Pressure-induced phase transitions of piezoelectric single crystals from langasite family: La3Nb0.5Ga5.5O14 and La3Ta0.5Ga5.5O14

A. Pavlovska,[a] S. Werner,[a]* B. Maximov[b] and B. Mill[c]

[a]Universität München, Institut für Kristallographie und Angewandte Mineralogie, Theresienstr. 41, D-80333 München, Germany, [b] Institute of Crystallography, RAS, Leninsky prospect 59, 117333 Moscow, Russia and [c]Moscow State University, 119899 Moscow, Russia. E-mail: swerner@epo.org

Synopsis [Click here to enter Synopsis]

Abstract The hydrostatic compression of piezoelectric single crystals of $La_3Nb_{0.5}Ga_{5.5}O_{14}$ (LNG), and $La_3Ta_{0.5}Ga_{5.5}O_{14}$ (LTG), was studied at pressures up to 23GPa in diamond anvil high pressure cells by means of single crystal X-ray diffraction techniques. The reflection intensity data for LNG and LTG were collected at pressures up to 22.8 and 16.7GPa, respectively. Both compounds show anisotropic behaviour under pressure, caused by different bonding parallel to *a*- and *c*- directions. The compression of strongly rigid structure due to high symmetry leads to increasing internal strains and results at pressures 12.4(3)GPa for LNG and 11.7(3)GPa for LTG in transition to lower symmetry. The compressibilities along the *c* axis are almost the same for LNG and LTG in the whole investigated pressure range. In contrast, the pressure dependencies of *a* axis of these materials are similar only for initial phase, whereas the axial compressibilities for the high-pressure polymorphs of LNG and LTG are significantly different to each other. The volume compressibilities of trigonal LNG and LTG (space group *P321*) are about $0.007GPa^{-1}$, respective bulk moduli are 145(3)GPa and 144(2)GPa. The monoclinic high pressure phases (space group *A2*) show differing to each other compressions, which can be explained through a Nb^{5+} to Ta^{5+} substitution. Thus bulk moduli for high pressure polymorphs of LNG and LTG are B_0=93(2)GPa and B_0=128(12)GPa, respectively. The respective volume compressibilities of the high pressure phases at $0.011GPa^{-1}$ for LNG and $0.008GP^{-1}$ for LTG are higher as compared to the initial phases, this effect being more pronounced in the case of LNG.

Keywords: high pressure, langasite family, phase transition, polyhedra

Deposit material:

Table 1 Unit cell parameters of LNG at various pressures

p (GPa)	*a* (Å)	*c* (Å)
0,07(5)	8,225(3)	5,1261(7)
0,15(2)	8,2205(12)	5,1219(6)
0,30(5)	8,2158(18)	5,1193(8)
0,52(2)	8,2113(23)	5,1188(9)
0,80(4)	8,204(3)	5,1172(14)
0,97(3)	8,2011(16)	5,1144(8)
1,60(3)	8,188(2)	5,1125(16)
1,80(2)	8,1831(13)	5,1074(6)
2,39(3)	8,1723(14)	5,1022(14)
3,12(2)	8,1573(23)	5,0992(10)
3,30(5)	8,157(24)	5,099(3)
3,46(2)	8,1487(21)	5,0929(5)
4,49(3)	8,1273(19)	5,0865(7)
4,51(3)	8,133(17)	5,0903(15)
4,50(3)	8,135(3)	5,0912(12)
4,5(3)	8,126(27)	5,083(3)
4,84(2)	8,1200(13)	5,0833(8)
5,08(3)	8,121(3)	5,0843(9)
5,21(5)	8,121(3)	5,0841(22)
5,7(3)	8,108(5)	5,0796(8)
5,89(2)	8,0976(15)	5,0742(8)
6,23(2)	8,1000(20)	5,0781(15)
6,5(3)	8,094(5)	5,0734(7)
6,71(3)	8,0846(28)	5,0695(12)
6,80(3)	8,084(3)	5,0692(12)
7,18(2)	8,0717(15)	5,0654(7)
7,2(3)	8,074(6)	5,0665(8)
7,41(3)	8,0790(18)	5,0682(17)
7,65(6)	8,0700(24)	5,0621(26)
7,80(3)	8,0691(23)	5,0623(13)
7,83(3)	8,070(3)	5,065(3)
8,13(6)	8,0592(25)	5,063(3)
8,64(6)	8,0488(21)	5,0595(15)
9,0(3)	8,035(6)	5,0529(12)
9,4(8)	8,0329(18)	5,0544(13)
9,7(3)	8,024(6)	5,049(4)
9,9(3)	8,014(5)	5,046(3)

10,8(3)	8,003(6)	5,0416(12)
11,7(3)	7,991(6)	5,0374(11)
12,2(3)	7,984(5)	5,0347(11)
12,6(3)	7,958(5)	5,022(3)
13,1(3)	7,956(5)	5,0236(11)
13,1(3)	7,953(5)	5,0232(10)
13,2(3)	7,946(6)	5,0226(11)
13,5(3)	7,932(8)	5,016(5)
13,7(3)	7,938(6)	5,0198(11)
15,2(3)	7,905(6)	5,0121(11)
15,6(3)	7,864(9)	5,007(5)
15,8(3)	7,885(7)	5,0089(12)
16,1(3)	7,879(10)	5,0091(22)
17,3(3)	7,838(9)	5,001(5)
18,5(3)	7,783(5)	4,994(3)
19,4(3)	7,777(6)	4,995(7)
21,7(3)	7,699(11)	4,984(7)
21,8(3)	7,694(9)	4,989(5)
21,85(30)	7,693(14)	4,985(8)
22,85(30)	7,664(7)	4,984(5)

Table 2 Unit cell parameters of LTG at various pressures

p (GPa)	a (Å)	c (Å)
0,70(2)	8,213(4)	8,167(3)
0,97(2)	8,2021(13)	5,1128(6)
1,80(1)	8,1857(15)	5,1072(9)
2,22(2)	8,1798(26)	5,1014(11)
2,34(1)	8,1665(14)	5,0981(15)
2,99(1)	8,1637(24)	5,0965(9)
3,00(1)	8,1587(24)	5,0995(9)
3,38(2)	8,1601(27)	5,0946(9)
3,3(3)	8,155(13)	5,091(5)
3,46(2)	8,1489(15)	5,0931(7)
4,49(2)	8,1295(15)	5,085(8)
5,10(1)	8,1160(15)	5,086(9)
5,13(2)	8,1142(19)	5,0757(9)
5,2(3)	8,113(7)	5,078(3)
5,60(1)	8,109(4)	5,0723(5)
5,96(1)	8,0935(17)	5,0684(9)
6,12(2)	8,1052(14)	5,0744(7)
6,64(1)	8,105(4)	5,064(2)

7,18(2)	8,0742(12)	5,0651(7)
7,30(1)	8,0653(20)	5,0589(7)
7,7(3)	8,061(8)	5,059(3)
7,81(1)	8,0529(22)	5,0532(8)
8,2(3)	8,052(8)	5,057(3)
8,36(1)	8,0478(18)	5,0526(10)
8,75(1)	8,0353(14)	5,0487(5)
9,5(3)	8,022(9)	5,046(4)
10,1(3)	8,017(9)	5,043(4)
11,5(3)	7,981(4)	5,024(3)
12,3(3)	7,976(5)	5,023(3)
12,7(3)	7,972(5)	5,021(3)
13,0(3)	7,969(5)	5,020(3)
13,2(3)	7,962(4)	5,018(4)
13,7(3)	7,947(7)	5,013(4)
14,4(3)	7,944(6)	5,012(3)
15,0(3)	7,939(8)	5,012(4)
16,3(3)	7,926(8)	5,008(4)
16,7(3)	7,872(7)	4,999(3)

Table 3 Structural parameters of LTG refined in the trigonal space-group *P321*

p (GPa)	La- 3e	Ga- 2d	Ga- 3f	O1-2d	O2- 6g			O3- 6g		
	(x; 0; 0)	(1/3; 2/3; z)	(x; 0; 1/2)	(1/3; 2/3; z)	(x; y; z)			(x; y,z)		
	X	Z	X	Z	X	Y	Z	X	Y	Z
0	.42492(7)	.4689(2)	.7617(1)	.822(2)	.4568(7)	.3089(8)	.694(1)	.2194(8)	.0787(8)	.241(1)
0.7	.42586(11)	.4687(6)	.7618(2)	.824(4)	.4518(14)	.3056(16)	.704(3)	.2172(13)	.0731(14)	.243(2)
1.4	.4260(2)	.4698(12)	.7622(5)	.838(7)	.460(2)	.307(2)	.693(3)	.215(2)	.077(2)	.235(3)
2.3	.42651(11)	.4691(3)	.7628(3)	.824(2)	.4566(16)	.3095(16)	.6958(14)	.2195(13)	.0766(16)	.2389(11
3	.42713(10)	.4694(4)	.7634(2)	.822(2)	.4568(12)	.3077(15)	.6969(17)	.2188(13)	.0749(14)	.2404(14
3.3	.42707(11)	.4696(7)	.7636(2)	.833(5)	.4536(13)	.3064(11)	.704(3)	.2188(12)	.0742(12)	.239(2)
5.1	.42799(8)	.4693(5)	.76424(15)	.827(3)	.4539(9)	.3052(9)	.703(2)	.2188(8).	.0736(9)	.2426(18
6.1	.42883(14)	.4695(6)	.7643(3)	.834(4)	.455(16)	.3062(18)	.694(3)	.2166(16)	.0719(18)	.239(2)
6.64	.42912(10)	.4709(6)	.7649(2)	.832(4)	.4575(14)	.3059(14)	.703(3)	.2209(12)	.0749(13)	.243(2)
7.7	.43055(13)	.4742(6)	.7656(3)	.828(4)	.454(2)	.304(3)	.697(4)	.2178(18)	.072(2)	.242(3)
8.15	.43038(17)	.4715(8)	.7651(4)	.840(6)	.455(2)	.302(3)	.688(3)	.2165(2)	.071(2)	.239(3)
9.5	.43218(15)	.4738(5)	.7668(3)	.838(4)	.451(3)	.300(3)	.685(4)	.2170(17)	.071(3)	.241(2)
11.57	.43463(19)	.4795(5)	.7659(4)	.838(3)	.453(4)	.296(3)	.691(3)	.225(2)	.077(3)	.238(2)
11.57	.43460(18)	.4793(5)	.7661(3)	.838(3)	.719(2)	.168(2)	.293(3)	.227(3)	.081(3)	.237(2)
Split					.516(6)	.108(6)	386(8)			
13.2	.43528(17)	.4800(4)	.7660(3)	.834(3)	.452(2)	.293(4)	.695(3)	.225(2)	.076(3)	.238(2)
13.2	.43537(16)	.4801(4)	.7659(3)	.837(3)	.720(2)	.168(2)	.293(3)	.227(2)	.079(2)	.237(2)
Split					.518(5)	.098(5)	375(6)			
14.4	.4362(2)	.4810(6)	.7660(3)	.837(4)	.443(4)	.277(5)	.698(4)	.220(3)	.071(3)	.235(3)
14.4	.4364(2)	.4809(6)	.7665(3)	.842(4)	.726(3)	.172(2)	.289(4)	.226(3)	.078(3)	.239(3)

Split					.517(6)	.106(6)	.376(9)			
16.7	.4381(2)	.4879(9)	.7661(4)	.831(6)	.459(6)	.303(9)	.689(6)	.226(4)	.077(5)	.234(5)
16.7	.4382(3)	.4879(9)	.7660(4)	.833(6)	.721(5)	.169(4)	.291(7)	.227(4)	.076(4)	.242(4)
Split					.507(4)	.093(5)	.384(8)			

Table 4 Structural parameters of LNG refined in the trigonal space-group *P321*

p (GPa)	La-3e	Ga-2d	Ga-3f	O1-2d	O2-6g			O3-6g		
	(x;0;0)	(1/3;2/3;z)	(x;0;1/2)	(1/3;2/3;z)	(x;y;z)			(x;y;z)		
	X	Z	X	Z	X	Y	Z	X	Y	Z
0	.42459(2)	.53124(7)	.76176(4)	.1784(5)	.4563(3)	.3088(3)	.3054(3)	.2188(3)	.0773(3)	.7627(3)
0.8	.42528(12)	.5307(8)	.7624(2)	.182(5)	.4557(14)	.3083(14)	.300(3)	.2128(13)	.0708(18)	.760(3)
1.8	.42575(18)	.5310(2)	.76283(17)	.177(2)	.4548(8)	.3082(10)	.3064(10)	.2186(8)	.0765(10)	.7621(11
3.3	.42652(8)	.5308(5)	.76405(16)	.181(4)	.4546(9)	.3067(9)	.302(2)	.2145(9)	.0720(9)	.759(2)
4.5	.42700(11)	.5305(3)	.7644(2)	.179(2)	.4570(13)	.3093(13)	.3052(15)	.2205(10)	.0735(11)	.7613(14
4.8	.42746(10)	.5307(4)	.76376(19)	.182(3)	.4542(13)	.3089(14)	.3023(18)	.2201(11)	.0750(12)	.7602(19
5.2	.42755(14)	.5298(9)	.7647(3)	.182(7)	.4533(18)	.3083(13)	.304(4)	.2159(11)	.0691(15)	.760(4)
6.8	.42868(8)	.5291(6)	.76526(18)	.184(4)	.4574(10)	.3072(12)	.308(3)	.2180(11)	.0722(11)	.759(3)
7.8	.42902(13)	.5294(6)	.7657(3)	.173(4)	.4535(17)	.307(2)	.317(3)	.217(2)	.0721(14)	.757(3)
9.67	.43162(9)	.5252(5)	.76729(16)	.173(3)	.4537(16)	.306(2)	.311(3)	.2180(11)	.0714(15)	.760(3)
9.9	.43207(11)	.5250(5)	.7672(2)	.171(3)	.4538(18)	.305(2)	.309(3)	.2196(13)	.0719(18)	.760(3)
11.7	.43306(11)	.5231(4)	.7679(2)	.168(3)	.4530(16)	.3045(18)	.310(2)	.2191(17)	.0698(19)	.761(2)
13.1	.43418(15)	.5190(6)	.7666(3)	.168(4)	.447(2)	.295(2)	.302(3)	.2200(19)	.069(2)	.761(3)
13.1	.43427(14)	.5193(5)	.7664(3)	.165(4)	.4471(19)	.289(2)	.293(3)	.2213(18)	.0715(18)	.761(2)
Split					.486(6)	.385(6)	.397(8)			
15.6	.4361(3)	.5125(9)	.7661(4)	.160(7)	.445(4)	.295(7)	.319(5)	.221(4)	.074(4)	.766(4)
15.6	.4361(3)	.5133(9)	.7664(4)	.153(6)	.468(8)	.380(9)	.371(11)	.225(4)	.077(4)	.766(4)
Split					.443(3)	.277(4)	.301(5)			
18.5	.4390(5)	.5075(17)	.7650(8)	.168(8)	.439(8)	.279(8)	.332(8)	.228(7)	.074(7)	.765(6)
18.5	.4392(5)	.5088(16)	.7655(9)	.161(9)	.491(11)	.425(11)	.400(16)	.230(8)	.081(7)	.761(6)
Split					.450(7)	.275(7)	.311(9)			
21.8	.4372(8)	.505(3)	.7681(13)	.15(3)	.435(7)	.287(9)	.379(13)	.239(7)	.072(7)	.760(14)
21.8	.4379(9)	.506(3)	.7675(12)	.11(3)	.496(10)	.467(10)	.458(14)	.223(6)	.066(7)	.768(12)
Split					.412(9)	.290(8)	.369(12)			
22.8	.4405(10)	.501(2)	.7652(17)	.118(17)	.443(14)	.29(2)	.355(17)	.247(12)	.067(13)	.784(12)
22.8	.4398(10)	.501(2)	.7673(18)	.085(17)	.450(13)	.433(15)	.46(2)	.243(11)	.065(11)	.781(11)
Split					.402(12)	.238(12)	.322(15)			

Table 5 Structural parameters of LNG refined in the monoclinic space-group *A2*

p (GPa)		13.1	15.6	18.5	21.85	22.85
La1	x	.002(2)	.004(2)	.008(3)	.001(5)	.003(4)
	y	.2168(11)	.2173(12)	.2189(16)	.2201(14)	.2197(18)

	z	.7825(8)	.7810(7)	.7792(11)	.782(2)	.7787(16)
La2	y	.4345(14)	.4363(13)	.438(2)	.439(3)	.439(4)
Ga1/ Nb	y	.002(3)	.002(4)	.009(4)	.005(6)	.011(6)
Ga2	x	.4814(8)	.4877(12)	.491(3)	.496(5)	.498(3)
	y	.498(2)	.498(2)	.498(4)	.491(3)	.498(4)
	z	.1658(13)	.1657(14)	.165(2)	.168(3)	.168(3)
Ga3	y	.233(4)	.236(6)	.236(5)	.235(3)	.230(7)
Ga4	x	.502(3)	.500(3)	.512(4)	.500(7)	.503(10)
	y	.381(2)	.3843(19)	.385(2)	.379(3)	.385(3)
	z	.3841(13)	..3844(10)	.3840(14)	.384(6)	.383(3)

p (GPa)		13.1	15.6	18.5	21.85	22.85
O1	x	.167(5)	.167(10)	.157(14)	.17(3)	.14(2)
	y	.507(14)	514(13)	.50(2)	.534(11)	.528(16)
	z	.172(6)	.173(8)	.173(10)	.184(15)	.17(2)
O2	x	.281(10)	.29(2)	.35(3)	.39(3)	.31(3)
	y	.372(8)	.382(12)	.352(16)	.335(11)	.329(19)
	z	.092(3)	.078()	.064(13)	.100(13)	.078(13)
O3	x	.387(14)	.305(16)	.30(3)	.37(3)	.38(4)
	y	.142(12)	.051(8)	.055(16)	.130(12)	.167(19)
	z	.761(6)	.717(5)	.736(12)	.787(14)	.751(13)
O4	x	.290(8)	.40(3)	.41(2)	.43(4)	.36(4)
	y	.286(5)	.273(16)	.270(15)	.313(12)	.326(19)
	z	.145(3)	.198(10)	.219(9)	.129(13)	.161(12)
O5	x	.746(9)	.75(2)	.764(17)	.79(3)	.82(3)
	y	.123(6)	.125(14)	.132(11)	.136(10)	.117(18)
	z	.914(3)	.917(9)	.952(10)	.935(15)	.897(13)
O6	x	.207(8)	.21(3)	.235(17)	.23(3)	.21(4)
	y	.006(6)	.03(2)	.029(12)	.057(11)	.050(17)
	z	.115(3)	.112(12)	.129(10	.124(14)	.129(15)
O7	x	.736(18)	.80(3)	.81(3)	.69(4)	.71(3)
	y	.191(13)	.20(2)	.205(18)	.233(10)	.197(17)
	z	.967(8)	.938(13)	.996(13)	.910(16)	.926(17)

Table 6 Structural parameters of LTG refined in the monoclinic space-group *A2*

p (GPa)		11.57	13.2	14.4	16.7
La1	x	.0016(14)	.0003(17)	.0021(19)	.005(3)
	y	.7834(8)	.7811(9)	.781(1)	.2188(10)
	z	.2182(5)	.2178(6)	.2193(11)	.2202(7)

La2	y	.4339(13)	.4332(13)	.4326(9)	.4367(8)
Ga1/ Nb	y	.002(3)	.003(3)	.000(2)	.0046(15)
Ga2	x	.4799(8)	.4800(8)	.4822(14)	.497(2)
	y	.499(4)	.497(3)	.496(3)	.500(3)
	z	.1669(13)	.1659(13)	.165(2)	.166(2)
Ga3	y	.763(3)	.763(4)	.771(2)	.230(4)
Ga4	x	.496(3)	.495(3)	.495(5)	.500(2)
	y	.618(3)	.616(3)	.615(3)	.6160(13)
	z	.3848(12)	.3834(12)	.381(1)	.3815(7)

p (GPa)		11.57	13.2	14.4	16.7
O1	x	.164(5)	.167(6)	.166(8)	.169(10)
	y	.013(11)	.008(18)	.006(18)	.010(14)
	z	.334(8)	.326(7)	.330(9)	.336(9)
O2	x	.286(14)	.282(10)	.30(3)	.35(4)
	y	.640(15)	.648(8)	.64(2)	.64(2)
	z	.089(7)	.093(4)	.079(4)	.078(13)
O3	x	.298(10)	.304(11)	.297(16)	.39(2)
	y	.057(10)	.073(9)	.033(9)	.158(10)
	z	.776(5)	.779(5)	.778(11)	.756(6)
O4	x	.379(19)	.360(12)	.35(2)	.308(15)
	y	.282(17)	.288(10)	.285(14)	.28(4)
	z	.182(9)	.192(6)	.190(10)	.138(10)
O5	x	.254(15)	.266(12)	.276(14)	.23(3)
	y	.857(15)	.885(10)	.896(10)	.847(13)
	z	.920(9)	.921(6)	.917(6)	.919(9)
O6	x	.206(8)	.198(9)	.204(13)	.19(4)
	y	.986(9)	.989(11)	.988(8)	.991(18)
	z	.120(4)	.118(4)	.120(4)	.129(10)
O7	x	.26(2)	.249(11)	.226(16)	.27(3)
	y	.18(2)	.191(11)	.194(11)	.175(14)
	z	.978(8)	.964(4)	.968(5)	.975(8)