Growth, Structure and Piezoelectric Properties of $Ln_3Ga_5SiO_{14}$ (Ln= La, Nd) Single Crystals

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Piezoelectric $La_3Ga_5SiO_{14}$ (LGS) and $Nd_3Ga_5SiO_{14}$ (NGS) single crystals with a $Ca_3Ga_2Ge_4O_{14}$-type structure were grown by the Czochralski technique and their electric properties were investigated. The size of the grown crystals was 18-25 mm in diameter and 72-110 mm in length. The crystal structure of both crystals has been refined from the single crystal X-ray diffraction data. Except for the lanthanoide site, the cation distribution on each site in NGS is same as that of LGS. The dielectric, piezoelectric and elastic compliance constants of the LGS and NGS crystals were evaluated. The independent piezoelectric moduli d_{11} and d_{14} of the NGS crystal were approximately half that of the LGS one. The substitution of the lanthanoide site in the LGS-type crystals significantly affected the piezoelectric properties.

Key words: rare-earth element, langasite, crystal growth, crystal structure, piezoelectric properties

1. INTRODUCTION

$La_3Ga_5SiO_{14}$ (langasite, LGS) crystals [1] have been promising piezoelectric materials for the fabrication of filters with large passband widths and oscillators with large shifts or high frequency stabilities [2,3]. Actually, surface acoustic wave (SAW) filters made of LGS wafers have already been mass-produced for use in a wideband-code division multiple access (W-CDMA) station. Very recently, LGS-type crystals also have attracted the attention as pressure sensor materials usable at high temperature, because LGS shows no phase transitions up to its melting temperature. However, there are few reports about the physical properties at high temperature in LGS. Furthermore, since there are few data about the piezoelectric properties of other LGS-type crystals at room temperature, it has not been clarified that LGS is the most appropriate material for all LGS-type crystals. Under this situation, we have investigated the substitution effect of La^{3+} in LGS on the growth, structure and piezoelectric properties. We have been determining all the material constants of lanthanoide gallium silicates (LGS and $Nd_3Ga_5SiO_{14}$; NGS) and comparing them. Although the authors in ref.[4] have already reported one piezoelectric constant, other material constants have not yet been determined. The obtained data are useful for developing newer candidates for pressure sensor devices that work at high temperature.

In this paper, we report the growth of LGS and NGS crystals by the Czochralski (Cz) technique, and their detailed crystal structure and material constants.

2. CRYSTAL GROWTH

Single crystals were grown by the conventional RF-heating Cz technique using an iridium crucible (50 mm diameter and height). The starting materials were prepared by mixing 99.99% pure $La(Nd)_2O_3$, Ga_2O_3 and SiO_2 powders in a stoichiometric ratio. The powders were mixed in air, and then calcined at 1000°C for 2 h. They were then heated at 1350 °C for 5 h. The L(N)GS powders were uniaxially pressed in a disk form with a 48 mm diameter and ~30mm thickness, and were charged into the crucible. The growth atmosphere was an 1vol%O2+Ar gas flow of 10^{-3} m³/min. The pulling rate and the rotation rate were 1.0~1.5 mm/h and 10 rpm, respectively. The observation of bubbles and inclusions in the crystals was performed using an optical microscope. The density of the grown crystals was measured by the Archimedes method using distilled water at room temperature.

We have successfully obtained L(N)GS single crystals pulled in the <001> direction by the Cz technique. Since no growth instability such as spiral symptom appeared during the growth, the uniform diameter of the grown crystals was easily controlled. The grown LGS crystal had a 25 mm diameter and 110 mm length and the NGS had an 18 mm diameter and 72 mm length. Both crystals showed a smooth surface, and were transparent with a orange color for LGS and deep purple color for NGS. No cracks and inclusions were found inside the grown crystals. All peaks of the powder X-ray diffraction patterns of the boules were identified to be those of the LGS-type structure. The measured density (Dm) is 5.742(3) g/cm³ and 6.008(5) g/cm³ for the LGS and NGS crystals, respectively. (cf. Table 4)

3. STRUCTURE ANALYSIS

The L(N)GS crystals have the $Ca_3Ga_2Ge_4O_{14}$-type structure (space group $P321$) [1]. There are four kinds of

cation sites in the structure with the chemical formula $A_3BC_3D_2O_{14}$. A part of the crystal structure is schematically shown in Figure 1. The notations A and B represent a decahedral (twisted Thomson cube) site coordinated by eight oxygens, and an octahedral site coordinated by six oxygens, respectively. Moreover, C and D represent tetrahedral sites coordinated by four oxygens, the size of the D site is smaller than that of the C site. In the Ca$_3$Ga$_2$Ge$_4$O$_{14}$ crystal, Ca^{2+} occupies the A site, Ga^{3+} occupies the B and one of three C sites, and Ge^{4+} occupies the B and one of the three C and D sites.

Each single crystal, cut from the grown crystal, was ground into a spherical shape and used for the present single crystal structure analysis. X-ray intensity data were collected with MoKα radiation (λ=0.71069 Å) on a Rigaku AFC-6 four-circle diffractometer using a pyrolytic graphite monochromater in the incident beam path. The ω-2θ scan technique was used to collect the integrated intensity data up to 2θ = 90° with a scan speed of θ = 4 °/min. From the total of 1821-1875 reflections, measured within the ranges of $16\leq h \leq 0$, $0 \leq k \leq 16$ and $0 \leq l \leq 10$, 1414-1484 reflections with F$\geq 3\sigma$(F) were used for the refinement. The cell dimensions were determined by a least squares calculation of twenty 2θ values between $20°<2\theta<30°$. After corrections for the Lorentz, polarization and absorption effects, the anisotropic refinement with the corrections for an isotropic extinction (TYPE II) [5] were simultaneously carried out using the full matrix least-squares program *LSGC* [6]. The atomic scattering factors [7] for La(Nd), Ga, Si and O together with anomalous scattering factors were used so as to minimize the residuals of the function $\Sigma w_i(|F_o|-k|F_c|)^2$ where $w_i=1/\sigma^2$(F) and k is the scale factor. The final R and R_w values for the
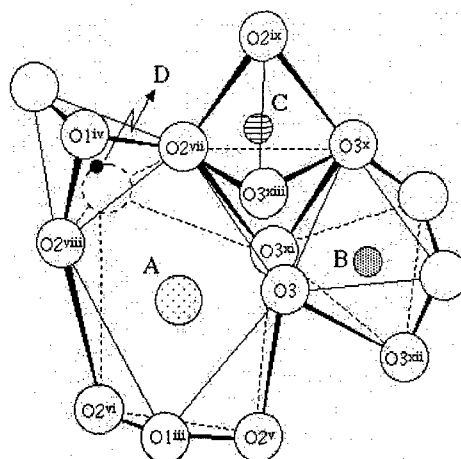
Fig.1 Schematic coordination polyhedra of oxygen atoms around cationic atoms in La$_3$Ga$_5$SiO$_{14}$-type structure. Open circle (◯), coarse dot circle (◉), fine dot circle (◍), hatched circle (⊜) and solid circle (●) represent oxygen atoms, the eight-(A), six-(B), four-(C) and smaller four-coordination (D) sites, respectively.

refinement with anisotropic temperature factors were 0.037-0.039 and 0.040-0.041, respectively. Detailed information of the data collection and refinement are summarized in Table I. The positional parameters, isotropic thermal parameters and selected interatomic distances are listed in Tables 2 and 3 for the LGS and NGS crystals, respectively.

For the LGS and NGS crystals, the distributions of Si and Ga were analyzed by common site-multiplicity refinement. For the first time, the distribution of Si within the octahedral (B;Ga1) and two tetrahedral

Table 1 Crystal Data and Intensity Collection for Ln$_3$Ga$_5$SiO$_{14}$ (Ln=La, Nd)

	La$_3$Ga$_5$SiO$_{14}$	Nd$_3$Ga$_5$SiO$_{14}$
Color	orange	purple
Diameter of specimen (mm)	0.115	0.146
Crystal system	Trigonal	
Space group	*P*321 (No.150)	
Lattice parameters	a = 8.161(1) Å	a = 8.062(1) Å
	c = 5.094(1) Å	c = 5.062(2) Å
Volume (Å^3)	293.8	284.93
Formula weight	1017.41	1033.41
Calculated density (g/cm^3)	5.750	6.019
Radiation	Mo Kα (λ = 0.71069 Å)	
Monochromator	Graphite (002)	
μ (Mo Kα) (mm^{-1})	22.04	25.26
Maximum 2θ (°)	90	
No. of reflections measured	1875	1821
No. of independent reflections	1619	1571
No. of used reflections [F^2 ? 3σ(F^2)]	1414	1484
R	0.039	0.037
R$_w$	0.040	0.041
Goodness of fit	1.111	1.326

Table 2 (a) Atomic parameters and (b) selected interatomic distances [Å] of $La_3Ga_5SiO_{14}$ with estimated standard deviations in parentheses.

(a)

Site		Atom	x	y	z	B
La	3e	La	0.41874(6)	0	0	0.669(8)
Ga1	1a	Ga	0	0	0	0.87(3)
Ga2	3f	Ga	0.7655(2)	0	1/2	0.68(2)
Ga3	2d	Ga+Si	1/3	2/3	0.4678(3)	0.60(3)
O1	2d	O	1/3	2/3	0.805(2)	1.22(13)
O2	6g	O	0.4649(8)	0.3117(8)	0.682(1)	1.50(9)
O3	6g	O	0.2220(8)	0.0802(8)	0.2376(9)	1.54(9)

(b)

Ga1 octahedron

Ga1	-	O3	×6	1.997(6)
O3	-	$O3^{x}$	×6	2.752(9)
	-	$O3^{xi}$	×3	2.673(7)
	-	$O3^{xii}$	×3	3.142(8)
$(O-O)_{av}$				2.830

Ga2 tetrahedron

$Ga2^{ii}$	-	$O2^{vii}$	×2	1.900(6)
	-	$O3^{x}$	×2	1.804(5)
$(Ga2-O)_{av}$				1.852
$O2^{vii}$	-	$O2^{ix}$	×1	2.854(8)
	-	$O3^{xiii}$	×2	2.982(9)
$O2^{ix}$	-	$O3^{x}$	×2	2.874(9)
$O3^{x}$	-	$O3^{xiii}$	×1	3.341(7)
$(O-O)_{av}$				2.985

Ga3 tetrahedron

$Ga3^{i}$	-	$O1^{iv}$	×1	1.715(9)
	-	$O2^{vii}$	×3	1.743(6)
$(Ga3-O)_{av}$				1.736
$O1^{iv}$	-	$O2^{vii}$	×3	2.934(9)
$O2^{vii}$	-	$O2^{viii}$	×3	2.712(9)
$(O-O)_{av}$				2.823

La polyhedron

La	-	$O1^{iii}$	×2	2.642(3)
	-	$O2^{iv}$	×2	2.504(6)
	-	$O2^{v}$	×2	2.876(6)
	-	O3	×2	2.350(5)
$(La-O)_{av}$				2.593
$O1^{iii}$	-	$O2^{viii}$	×2	3.611(6)
		$O2^{v}$	×4	3.046(10)
		O3	×2	3.160(7)
$O2^{v}$	-	O3	×2	2.986(8)
	-	$O2^{vi}$	×2	2.712(9)
	-	$O3^{xi}$	×2	3.428(8)
$O2^{vi}$	-	$O2^{viii}$	×1	3.893(8)
O3	-	$O3^{xi}$	×1	2.673(7)
$(O-O)_{av}$				3.519

Table 3 (a) Atomic parameters and (b) selected interatomic distances [Å] of $Nd_3Ga_5SiO_{14}$ with estimated standard deviations in parentheses.

(a)

Site		Atom	x	y	z	B
Nd	3e	Nd	0.41796(5)	0	0	0.690(8)
Ga1	1a	Ga	0	0	0	0.83(2)
Ga2	3f	Ga	0.7647(1)	0	1/2	0.73(2)
Ga3	2d	Ga+Si	1/3	2/3	0.4651(3)	0.62(3)
O1	2d	O	1/3	2/3	0.803(2)	1.24(13)
O2	6g	O	0.4663(8)	0.3171(8)	0.689(1)	1.72(10)
O3	6g	O	0.2230(8)	0.0756(8)	0.2403(9)	1.45(9)

(b)

Ga1 octahedron

Ga1	-	O3	×6	1.997(6)
O3	-	$O3^{x}$	×6	2.743(9)
	-	$O3^{xi}$	×3	2.652(7)
	-	$O3^{xii}$	×3	3.187(8)
$(O-O)_{av}$				2.830

Ga2 tetrahedron

$Ga2^{ii}$	-	$O2^{vii}$	×2	1.895(7)
	-	$O3^{x}$	×2	1.808(5)
$(Ga2-O)_{av}$				1.852
$O2^{vii}$	-	$O2^{ix}$	×1	2.827(8)
	-	$O3^{xiii}$	×2	2.996(9)
$O2^{ix}$	-	$O3^{x}$	×2	2.871(9)
$O3^{x}$	-	$O3^{xiii}$	×1	3.339(7)
$(O-O)_{av}$				2.983

Ga3 tetrahedron

$Ga3^{i}$	-	$O1^{iv}$	×1	1.711(9)
	-	$O2^{vii}$	×3	1.737(7)
$(Ga3-O)_{av}$				1.731
$O1^{iv}$	-	$O2^{vii}$	×3	2.934(10)
$O2^{vii}$	-	$O2^{viii}$	×3	2.690(9)
$(O-O)_{av}$				2.812

Nd polyhedron

Nd	-	$O1^{iii}$	×2	2.617(3)
	-	$O2^{iv}$	×2	2.433(6)
	-	$O2^{v}$	×2	2.859(7)
	-	O3	×2	2.230(7)
$(Nd-O)_{av}$				2.535
$O1^{iii}$	-	$O2^{viii}$	×2	3.528(6)
		$O2^{v}$	×4	3.005(10)
		O3	×2	3.119(7)
$O2^{v}$	-	O3	×2	2.937(8)
	-	$O2^{vi}$	×2	2.690(10)
	-	$O3^{xi}$	×2	3.409(8)
$O2^{vi}$	-	$O2^{viii}$	×1	3.778(9)
O3	-	$O3^{xi}$	×1	2.673(7)
$(O-O)_{av}$				3.114

(C;Ga2 and D;Ga3) sites was examined. The obtained s tructural parameters clearly indicated that the Si atoms occupy all the smaller tetrahedral (D) sites within the estimated error. Therefore, it was suggested that the Ga atoms occupy another tetrahedral (C) site. Moreover, the decahedral (A) and octahedral(B) sites are fully occupied by La(Nd) and Ga, respectively. The chemical composition determined from the X-ray diffraction data agreed well with that determined from the chemical analysis within the estimated error. Therefore, the chemical formula of $La(Nd)_3Ga_2Ge_4O_{14}$ can be represented as $(La(Nd)_3)^{3e}(Ga_1)^{1a}(Ga_3)^{3f}(Ga_1Si_1)^{2d}O_{14}$

Table 4 Properties of $Ln_3Ga_5SiO_{14}$ (Ln=La, Nd)

	$La_3Ga_5SiO_{14}$	$Nd_3Ga_5SiO_{14}$
D_m	5.742	6.008
k_{12}	14.75	9.68
k_{25}	8.88	2.85
k_{26}	13.82	12.13
$\varepsilon^T_{11}/\varepsilon_0$	19.88±0.6	20.22±0.4
$\varepsilon^T_{33}/\varepsilon_0$	50.83±0.1	63.36±0.1
d_{11}	5.95	4.05
d_{14}	-5.38	-2.07
s^E_{11}	9.19	9.78
s^E_{12}	-3.95	-3.69
s^E_{13}	-1.78	-2.00
s^E_{14}	-3.40	-3.43
s^E_{33}	5.42	6.34
s^E_{44}	20.3	19.1
s^E_{66}	26.28	26.93

D_m : Experimental density [g/cm³]
k_{ij} : Electromechanical coupling factor
$\varepsilon^T_{ij}/\varepsilon_0$: Relative dielectric constant
d_{ij} : Piezoelectric constant [pC/N]
s^E_{11} : Elastic compliance constant [×10¹² m²/N]

with the Wyckoff-site notation superscripted.

As can be seen in Tables 2 and 3, for the LGS and NGS crystals, the average B-O distance (1.997 Å) is closer to the estimated Ga^{VI}-O distance (2.000 Å) [8]. This result supports the full occupation of Ga atoms at the B site in both crystals. The mean C-O distance (1.852 Å) is longer than the mean D-O distance (1.731-1.736 Å). This result suggests that the Si atoms occupy the D site. The shape of the Ga3 tetrahedron appears to be more distorted. The average B, C and D-O distances in LGS are the same as the corresponding ones in NGS, whereas the average A-O one (2.593 Å) of LGS is apparently longer than that (2.535 Å) of NGS. This decrease is due to the ionic size (1.109 Å) of Nd^{3+} (1.160 Å for La^{3+}) [8]. Moreover, there is very small difference in the average O-O distance of the octahedral and two tetrahedral sites. These results show that the substitution of La^{3+} with Nd^{3+} only affects the size of the decahedral site (A-site).

4. EVALUATION OF MATERIAL CONSTANTS

LaCOB crystals belong to the torigonal system P321. Independent material constants in point group 32 consist of two dielectric, two piezoelectric and six elastic compliance constants (ε_{ij}, d_{ij} and s_{ij}, respectively). The total number of constants that should be obtained is ten. The material constants were determined using an impedance/gain phase analyzer (HP 4194A: Agilent) as reported in refs.[9,10]. The electromechanical coupling factor k_{ij} and the piezoelectric modulus were evaluated by measuring the mechanical series resonance frequency f_s and parallel resonance frequency f_p of equivalent resonators. The equivalent resonators were fabricated in the form of bars, plates and rotating cuts according to each vibration mode such as the thickness-extensional

mode. The dielectric constants ε_{ij} were determined by measuring the capacitances of the resonators by taking the parasitic capacitance into account.

All the evaluated material constants of the LGS and NGS crystals are shown in Table 4. All the constants of LGS and the piezoelectric constant d_{11} of NGS agreed with those reported in refs.[11] and [4], respectively. About the piezoelectric constants d_{11} and d_{14}, we found the dependence of the piezoelectric constant on the rare earth elements occupying the decahedral site in $Ln_3Ga_5SiO_{14}$ (Ln = La and Nd) crystals. In ref.[4], it is reported that the absolute piezoelectric modulus $|d_{11}|$ decreases with the decreasing ionic radius of a rare-earth element occupying the A-site in $Ln_3Ga_5SiO_{14}$ (Ln = La, Pr and Nd). Moreover, we found higher decreases in the d_{14} value. In the crystal structure data, we determined the decrease in the size of the decahedral site (A-site) by the substitution of La^{3+} with Nd^{3+}. Hence, the substitution of the A-site in the LGS-type crystal significantly affected the piezoelectric properties. This observation will give a hint to developing new LGS-type crystals with superior piezoelectric properties.

5. SUMMARY

Piezoelectric LGS and NGS single crystals were grown by the Czochralski technique. The results of a single-crystal X-ray structure analysis indicated that the cation distribution on each site in NGS is the same as that of LGS. Using the grown crystals, all material constants of the LGS and NGS crystals were evaluated. The determined piezoelectric constants decreased with the decreasing ionic radius of the rare earth element occupying the A-site in $Ln_3Ga_5SiO_{14}$.

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