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Origin of piezoelectricity for langasite $A_3Ga_5SiO_{14}$ (A = La and Nd)under high pressure

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Abstract

The origin of piezoelectricity for langasite stated by a previous article has been clarified from the crystal structure under high pressure. The crystal structure of langasite with trigonal symmetry has the special empty-spaces located between A- and B-sites which are two large cation sites. The empty-space works for piezoelectricity. When a force is applied to the [1 0 0] direction, piezoelectricity was produced by the formation of polarity due to the shift of the A-cation in the [1 0 0] direction towards empty-space and deformation of the A-decahedron in the [−1 0 0] direction. In spite of the deformation of the A-site, the atomic distance between A- and B-ions is not changed due to the electrostatic repulsion.

The empty-space plays a role keeping of the A–B adjacent atomic distance and decreasing the B–A atomic distance throughout the empty-space. Under high pressure, it was clarified that the linear compressibility of the *a*-direction including the empty-space is larger than that of the *c*-direction. This shows the empty-space is contributing to the piezoelectricity. Also, it was clarified that the compressibility of the bond distance between A- and B-cations is smaller than that of the bond distance between A- and B-cations over the empty-space.

Keywords: X-ray methods; Piezoelectric properties; Silicate; Sensors; SAW filter

1. Introduction

For the next generation of advanced digital communications, high-performance surface acoustic wave (SAW) devices available to higher frequencies, wider bandwidth and higher bit rates are strongly needed. Langasite crystals, $A_3Ga_5SiO_{14}$ (A = La, Pr and Nd) have been expected to be one of the important candidates for such SAW devices, because of the excellent piezoelectric properties with larger electromechanical coupling factor and lower temperature coefficient than those of quartz.

Langasite crystals belong to the trigonal system with space group $P321$[1] and show lattice parameters of $a = 8.1674(4)$ Å and $c = 5.0964(8)$ Å. Fig. 1 shows the crystal structure of langasite crystal $La_3Ga_5SiO_{14}$. The A site containing La^{3+} forms a decahedron, B and C sites containing Ga^{3+} form an octahedron and tetrahedron, respectively. The D site containing Ga^{3+} and Si^{4+} with 1:1 ratio forms a tetrahedron. As shown in the *a*–*c* plane, the crystal structure consists of two different layers in the [0 0 1] direction. One is the layer consisting of a decahedron (A site), octahedron (B site) and an empty-space surrounded by A, B and C sites. The other is tetrahedral layers (C and D sites) sandwiched between two decahedral (A site) and octahedral (B site) layers.[2,3]

The piezoelectricity of langasite generates along the [1 0 0] direction, including a piezoelectric constants d_{11} and an electromechanical coupling coefficient k_{12}. These values of piezoelectricity for La-, Pr- and Nd-analogies (LGS, PGS and NGS) were reported by Sato et al.[4] These piezoelectric properties are strongly dependent on the width of decahedron (A_L) and octahedron (B_L) along the [1 0 0] direction in Fig. 1. According to our previous report,[5] these piezoelectric properties were depended on the ratio of A_L to B_L (A_L/B_L), as shown in Fig. 2.

In this paper, the origin of the piezoelectricity for langasite crystals were clarified by the atomic distances between A- and B-cations, as well as the width of decahedron (A_L) and octahedron (B_L) of crystal structure with applied pressure. The effects

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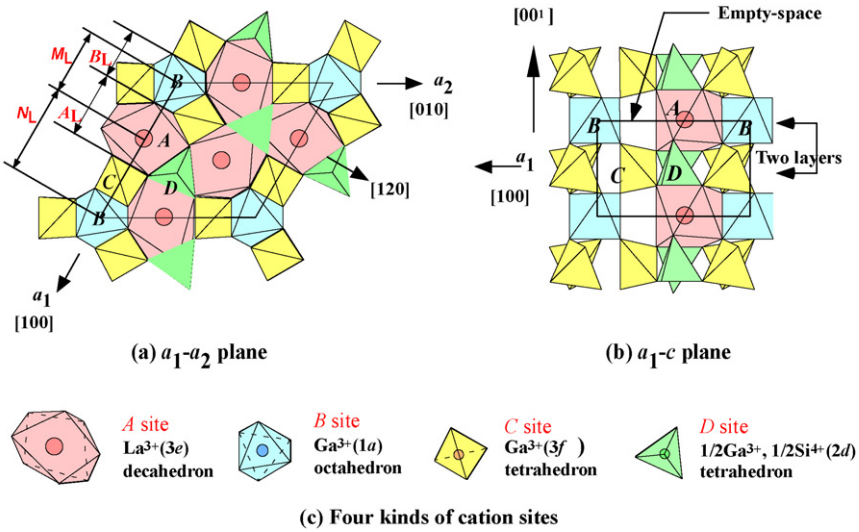

Fig. 1. Crystal structure of langasite: (a) projection from [0 0 1], (b) projection from [1 2 0] and (c) cation sites.

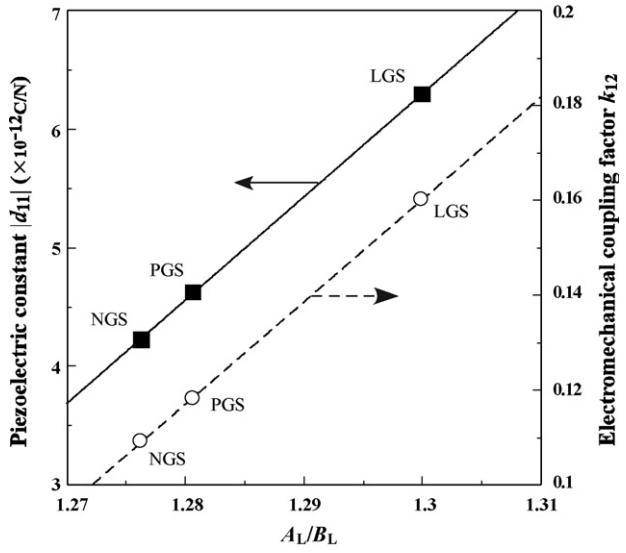

Fig. 2. Piezoelectric constant $|d_{11}|$ and electromechanical coupling factor $|k_{12}|$ as a function of the A_L/B_L.

of the empty-space surrounded by A, B and C sites on the piezoelectricity were also discussed.

2. Experimental

The single crystals of La- and Nd-analogies were prepared by the Czochralski method. Details of single crystal preparation method were described in a previous report.[4] Crystal structural analyses of these single crystals were performed by the four-circle X-ray diffractometer (Rigaku AFC-7R, Japan) with Mo Kα radiation monochromatized by graphite. Pressures applied to the single crystals using a diamond anvil cell (DAC)[6] were calibrated by the ruby fluorescence technique.[7] The unit cell parameters were refined by using approximately 20 reflections in the 2θ range from 12° to 28°. Reflection intensity data were collected by using the 2θ–ω step scan technique. Refinements of the crystal structure were performed by the full-matrix least-squares program "RADY".[8]

3. Results and discussion

Fig. 3 shows lattice parameters (a and c) and unit cell volumes of La- and Nd-analogies as a function of pressure. Both of the lattice parameters of the a- and c-axis, and the volumes of unit cell shrunk linearly with increase of applied pressure. It is noteworthy that the a-axis is the preferentially shrunk direction compared to the c-axis. The linear compressibility β of the a- and c-axis are $\beta_a = 2.44$ and $\beta_c = 1.46$ for the La-analogy and $\beta_a = 2.56$ and $\beta_c = 1.51$ for Nd-analogy. The compressibility β_a in the a-direction is more dominant than β_c. This indicates that the compression of langasite crystals occurs preferentially in the a_1–a_2 plane.

Table 1 shows the lattice parameter a and variation of M_L, and N_L for La- and Nd-analogies along the [1 0 0] direction at various pressure. Here, M_L is defined as the B–A adjacent atomic distance and N_L as the A–B atomic distance throughout the empty-space, as shown in Fig. 1. For both La- and Nd-analogies, the changes of N_L are much larger than those of M_L. The compressibility and normalized compressibility depending on *a-axis* length shown in Table 1 reveal clearly the larger compressibility of the atomic distance of A and B over empty-space, indicating a larger contribution to shrinkage of the empty-space. Comparing with the edge-shared A- and B-sites, it can be speculated that the empty-space is easily distorted when the pressure is induced in the [1 0 0] direction.

Piezoelectricity is originated from polarization caused by the destruction of charge balance depending on the displacement of ions when pressure is induced. The piezoelectricity of langasite is known to be generated in the [1 0 0] direction. From the rule of symmetrical operation, langasite should have polarization in the A- and C-sites in contrast with no polarization in the B- and D-sites with three-fold site symmetry.

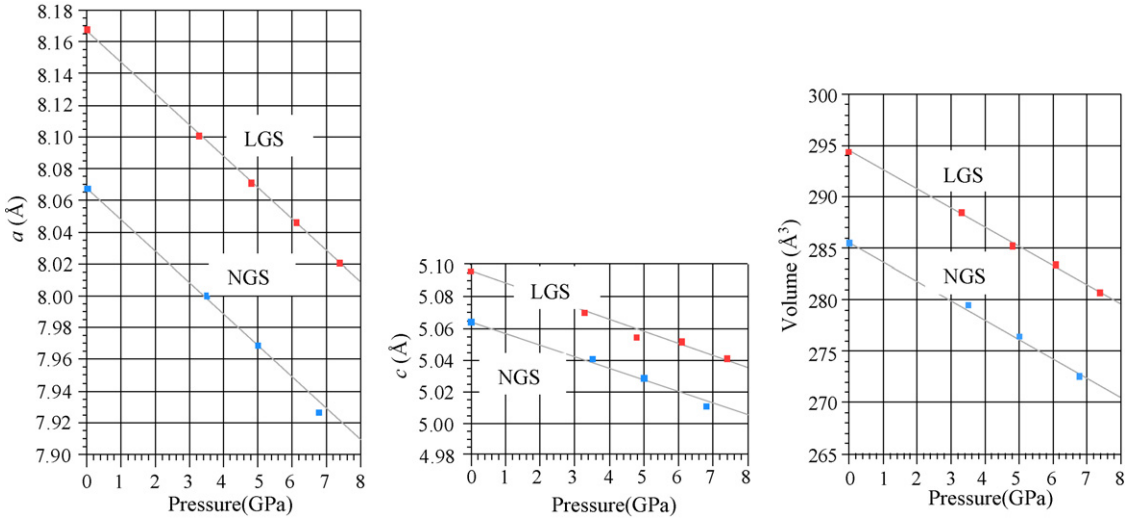

Fig. 3. Lattice parameters and unit cell volumes as a function of the pressure.

Table 1
Atomic distances (M_L and N_L) depending on the pressure

	Pressure (GPa)			Compressibility	Normalized compressibility
	atm.	3.3	6.1		
(a) LGS					
M_L (Å)	3.419	3.413	3.392	0.80	0.54
N_L (Å)	4.748	4.690	4.654	1.98	1.34
a (Å)	8.167	8.103	8.046	1.48	1.0
	Pressure (GPa)			Compressibility	Normalized compressibility
	atm.	3.5	6.8		
(b) NGS					
M_L (Å)	3.372	3.354	3.350	0.64	0.37
N_L (Å)	4.696	4.645	4.576	2.56	1.46
a (Å)	8.067	7.999	7.926	1.75	1.0

With an induced pressure, the movements of A-site cation to the [1 0 0] direction and oxygen ions to the [−1 0 0] direction were confirmed by crystal structural refinements, finally the charge centers of cations and anions move to the opposite directions, which may relate with the shrinkage of the empty-space. Dipole moment should be enhanced if the distance between the charge centers of cations and anions become large. Therefore, the enhancements of piezoelectric properties are strongly related with the shrinkage of empty-space in langasite crystal structure, and it is clear that the increase of polarization is caused by the induced pressure in [1 0 0] direction of langasite structure, as shown in Fig. 4.

The piezoelectric properties of the langasite crystals were improved by the A_L/B_L ratio,[2] which mentioned in the introduction section. The present work also showed the dependence of A_L/B_L ratio on the various pressures, as shown in Table 2. The ratios for LGS are larger than those of NGS and are increased with the pressure. At high pressure, the piezoelectric-

Table 2
A and B-site width along [1 0 0] direction

	Pressure (GPa)		
	atm.	3.3	6.1
(a) LGS			
A_L (Å)	3.516	3.545	3.529
B_L (Å)	2.717	2.717	2.625
A_L/B_L (Å)	1.29	1.30	1.34
	Pressure (GPa)		
	atm.	3.5	6.8
(b) NGS			
A_L (Å)	3.411	3.324	3.325
B_L (Å)	2.703	2.719	2.669
A_L/B_L (Å)	1.26	1.22	1.25

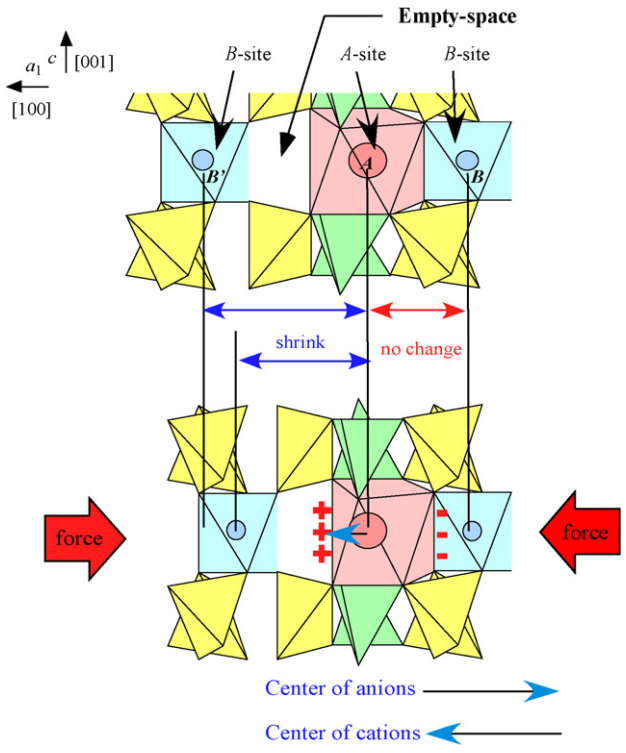

Fig. 4. Mechanisms of the piezoelectricity.

ity of LGS might be larger than that of NGS based on these phenomena.

4. Conclusion

The following results were confirmed based on crystal structure analysis with applied pressure for langasite crystals, La- and Nd-analogies:

(1) With an increase of applied pressure, the unit cell volume was decreased due to the decrease of lattice parameters of the *a*- and *c*-axis. The compression of langasite crystals occurs preferentially in the a_1–a_2 plane.
(2) The compressibility of the A–B atomic distance over empty-space (N_L) was larger than that of *B*–*A* adjacent atomic distance (M_L), indicating a larger contribution to shrinkage of the empty-space.
(3) For the [1 0 0] direction of langasite crystals, the ratios of the decahedron width (A_L) to the octahedron width (B_L) were increased with the pressure. The ratios for LGS are larger than those of NGS.
(4) The piezoelectricity of langasite crystals were attributed to the compressibility of A–B atomic distance throughout the empty-space and dependence of the ratios of the decahedron width to the octahedron width (A_L/B_L) on the pressure.

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