

# Single-crystal neutron diffraction investigation on crystals belonging to the langasite family: a comparative study

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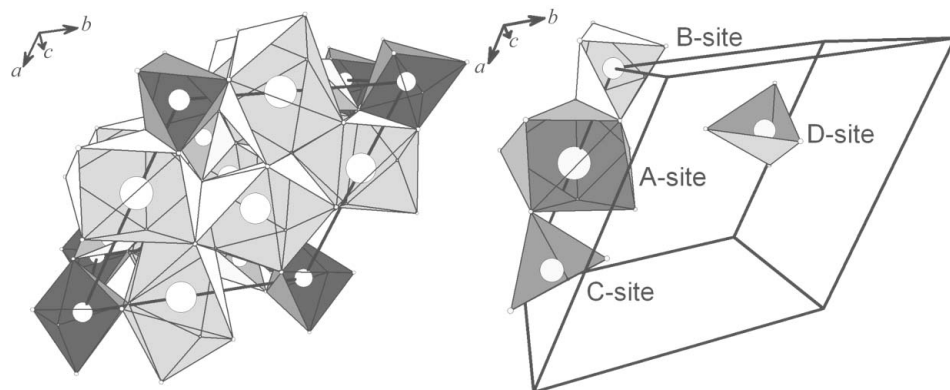
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Crystals of the langasite family are of interest as they are piezoelectric in different devices. The properties of these classes of crystals can be modified within certain limits by isomorphous substitution. Single-crystal neutron diffraction studies were carried out for LGT ( $\text{La}_3\text{Ga}_{5.5}\text{Ta}_{0.5}\text{O}_{14}$ ), LGST ( $\text{La}_3\text{Ga}_{5.25}\text{Ta}_{0.25}\text{Si}_{0.5}\text{O}_{14}$ ) and LGZrT ( $\text{La}_3\text{Ga}_{5.25}\text{Ta}_{0.25}\text{Zr}_{0.5}\text{O}_{14}$ ) as the neutron study gives a better average picture of the crystal properties over a macroscopic region of the grown crystal. The effect of small substitutions at various sites on the piezoelectric properties of the crystal was studied.

## 1. Introduction

The  $\text{La}_3\text{Ga}_{5.5}\text{Ta}_{0.5}\text{O}_{14}$  crystals belong to the large group of compounds with the structure of calcium gallium germanate,  $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$  (Belokoneva *et al.*, 1980). Later these compounds were called langasites with the chemical formulae of LGS ( $\text{La}_3\text{Ga}_5\text{SiO}_{14}$ ) crystals. More than a hundred compounds of different chemical composition with the langasite structure have been synthesized so far (Mill & Pisarevsky, 2000). Interest in these crystals grew because of their unique physical properties, which can be modified within certain limits by isomorphous substitutions. The crystals can be doped with elements from the iron and lanthanide groups. Compounds of the langasite family form an important class of promising commercial materials because of their interesting material properties like high piezoelectric coupling, unique temperature compensation and low acoustic losses. The langasite crystals are of greatest interest as piezoelectrics in different devices for the control of the radio signal frequency. In particular, the resonators were made out of these crystals as they were found to have higher relative bandwidths (Smythe *et al.*, 1999; Kludzin *et al.*, 2005).

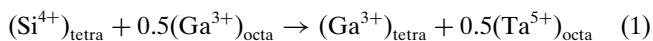
The mechanism for the piezoelectricity of langasite could be successfully explained by careful analysis of the crystal structure (Iwataki *et al.*, 2001). The structure of langasite contains four distinct cationic sites with the general formula  $A_3BC_3D_2O_{14}$ , where *A* is the dodecahedral site, *B* is the octahedral site, *C* is the large tetrahedral site and *D* is the small tetrahedral site. Fig. 1 shows the langasite structure with four kinds of cationic sites. The piezoelectricity of langasite is generated along the [100] direction and is found to be strongly dependent on the width of the dodecahedron ( $A_L$ ) and octahedron ( $B_L$ ) along the [100] direction (Araki *et al.*, 2007). Owing to the availability of a number of sites, which allow easy substitution, over 100 combinations of compositions with the langasite structure have been reported. It was indicated that cation size tolerance is higher for *A* and *D* sites compared with *B* and *C* sites (Chai *et al.*, 2000); it was further shown that the *C*



**Figure 1**  
Langasite structure with four different cations.

site is the most critical, and all the ions which can be substituted in the *C* site should have a nearly identical ionic size.

In the LGS crystal the *A* site is occupied by  $\text{La}^{3+}$  ions, *B*, *C* and half the *D* sites are occupied by  $\text{Ga}^{3+}$  ions and the remaining half by  $\text{Si}^{4+}$  ions. It was found that langatate (LGT:  $\text{La}_3\text{Ga}_{5.5}\text{Ta}_{0.5}\text{O}_{14}$ ) showed better technical characteristics compared with LGS crystals (Kludzin *et al.*, 2005; Dudka *et al.*, 2009). LGT crystals were obtained by substituting  $\text{Si}^{4+}$  in LGS with  $\text{Ga}^{3+}$  and  $\text{Ta}^{5+}$ , as described below.



The electronic structures of LGS and LGT are similar. In this manuscript we have studied and compared single-crystal neutron structures of LGT, LGST ( $\text{La}_3\text{Ga}_{5.25}\text{Ta}_{0.25}\text{Si}_{0.5}\text{O}_{14}$ ) and LGZrT ( $\text{La}_3\text{Ga}_{5.25}\text{Ta}_{0.25}\text{Zr}_{0.5}\text{O}_{14}$ ). This study is expected to provide insight into structural changes due to substitution in LGT, LGST and LGZrT, and the effect of this change on the corresponding change in material properties. The crystal structure of LGT has already been studied using X-rays (Dudka *et al.*, 2009). Since the crystals used for single-crystal neutron diffraction are much larger than those used for single-crystal X-ray investigations, a neutron study gives a better average picture of the crystal properties (Kuz'michva *et al.*, 2008) over a macroscopic region of the grown specimen.

## 2. Crystal growth

LGT and LGST crystals melt congruently at 1753 K. They were grown in platinum or iridium bowls with crystal diameters of up to 30 and 100 mm. The crystals were grown by Chokhralskii's method with the use of high-frequency heating. The blend was synthesized by fritting the particularly pure lanthanum, gallium and tantalum oxides at a temperature of  $\sim 1473$  K. The crystals grow better with the orientation along the threefold axis, in air or in a stream of oxygen and nitrogen admixture. As a rule crystals without electrical and optical twins can be grown. The crystals are transparent in the 450–5000 nm area. They have a very high refractive index (1.96–1.98) at the birefringence value 0.01 and a relative rotation of

the plane of polarization almost five times less than that of quartz crystals (Molchanov *et al.*, 2001).

## 3. Single-crystal neutron diffraction

Colourless transparent cuboidal crystals of LGT, LGST and LGZrT with approximate dimensions  $3 \times 3 \times 3$  mm were used to collect the single-crystal data at room temperature. The crystals were mounted on a four-circle single-crystal diffractometer with a  $\text{BF}_3$  point detector located at the Dhruva Reactor at Trombay. The

neutron wavelength used was  $0.995 \text{ \AA}$  obtained from the Cu(220) monochromator crystal. The unit-cell values and orientation matrix were refined by the least-squares technique from optimized  $2\theta$  angles of 50 reflections using the *REFINE* program (Srikanta & Sequeira, 1968). The reflections were chosen to randomly sample reciprocal space. The integrated neutron counts for Bragg reflections were measured in the symmetrical setting of the diffractometer using the  $\theta$ – $2\theta$  coupled step-scan mode ( $0.1^\circ$  step in  $2\theta$ ). The background was scanned for a minimum of  $1^\circ$  on either side. The standard reflections were measured after every 25 reflections. The variation of the standard reflection intensity was within 3%. Squared observed structure factors were obtained from integrated intensities using the program *DATRED* (Srikanta, 1968). These were corrected for absorption. The structural parameters obtained using X-rays were used as the starting parameters and were subjected to a series of isotropic and anisotropic full-matrix least-squares refinement using *SHELXL* (Sheldrick, 2008). In the initial stages of refinement the weight ( $w$ ) was taken to be  $1/\sigma(F_o^2)$ , which was derived using counting statistics. In the case of LGT, Ga1 (0, 0, 0) and Ta occupy the same site. Similarly in the case of LGST, Ga1 (0, 0, 0) and Ta occupy the same site, and Ga3 (0.3333, 0.6667, 0.5320) and Si occupy the same site, whereas in the case of LGZrT, Zr occupies the Ga1 (0, 0, 0) and Ga2 (0.7583, 0, 0.5) site. Hence these atoms were constrained to have the same coordinates and atomic displacement parameters. Their occupancies were refined using the SUMP instruction. Crystallographic and refinement details are summarized in Table 1.<sup>1</sup>

## 4. Results and discussion

The cell volume follows the order LGS ( $294.22 \text{ \AA}^3$ ; Kuz'michva *et al.*, 2008) < LGST ( $297.7 \text{ \AA}^3$ ) < LGT ( $300.2 \text{ \AA}^3$ ) < LGZrT ( $303.4 \text{ \AA}^3$ ), with the lowest being LGS and the

<sup>1</sup> Supplementary data for this paper are available from the IUCr electronic archives (Reference: BP5031). Services for accessing these data are described at the back of the journal.

**Table 1**

Crystallographic and refinement details.

For all structures: trigonal,  $P3_21$ ,  $Z = 1$ . Experiments were carried out at 300 K with neutron radiation,  $\lambda = 0.99500 \text{ \AA}$  using a four-circle diffractometer.

	LGT	LGST	LGZrT
Crystal data			
Chemical formula	$\text{La}_3\text{Ga}_{5.61}\text{Ta}_{0.41}\text{O}_{14}$	$\text{La}_3\text{Ga}_{5.34}\text{Ta}_{0.29}\text{Si}_{0.36}\text{O}_{14}$	$\text{La}_3\text{Ga}_{5.48}\text{Ta}_{0.03}\text{Zr}_{0.5}\text{O}_{14}$
$M_r$	1106.05	1075.12	1073.18
$a, c$ ( $\text{\AA}$ )	8.224 (4), 5.126 (1)	8.195 (7), 5.118 (1)	8.256 (5), 5.141 (2)
$V$ ( $\text{\AA}^3$ )	300.2 (2)	297.7 (4)	303.5 (3)
$\mu$ ( $\text{mm}^{-1}$ )	0.02	0.02	0.01
Crystal size (mm)	$3 \times 3 \times 3$	$3 \times 3 \times 3$	$3 \times 3 \times 3$
Data collection			
Absorption correction	Integration dated	Integration dated	Integration dated
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	374, 366, 355	461, 454, 440	354, 354, 341
Completeness (%)	99	99	100
$R_{\text{int}}$	0.025	0.022	0.000
Refinement			
$R[F^2 > 2\sigma(F^2)]$ , $wR(F^2)$ , $S$	0.043, 0.135, 1.17	0.045, 0.134, 1.14	0.027, 0.071, 1.14
No. of reflections	366	454	354
No. of parameters	40	42	43
No. of restraints	1	2	2
$\Delta\rho_{\text{max}}$ , $\Delta\rho_{\text{min}}$ ( $\text{e \AA}^{-3}$ )	1.15, -1.06	0.83, -0.83	0.60, -0.71

Computer programs: SCAD, REFINE, DATRED, SHELXL97 (Sheldrick, 2008), DIAMOND (Crystal Impact GbR, 2009).

**Table 2**

Atomic parameters of LGT, LGST and LGZrT.

Structure	Atoms	$x/a$	$y/b$	$z/c$	Occupancy	$U_{\text{eq}}$
LGT	La	0.4246 (3)	0.0	0.0	1.0	0.0121 (6)
LGST	La	0.4222 (3)	0.0	0.0	1.0	0.0077 (6)
LGZrT	La	0.4258 (2)	0.0	0.0	1.0	0.0096 (4)
LGT	Ga1, Ta	0.0	0.0	0.0	0.61 (3), 0.41 (2)	0.0119 (10)
LGST	Ga1, Ta	0.0	0.0	0.0	0.75 (3), 0.28 (1)	0.0104 (10)
LGZrT	Ga1, Ta, Zr1	0.0	0.0	0.0	0.55 (4), 0.027 (3), 0.42 (5)	0.0099 (9)
LGT	Ga2	0.7608 (3)	0.0	0.5	1.0	0.0132 (6)
LGST	Ga2	0.7640 (3)	0.0	0.5	1.0	0.0081 (6)
LGZrT	Ga2, Zr2	0.7583 (2)	0.0	0.5	0.977 (8), 0.026 (5)	0.0103 (4)
LGT	Ga3	0.3333	0.6667	0.4696 (5)	1.0	0.0098 (6)
LGST	Ga3, Si	0.3333	0.6667	0.5321 (6)	0.79 (1), 0.18 (2)	0.0067 (7)
LGZrT	Ga3	0.3333	0.6667	0.5309 (3)	1.0	0.0091 (4)
LGT	O1	0.3333	0.6667	0.8193 (6)	1.0	0.0133 (8)
LGST		0.3333	0.6667	0.8127 (7)	1.0	0.0122 (8)
LGZrT		0.3333	0.6667	0.8194 (4)	1.0	0.0118 (5)
LGT	O2	0.4565 (3)	0.3097 (3)	0.6936 (5)	1.0	0.0190 (7)
LGST		0.4609 (3)	0.3108 (3)	0.6887 (4)	1.0	0.161 (6)
LGZrT		0.4578 (2)	0.3108 (3)	0.6949 (3)	1.0	0.0151 (4)
LGT	O3	0.2193 (3)	0.0777 (3)	0.7644 (4)	1.0	0.0165 (7)
LGST		0.2211 (4)	0.0794 (4)	0.7633 (4)	1.0	0.0171 (7)
LGZrT		0.2232 (2)	0.0796 (2)	0.7597 (3)	1.0	0.0148 (4)

highest being LGZrT. Hence, it is seen that the substitution of  $\text{Ga}^{3+}$  ions of LGS by  $\text{Ta}^{5+}$  ions in the  $B$ -site octahedra in LGST requires the expansion of the lattice. Similarly, the substitution of  $\text{Ga}^{3+}$  and  $\text{Ta}^{5+}$  ions of LGT by  $\text{Zr}^{4+}$  ions in the octahedral  $B$  site and the tetrahedral  $C$  site of LGZrT requires expansion of the lattice. Table 1 indicates that the change in size of the unit cell along the  $a$  and  $b$  direction is much more (0.029  $\text{\AA}$ ) than that along the  $c$  direction (0.008  $\text{\AA}$ ) as the composition changes from LGST to LGT. Similarly the change in size of

the unit cell along the  $a$  and  $b$  direction is much more (0.032  $\text{\AA}$ ) compared with that along the  $c$  direction (0.015  $\text{\AA}$ ) as the composition changes from LGT to LGZrT. This is consistent with the recent experimental study (Araki *et al.*, 2007) demonstrating that the compression of the langasite structure is preferential in the  $ab$  plane. Table 2 gives the atomic parameters of LGS, LGST and LGZrT crystals.

The isostructurality index [ $I_i(n)$ ; Fábíán & Kálmán, 1999] defined by the following equation gives a measure of similarity between two structures.

$$I_i(n) = \left| \left[ \frac{\sum \Delta R_i^2}{n} \right]^{1/2} - 1 \right| \times 100, \quad (2)$$

where  $\Delta R_i$  are the differences between the orthogonalized coordinates of common atoms within the same section of asymmetric units of the related structures.

For the LGS crystal the neutron coordinates were taken from Kuz'michva *et al.* (2008). The value of  $I_i(7)$  for these crystals (Table 3) indicates a very high isostructurality index between the combination of two structures, with LGT and LGST showing the highest isostructurality index.

The influence of small structural differences on the sizes of the various polyhedra was analyzed; the details are listed in Table 4. Geometrical calculations were performed with the program 'VOLCAL' (Finger, 1971). This program calculates polyhedral volumes for all coordination groups, but polyhedral distortion indices are generated only for tetrahedral and octahedral cases. The distortion parameters characterize the deviations of polyhedra from regular

geometrical forms. Two kinds of polyhedral distortion indices were calculated, such as quadratic elongation (QE) and bond-angle variance (BV), which are based on bond distances and angles (Hazen & Finger, 1982). Quadratic elongation,  $\langle \lambda \rangle$ , is defined as:  $\langle \lambda \rangle = \sum_{i=1}^n [(l_i/l_o)^2/n]$ , where  $l_o$  is the centre-to-vertex distance of a regular polyhedron of the same volume,  $n$  is the coordination number of the central atom and  $l_i$  is the distance from the central atom to the  $i$ th coordinating atom. A regular polyhedron has a quadratic elongation of 1, whereas

**Table 3**

Isostructurality index.

Crystal label	$I_i(7)$ (%)
LGT-LGST	97.2
LGS-LGST	96.3
LGT-LGZrT	96.2
LGST-LGZrT	94.6
LGS-LGT	93.8
LGS-LGZrT	91.2

distorted polyhedra have values greater than 1. Bond-angle variance,  $\sigma^2$ , is defined as

$$\sigma^2 = \sum_{i=1}^n [(\theta_i - \theta_0)^2 / (n - 1)], \quad (3)$$

where  $\theta_0$  is the ideal bond angle for the regular polyhedron,  $n$  is the coordination number and  $\theta_i$  is the  $i$ th adjacent bond angle from the outer to the central atoms. Angle variance is zero for a regular polyhedron and positive for a distorted polyhedron.

It is seen that in LGS, Si substitution occurs in the  $D$  site. In LGT the substitution of Ta occurs in the  $B$  site, and in the intermediate composition of LGST the substitution of Ta and Si occurs both in  $B$  and  $D$  sites. The case of LGZrT seems to be slightly different in that the substitution of Zr occurs in  $B$  and  $C$  sites.

It is seen from Table 4, even though there is a substitution in the  $C$  site in the case of LGZrT, the volumes of  $C$  sites are similar in all four crystals, indicating that a small substitution (*i.e.* 3% of Zr in LGZrT) does not affect the volume of the  $C$  site.

It is also observed from Table 4 that even though there is no substitution taking place in the  $A$  site, there is still variation in the dodecahedral volumes of the four structures, with the volume being lowest for LGS and highest for LGZrT, and

LGT and LGST having similar volumes. The dodecahedron shares common edges with  $B$  and  $D$  sites that have substitutions. This may result in a change in dodecahedral volume.

Comparing the tetrahedral volumes of the  $D$  site it is seen that LGT and LGZrT have higher volumes followed by LGST and LGS, indicating that substitution at this site by a cation of smaller radii reduces the volume of the tetrahedra. It is observed that all the polyhedra are distorted as they have a larger angle-variance parameter.

The property that attracts the primary interest for material application is the electromechanical coupling coefficient  $k_{12}$ . This is related to the piezoelectric constant  $d_{11}$  by the following relation (Sato *et al.*, 1998)

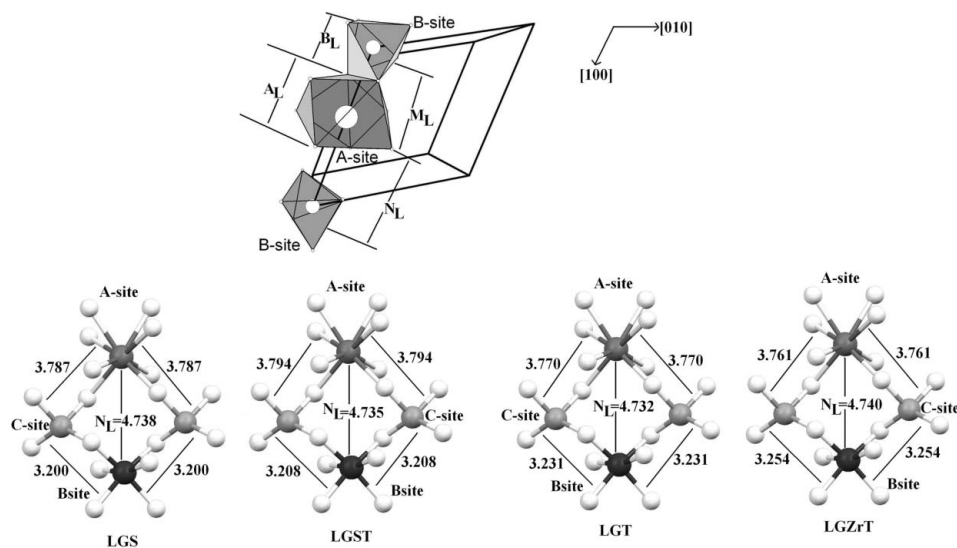
$$k_{12}^2 = d_{12}^2 / (s_{22}^E - \varepsilon_{11}^T); \quad d_{12} = -d_{11}, \quad (4)$$

where  $d_{ik}$  are the piezoelectric strain constants,  $s_{ik}^E$  are elastic compliances in a constant electric field and  $\varepsilon_{ik}^T$  are the dielectric constants at a given temperature.

Earlier studies (Iwataki *et al.*, 2001; Araki *et al.*, 2007) have demonstrated that the piezoelectric property of this class of crystal is strongly dependent on the width of the dodecahedron ( $A_L$ ) and octahedron ( $B_L$ ) along the  $[100]$  direction (Fig. 2). These studies illustrate that the piezoelectric coefficient ( $d_{11}$ ) increases with an increase in the  $A_L/B_L$  ratio. Moreover, it was found that the dipole moment is enhanced if the distance between the charge centers of the cations and anions becomes large, and hence the enlargement of piezoelectric properties is strongly related to the shrinkage of the empty space (Fig. 3) surrounded by  $A$ ,  $B$  and  $C$  sites (Araki *et al.*, 2007).  $A_L$  and  $B_L$  for the LGS, LGT, LGST and LGZrT structures were obtained (Table 5) along with the distances  $M_L$  and  $N_L$  defined as the adjacent atomic distance  $B-A$  and atomic distance  $A-B$  through empty space (Fig. 2). The values of  $k_{12}$  and  $d_{11}$  for LGS and LGT have been taken from the literature (Mill & Pisarevsky, 2000). These values for two other crystals (LGST and LGZrT) have not yet been determined experimentally.

Table 5 indicates that the piezoelectric properties of these crystals should improve as the composition gradually changes from LGS to LGT. It is also observed from Table 5 that LGZrT has an  $A_L/B_L$  ratio similar to that of LGS. It has been confirmed experimentally that LGT has improved piezoelectric properties compared with LGS (Kludzin *et al.*, 2005; Dudka *et al.*, 2009). Hence, the result of this study shows that a slight change in structure can lead to an improvement of the material properties.

The  $N_L$  values listed in Table 5 and Fig. 3 indicate that the size of the empty space surrounded by  $A$ ,  $B$  and  $C$  sites is not altered significantly with a change in composition.



**Figure 2**

Crystal structure of LGS, LGST, LGST and LGZrT showing the empty space.

**Table 4**  
Polyhedron volumes and polyhedron distortions in LGT, LGST, LGS and LGZrT.

Bonds	LGT	LGST	LGS	LGZrT
<b>A-site dodecahedral</b>				
La–O1 × 2 (Å)	2.623	2.631	2.640	2.630
La–O2 × 2 (Å)	2.462	2.479	2.511	2.454
La–O2 × 2 (Å)	2.890	2.885	2.873	2.905
La–O3 × 2 (Å)	2.408	2.384	2.349	2.420
(La–O) <sub>av.</sub> (Å)	2.595	2.595	2.593	2.602
O1–O2 × 4 (Å)	2.987	3.013	3.043	2.987
O1–O2 × 2 (Å)	3.610	3.612	3.633	3.622
O2–O2 × 2 (Å)	2.840	2.775	2.685	2.839
O3–O2 × 2 (Å)	2.956	2.975	2.992	2.978
O3–O2 × 2 (Å)	3.383	3.406	3.421	3.400
O3–O2 × 2 (Å)	3.946	3.921	3.909	3.934
O3–O3 (Å)	2.657	2.673	2.641	2.720
O2–O2 (Å)	3.774	3.612	3.927	3.776
O3–O1 × 2 (Å)	3.209	3.183	3.160	3.196
(O–O) <sub>av.</sub> (Å)	3.237	3.171	3.241	3.243
Volume (Å <sup>3</sup> )	28.697	28.686	28.550	28.945
<b>B-site octahedral</b>				
Ga1–O × 6	1.992	1.999	1.987	2.035
O3–O3 × 6	2.743	2.753	2.753	2.802
O3–O3 × 3	2.657	2.673	2.641	2.720
O3–O3 × 3	3.147	3.149	3.113	3.213
(O–O) <sub>av.</sub>	2.823	2.832	2.815	2.884
Volume (Å <sup>3</sup> )	10.205	10.332	10.175	10.898
Quad elongation	1.02	1.02	1.02	1.02
Angle variance	71.95	67.87	62.31	70.40
<b>C-site large tetrahedral</b>				
Ga2–O2 × 2 (Å)	1.865	1.891	1.896	1.869
Ga2–O3 × 2 (Å)	1.847	1.822	1.826	1.842
(Ga2–O) <sub>av.</sub> (Å)	1.856	1.857	1.861	1.855
O2–O2 (Å)	2.883	2.875	2.874	2.904
O3–O3 (Å)	3.379	3.362	3.371	3.369
O2–O3 × 2 (Å)	2.841	2.857	2.893	2.850
O2–O3 × 2 (Å)	3.039	3.014	2.993	3.027
(O–O) <sub>av.</sub> (Å)	3.003	2.997	3.003	3.004
Volume (Å <sup>3</sup> )	3.110	3.097	3.123	3.117
Quad elongation	1.04	1.04	1.04	1.03
Angle variance	154.99	180.53	176.91	148.33
<b>D-site small tetrahedral</b>				
Ga3–O2 × 3 (Å)	1.841	1.791	1.733	1.844
Ga3–O1 (Å)	1.793	1.764	1.704	1.801
(Ga3–O) <sub>av.</sub> (Å)	1.829	1.784	1.726	1.833
O2–O2 × 3 (Å)	2.840	2.775	2.685	2.839
O2–O1 × 3 (Å)	3.099	3.025	2.923	3.111
(O–O) <sub>av.</sub> (Å)	2.970	2.900	2.804	2.979
Volume (Å <sup>3</sup> )	3.062	2.851	2.578	3.077
Quad elongation	1.02	1.02	1.01	1.02
Angle variance	77.61	68.23	66.99	81.99

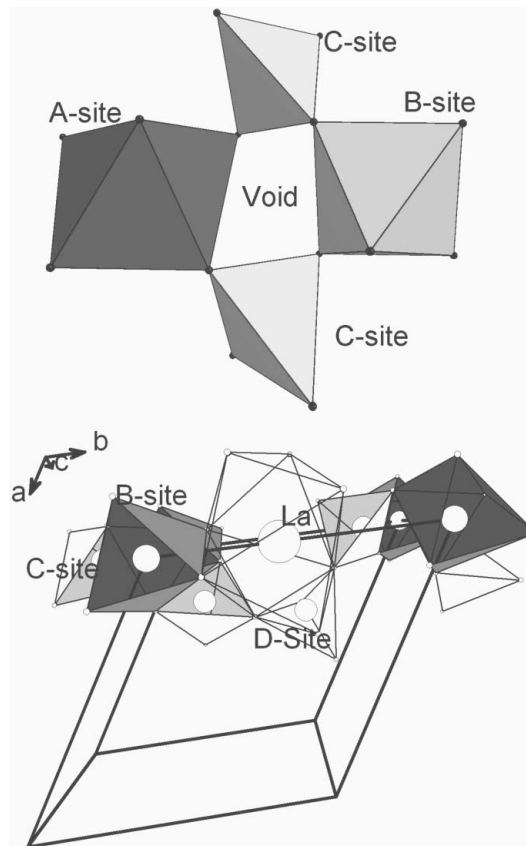
From Table 5 it is evident that the most significant change occurs in the value of  $A_L$ , *i.e.* the width of the dodecahedron along the [100] direction.

An earlier structural analysis of the langsite structure (Chai *et al.*, 2000) indicates that the structure is controlled by the *B* and *C* sites (Fig. 3). These are linked by the large dodecahedral *A* site as well as the small tetrahedral *D* site.

Hence the *A* and *D* sites are actually linkage sites. The size and charge of the *D*-site affects the size and charge of the *A* site. Although the *A* site for the LGS, LGT, LGST and LGZrT is occupied by the same  $\text{La}^{3+}$  ion, the difference lies in the *D* site. The *D* site of LGT and LGZrT has  $\text{Ga}^{3+}$  ions, whereas it has  $\text{Ga}^{3+}$  and  $\text{Si}^{4+}$  ions in the case of LGS and LGST. The significant change in the size of the *D* site affects the orientation of the *A*-site dodecahedra, so that its width along the [100] direction changes thus significantly affecting the piezoelectric properties of the crystals.

## 5. Conclusion

The crystal structures of LGS, LGT, LGST and LGZrT crystals obtained from single-crystal neutron diffraction have been analyzed. These crystals have very slight structural differences resulting from the difference in composition. These small structural changes are enough to bring about a noticeable change in their piezoelectric properties. This study attempts to correlate these structural changes to the changes in the material properties. It is shown that the significant change in the *D* site affects the orientation of the *A* site along the [100] direction leading to a change in the piezoelectric property.



**Figure 3**  
 $A_3BC_3D_2O_{14}$  structure.

**Table 5**

*A* and *B* side width along the [100] direction and atomic distances  $M_L$  and  $N_L$ .

Parameters	LGS	LGST	LGT	LGZrT
$B_L$	2.719	2.718	2.705	2.764
$A_L$	3.508	3.546	3.589	3.569
$A_L/B_L$	1.290	1.305	1.327	1.291
$M_L$	3.427	3.460	3.492	3.516
$N_L$	4.738	4.735	4.732	4.740
$k_{12}$ (Nm <sup>-2</sup> )	0.160 <sup>†</sup>		0.168 <sup>†</sup>	
$d_{11} \times 10^{-12}$ (CN <sup>-1</sup> )	-6.16 <sup>†</sup>		-6.98 <sup>†</sup>	

<sup>†</sup> See Mill & Pisarevsky (2000).

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