		3.08	0.79
															586.5	588 w	589	592	594	599	604	607	607		5.83	1.25
Ga-O-Ga bend (GaO_4)	591.5 s	591	595.5	600.5	608	612	619	622	625	630	635	638	642	653	644.5	645	643.5	644.5	646	650	651	654	656		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	687	661.5	656.5	658.5	658.5	664	665	669	669		5.05	0.74
Ga-O stretch (GaO_6) [001]	781 w	792.5	797	797	807	812	820.5	825	829	836	841	843	848	858.5	775.5	871.5 vw	870.5	870.5	872	875	875.5	876	879		4.79	0.63
																886.5 vw	886.5	890							4.79	0.63

†

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