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Mechanism of the piezoelectricity of langasite based on the crystal structures

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Abstract

Langasite family crystals ($R_3Ga_5SiO_{14}$, R = rare earth) are expected as the new piezoelectric material for SAW filter. $La_3Ga_5SiO_{14}$ has the largest piezoelectric modulus in these crystals. It is reported that the piezoelectric properties of these crystals improved with the increase of the ionic radius of R. In this work, we clarified the crystal structures of three kinds of langsite family crystals (R = La, Pr and Nd) by X-ray diffraction analysis. We investigated the differences among these crystal structures and clarified the reason why the piezoelectric properties improved with the increase of the ionic radius of R on the basis of these structural differences. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Recently, as a result of the rapid development of mobile communications, new piezoelectric crystals for surface acoustic wave (SAW) microwave filter have become greatly desired in the next generation system. The properties required for the new crystals are large electromechanical coupling factors and high thermal stability of frequency and so on. Langasite ($La_3Ga_5SiO_{14}$, La-langasite, LGS) is one material that satisfies this demand. The mechanical coupling factor of LGS is 3 times as large as that of quartz. LGS has also a low temperature coefficient of resonant frequency.

LGS also has another interesting property: the new crystals with the same structure can be made by the substitution of cation of LGS relatively easily. $Pr_3Ga_5SiO_{14}$ (Pr-langasite, PGS) and $Nd_3Ga_5SiO_{14}$ (Nd-langasite, NGS) were made by the substitution Pr and Nd for La, respectively. These crystals are called the langasite family ($R_3Ga_5SiO_{14}$, R = rare earth) crystals. It is reported that the piezoelectric properties of these langasite family crystals improved with the increase of the ionic radius of R.[1] This relationship is shown in Fig. 1.

The langasite family crystals belong to the trigonal system, space group $P321$ (No. 150), and are isostructural to $Ca_3Ga_2Ge_4O_{14}$.[2] The crystal structure is shown in Fig. 2. There are four kinds of cation sites in this structure, as shown in Fig. 3. This structure can be represented by the chemical formula, $A_3BC_3D_2O_{14}$. In this chemical formula, A and B represent a decahedral site coordinated by eight oxygen anions, and an octahedral site coordinated by six oxygen anions, respectively. While both C and D represent tetrahedral sites coordinated by four oxygen anions, the size of D site is slightly smaller than that of C site. In the case of the LGS, La^{3+} occupies the A sites, Ga^{3+} occupies the B, C and half of the D sites, and Si^{4+} half of the D sites, respectively.

In this work, we investigated the crystal structures of LGS, PGS and NGS and clarified the differences of crystal structures among these crystals. We clarified the generation mechanism of the piezoelectricity and the reason why LGS has the best piezoelectric properties.

2. Experimental

The crystals used for crystal structure analysis were grown by the Czochralski method. The conditions of the growth are shown in Table 1. A single crystal cut from the grown crystal was ground into a sphere and used for the single-crystal structure analysis. X-ray

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intensity data were obtained with MoK_α radiation ($\lambda = 0.71069$ Å) on a four-circle diffractometer using a graphite monochromator. After Lp and absorption correction, the refinement of the crystal structure was performed by the full-matrix least-squares program RADY[3]. The unit cell parameters were refined and determined by a least-square calculation of 20 values of 2θ between $70^\circ \leqslant 2\theta \leqslant 80^\circ$. The crystallographic data and the experimental conditions are shown in Table 2.

3. Results and discussion

The atomic coordinates of LGS, PGS and NGS are presented in Tables 3–5, respectively. The differences of the crystal structure among LGS, PGS and NGS were clarified by the crystal structure analysis. The crystal structures differ mostly in shape of each site. In particular, the change of the *A* site is remarkable.

The decahedral *A* site expands with the increase of ionic radius of *R* that occupies the *A* site. The *A*-site expands greatly in [100] direction as compared to the expansion in [120], which is perpendicular to [100], with the increase of the ionic radius of *R*.

In this study, the reason was clarified why LGS has the best piezoelectric properties among LGS, PGS and NGS. We represented the change of the *A* site by the ratio of the site length in [100] direction, L1, to the site length in [120], L2, as shown in Fig. 4(a). As seen from Fig. 4(b), the ratio L1/L2 increases with the increase of the ionic radius of *R* and the piezoelectric modulus also increases. It could be deduced from Fig. 4(b) that the change of the ratio L1/L2 is proportional to the change

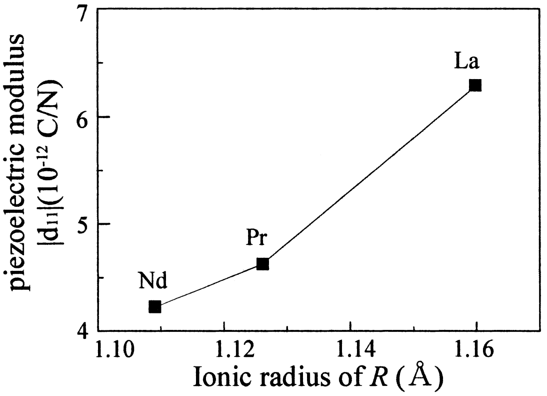

Fig. 1. The relationship between the piezoelectric modulus d_{11} and the ionic radius of *R* ion.

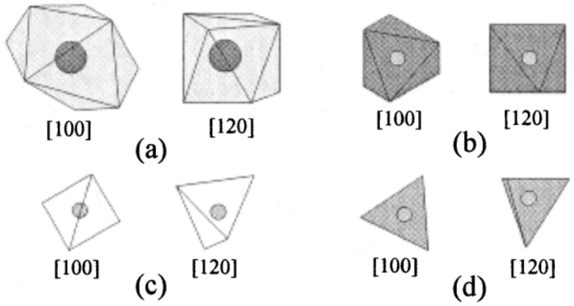

Fig. 3. The four sites in the crystal structure: (a) the decahedral *A* site is occupied by *R* ion; (b) the octahedral *B* site is occupied by Ga ion; (c) the tetrahedral *C* site is occupied by Ga ion; and (d) the tetrahedral *D* site is occupied by 1/2 Ga and 1/2 Si ions, respectively.

Table 1
Description of the crystal growth conditions

Growth material	$R_3Ga_5SiO_{14}$(R = La,Pr and Nd)
Method	Czochralski method
Mixture composition	*R*: Ga: Si = 3.0: 5.0: 1.0
Pilling rate	1.5 mm/h
Rotation rate	10 rpm
Growth orientation	[001]
Atmosphere	Ar + 1%O_2
Crucible	Ir

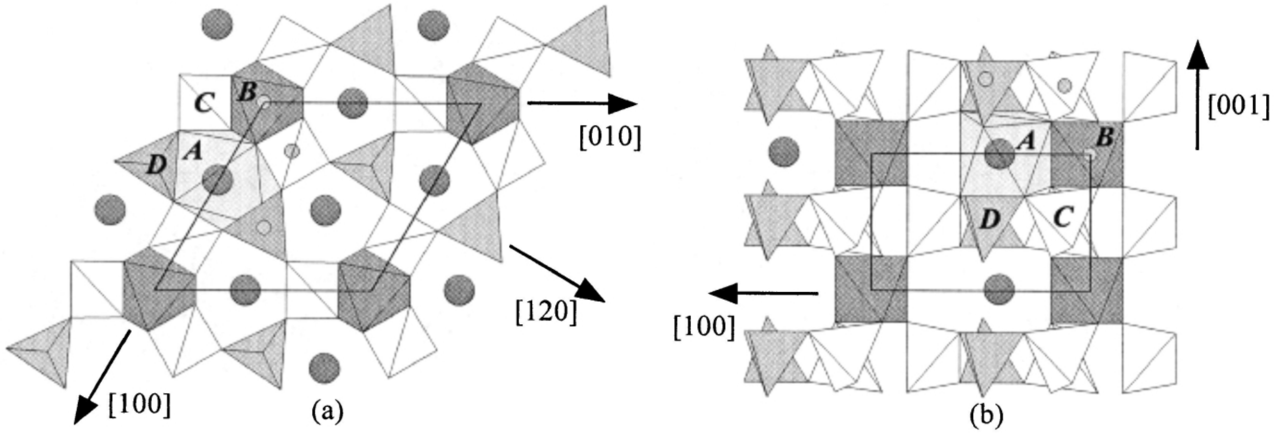

Fig. 2. The crystal structure of langasite family crystals from (a) the [001] direction and (b) the [120] direction.

Table 2
The crystallographic data and experimental conditions for single crystal XRD analysis of LGS, PGS and NGS

	LGS	PGS	NGS
Diameter of the specimen (mm)	0.133	0.110	0.150
Crystal system	Trigonal	Trigonal	Trigonal
Space group	$P321$ (No. 150)	$P321$ (No. 150)	$P321$ (No. 150)
Lattice parameter (Å)	$a = 8.1681(3)$	$a = 8.0956(2)$	$a = 8.0676(3)$
	$c = 5.1975(9)$	$c = 5.073(1)$	$c = 5.0622(9)$
Volume (Å^3)	294.54(6)	287.94(6)	285.33(6)
Formula weight	1017.409	1023.415	1033.412
Calculated density (g/cm^3)	5.736	5.902	6.014
Radiation	MoK_α ($\lambda = 0.71069$)	MoK_α($\lambda = 0.71069$)	MoK_α($\lambda = 0.71069$)
Monochrometor	Graphite	Graphite	Graphite
μ(MoK_α) (cm^{-1})	228.4	247.17	258.67
Maximum 2θ (°)	95	120	120
Scan speed in ω (°/min)	4	6	4
No. of use reflections [$\lvert F\rvert \geqslant 3\sigma(F)$]	1048	1022	1239
R	0.033	0.031	0.036
Rw	0.039	0.032	0.037

Table 3
The atomic coordinates of LGS

Atom	Site	x	y	z	B(EQ)
La	$3e$	0.41876(5)	0	0	0.938(3)
Ga1	$1a$	0	0	0	1.306(9)
Ga2	$3f$	0.7635(1)	0	1/2	1.096(7)
Ga3,Si	$2d$	1/3	2/3	0.4680(3)	0.969(8)
O1	$2d$	1/3	2/3	0.803(2)	1.62(6)
O2	$6g$	0.4649(9)	0.3107(9)	0.682(1)	1.96(7)
O3	$6g$	0.2223(9)	0.0817(9)	0.236(1)	1.95(7)

Table 4
The atomic coordinates of PGS

Atom	Site	x	y	z	B(EQ)
Pr	$3e$	0.41791(5)	0	0	0.996(3)
Ga1	$1a$	0	0	0	1.287(8)
Ga2	$3f$	0.76465(9)	0	1/2	1.140(6)
Ga3,Si	$2d$	1/3	2/3	0.4651(3)	1.036(8)
O1	$2d$	1/3	2/3	0.803(2)	1.66(6)
O2	$6g$	0.4660(8)	0.3164(8)	0.687(1)	2.06(6)
O3	$6g$	0.2233(8)	0.0782(8)	0.2379(9)	2.07(6)

Table 5
The atomic coordinates of NGS

Atom	Site	x	y	z	B(EQ)
Nd	$3e$	0.41794(4)	0	0	0.853(2)
Ga1	$1a$	0	0	0	1.033(7)
Ga2	$3f$	0.76473(9)	0	1/2	0.956(5)
Ga3,Si	$2d$	1/3	2/3	0.4650(2)	0.857(6)
O1	$2d$	1/3	2/3	0.799(2)	1.52(5)
O2	$6g$	0.4671(8)	0.3176(8)	0.686(1)	2.10(6)
O3	$6g$	0.2227(8)	0.0769(9)	0.2386(8)	1.86(6)

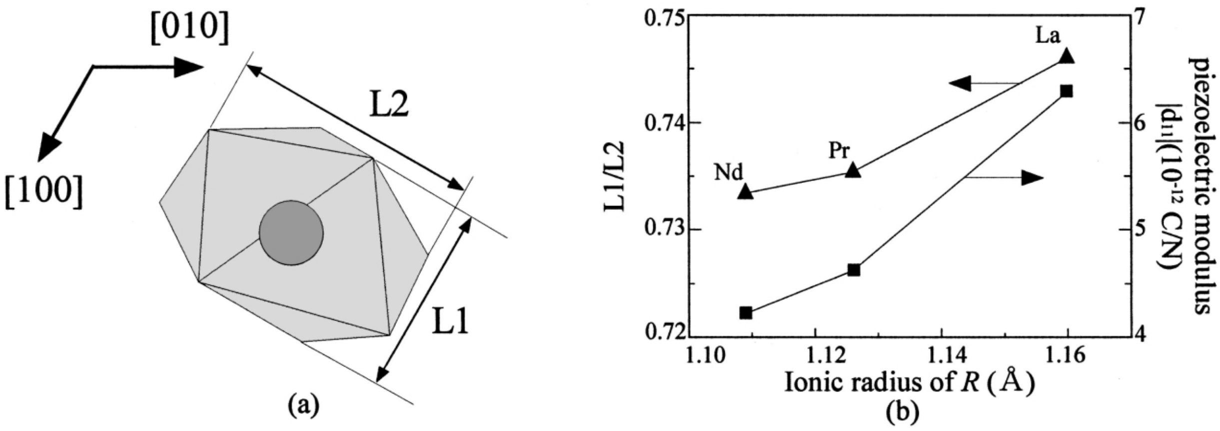

Fig. 4. The change of the *A* site with an increase of the ionic radius of the *R* ion: (a) the length L1 and L2; (b) the change of the L1/L2 and piezoelectric modulus versus the increase of the ionic radius of *R*.

of the piezoelectric modulus. The ratio L1/L2 shows the extent of the distortion of the crystal structure. When the external force is applied in the [100] direction, the structure with the large L1/L2 becomes distorted more greatly than the structure with the small L1/L2 because *A*-site with long L1 has more space to be compressed in the [100] direction. As a result, this causes the large polarization that generates piezoelectricity.

4. Conclusion

The crystal structures of langasite family crystals were investigated by single crystal structure analysis using a four-circle diffractometer. The crystal structure and unit cell parameters were refined and determined by least-square calculation. We investigated the differences of crystal structure among LGS, PGS and NGS with the change of ionic radius of *R*. The difference of crystal structure was due to changes of the sites shape. In particular, the change of the *A* site is remarkable. We clarified the relationship between the ionic radius of *R* and the piezoelectric properties. The *A* site expands in direction of [100] greatly with the increase of ionic radius of *R*. Therefore, the *A* site has more space to be compressed in the [100] direction. As a result, this causes the largest polarization that generates piezoelectricity in case of the LGS.

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