Available online at www.sciencedirect.com
SciVerse ScienceDirect
Ceramics International 39 (2013) S87–S90
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Piezoelectric properties of langasite group based on the ionic size of cation

Hitoshi Ohsato[a,b,c,*], Tsuyoshi Iwataki[c], Hiroki Morikoshi[d], Ken-ichi Kakimoto[c]

[a] BK21 Graduate School, Hoseo University, Asan-si, Republic of Korea
[b] Department of Research, Nagoya Industrial Science Research Institute, Nagoya, Japan
[c] Material Science and Engineering, Nagoya Institute of Technology, Nagoya, Japan
[d] Materials Research Center, TDK Co., Chiba 286-8588, Japan

---

Abstract

As langasite $A_3BC_3D_2O_{14}$ compounds group with piezoelectric properties has no phase transition up to the melting point of 1400–1500 °C, they have been applied for the combustion pressure sensor. As they also have a larger electromechanical coupling factor compared to quartz and nearly the same temperature stability as quartz, the surface acoustic wave (SAW) filters are expected based on the digital transformation of wider bandwidth and higher-bit rates. In the case of three-element compounds such as $[R_3]_A[\mathrm{Ga}]_B[\mathrm{Ga}_3]_C[\mathrm{GaSi}]_D\mathrm{O}_{14}$ (R=La, Pr and Nd), the piezoelectric constant increases with the ionic radius R. In the case of four-element compounds such as $[A_3]_A[B]_B[\mathrm{Ga}_3]_C[\mathrm{Si}_2]_D\mathrm{O}_{14}$ (A=Ca or Sr, B=Ta or Nb), $|d_{11}|$ and k_{12} values as a function of A_L/B_L ratio showed a linear relationship completely. There are two effects for the substitutions of A- and B-site cations: the substitution of Sr for Ca brings expansion toward [100] and enlargement in $|d_{11}|$ and k_{12}. On the other hand, as the substitution of Ta for Nb brings not much change, the properties are similar. In this study, five-element compounds such as $\mathrm{La}_{3-x}\mathrm{Sr}_x\mathrm{Ta}_y\mathrm{Ga}_{5-x+y}\mathrm{Si}_{1+x-2y}\mathrm{O}_{14}$ ($0 \le x \le 3$, $0 \le y \le 1$) solid solutions analysed by a single crystal X-ray diffraction are compared with the three- and four-element compounds on the coordinates of oxygen ions. As the coordinates positions are located on the extended line of coordinate positions on the three-element compounds as increasing ionic radius of R-ions in A-site, the piezoelectric properties $|d_{11}|$ and k_{12} are expected become large.

Keywords: B. X-ray methods; C. Piezoelectric properties; D. Silicate; E. Actuators

---

1. Introduction

Langasite $La_3Ga_5SiO_{14}$ (LGS) group crystals are now attracting researchers attention on the properties of high temperature performance, because they exhibit no curie point and no phase transition up until a melting point of 1400–1500 °C and also no pyroelectricity depending on the point group 32 which is the same as quartz [1]. The properties are applied to the direct measuring of the combustion (burning) pressure sensor at high temperature and the high pressure in combusting engines [2]. The piezoelectric constant of langasite is a superior sensitivity characteristic $k \sim 15$–25 approximately three times to that of quartz crystal $k \sim 7\%$ [1]. On the other hand, langasite has been expected for the surface acoustic wave (SAW) filter, because of low loss (high Q) and near zero temperature coefficient of frequency (*TCf*). The Q values of LGS and $La_3Ga_{5.5}Nb_{0.5}O_{14}$ (LGN) are 30,000–40,000 and 60,000–120,000, respectively [1].

We presented three-element compounds such as $R_3Ga_5SiO_{14}$ (RGS) (R=La, Pr and Nd) [3], which are analysed by single crystal X-ray diffraction. The structure as shown in Fig. 1 has four oxygen polyhedra including cations: A-site of decahedron including R^{3+}. B-site of octahedron with Ga^{3+}, and two C- and D-sites of tetrahedra with Ga^{3+} and Si^{4+}. The crystal structural formulae are shown as $A_3BC_3D_2O_{14}$. These sites include many kinds of ions, which create many compounds of more than 150 species.

---

*Corresponding author at: Nagare College, Nagoya Institute of Technology, Nagoya 466-8555, Japan. Tel./fax: +81 52 735 7511, +81 52 802 4070.
E-mail address: ohsato@naa.att.ne.jp (H. Ohsato).

0272-8842/$ - see front matter © 2012 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
http://dx.doi.org/10.1016/j.ceramint.2012.10.040

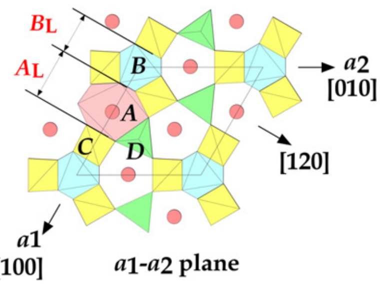

Fig. 1. Crystal structure of langasite viewed from [001].

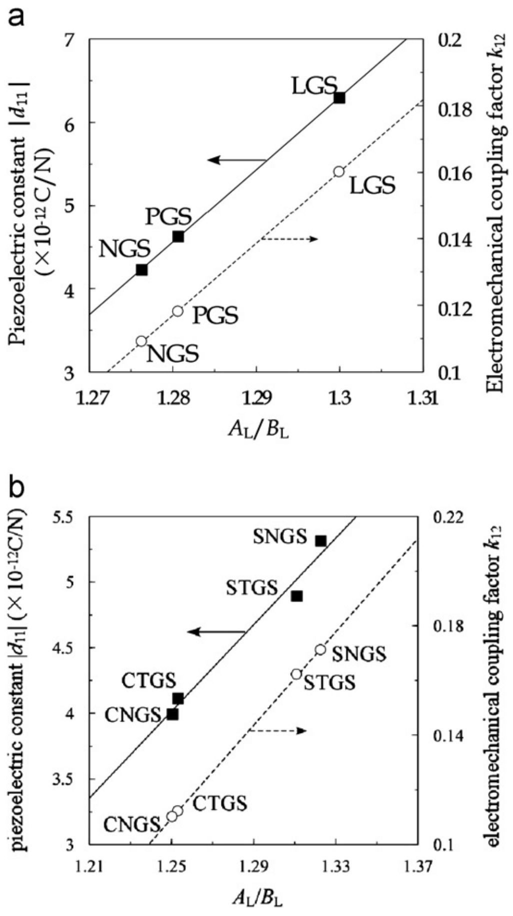

Fig. 2. (b) Piezoelectric constant $|d_{11}|$/electromechanical coupling factor of three-(a) and four-element compound (b) as a function of A_L/B_L which is shown in Fig. 1.

The piezoelectric constant $|d_{11}|$ and the electromechanical coupling factor k_{12} are shown as a function of A_L/B_L (Fig. 1) as shown in Fig. 2 [4,5]. Also, we presented the mechanism of piezoelectric properties based on the crystal structure as shown in previous papers [3,5,6].

We also presented four-element compounds langasite crystals such as $Sr_3TaGa_3Si_2O_{14}$ (STGS), $Ca_3TaGa_3Si_2O_{14}$ (CTGS), $Sr_3NbGa_3Si_2O_{14}$ (SNGS), and $Ca_3NbGa_3Si_2O_{14}$ (CNGS) which are denoted as (SC)(TN)GS, and clarified the effects for *A*-site substitution of Sr for Ca on STGS/SNGS and CTGS/CNGS, and for *B*-site substitution of Ta for Nb on STGS/CTGS and SNGS/CNGS [7]. $|d_{11}|$ and k_{12} values as a function of A_L/B_L ratio showed a linear relationship completely as shown in Fig. 2(b). There are two effects for substitutions of *A*- and *B*-site cations: the substitution Sr for Ca brings expansion toward [100] and enlargement in $|d_{11}|$ and k_{12}. On the other hand, as the substitution Ta for Nb brings not much change, the properties are similar. In this study, a five-elements single crystal of $[La_2Sr]_A[Ta_{0.5}Ga_{0.5}]_B[Ga_3]_C[GaSi]_DO_{14}$ which has a composition with $x=1$ and $y=0.5$ on $La_{3-x}Sr_xTa_yGa_{5-x+y}Si_{1+x-2y}O_{14}$ ($0 \le x \le 3$, $0 \le y \le 1$) solid solutions is grown, and five pieces of grounded spheres made from a single crystal are analysed by a single crystal X-ray diffraction, which have different compositions deviated from synthesized composition. And effects of ionic size of cations substituted are discussed based on three-, four- and five-element compounds, which affect the piezoelectric properties.

2. Experimental

The crystal used for crystal structure analysis was grown by the Czochralski method. The conditions of the growth are shown in the previous paper [4]. Five single crystals cut from a grown crystal have been analysed by the single-crystal X-ray structure analysis. The compositions of the five single crystals were determined from the multiplicity of cations.

The piezoelectric properties were measured by the resonance method using rectangular plates of $9.0 \times 1.5 \times 0.3$–$0.5\ \mathrm{mm}^3$. The orientation of the long side was varied in each plate being (i) parallel to the (010) plane and [100] direction, and (ii) parallel to the $(2\bar{1}0)$ plane and [120] direction as well as $-15°$, $+15°$ and $+30°$ tilted to [120]. Two aluminium electrodes of 100 nm thickness were deposited on both plate areas by vacuum evaporation [4].

3. Results and discussions

3.1. Coordinates of oxygen ions on the decahedron

The compositions of the five piece single crystals are shown in Table 1. The deviations of crystal structure for the five piece single crystals with near composition $La_2SrTa_{0.5}Ga_{4.5}SiO_{14}$ on $La_{3-x}Sr_xTa_yGa_{5-x+y}Si_{1+x-2y}O_{14}$ ($0 \le x \le 3$, $0 \le y \le 1$) solid solutions are smaller than those of other three- and four-element compounds. In this section, the

Table 1
Compositions of five-element compounds LSTGS #1–#5 by refined multiplicity.

	La	Sr	Ta	Ga	Si
#1	2.124(6)	0.876(6)	0.476(3)	4.600(9)	0.92(1)
#2	2.070(6)	0.930(6)	0.497(3)	4.567(9)	0.94(1)
#3	2.08(1)	0.92(1)	0.482(3)	4.56(2)	0.95(2)
#4	2.03(1)	0.97(1)	0.499(3)	4.53(2)	0.97(2)
#5	2.00(1)	1.00(1)	0.492(4)	4.50(2)	1.01(2)

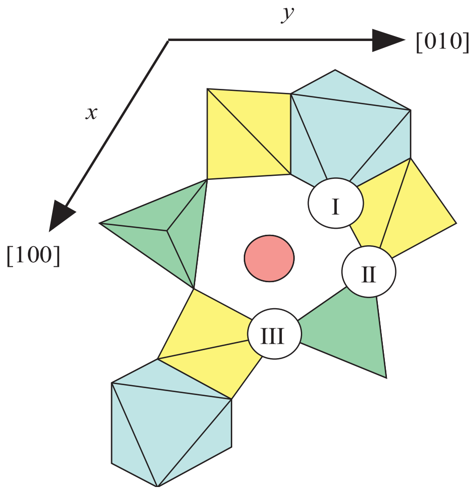

Fig. 3. Three kinds of oxygen ions I, II and III.

five piece single crystals of the five-element compounds are compared with the three- and four-element compounds based on the oxygen I, II and III as shown in Fig. 3.

The coordinates of oxygen ions I, II and III of the three- and four- and five-element compounds, are shown in Fig. 4(a)–(c). In the oxygen I, the coordinates x of the five-element compounds are a little smaller than those of the three- and the four-element compounds, and coordinates y of them locate between the three- and the four-element compounds, and near the three-element compounds as shown in Fig. 4(a). In the oxygen II, the coordinates x locate near the three-element compounds, and the coordinates y locate in intermediate positions between the three- and four-element compounds. In the oxygen III, the coordinates x and y locate near and larger than the three-element compounds. All coordinates of oxygen ions I, II, and III of five-element compounds are located near the three-element compounds, because the compositions of five-element compounds are similar to the three-element compounds, that is, the site occupancies of A-site are R:Sr = 2:1 which is near the three-element compounds, and B-sites are occupied by Ta:Ga with 1:1 similar with Ga, and D-sites are occupied by Ga:Si = 1:1 with same occupancy with the three-element compounds.

3.2. Effects of ionic size of cations for the piezoelectric properties

Fig. 4 shows coordinates of oxygen I, II and III (Fig. 3) on the three-element compounds RGS (R = La, Pr, and Nd), four-element compounds (SC)(TN)GS, and five-element compounds LSTGS #1–#5 (Table 1). In the case of the three-element compounds whose structure were presented by Iwataki et al.[3], coordinates of oxygen I, II, and III are distributed depending on the R-ion in the A-site. The coordinate x of oxygen I decreases and y increases as the radii of R-ions increase. x of oxygen II decreases a little, and y greatly as the radii of R-ions increase. As oxygen III is equivalent with oxygen II by the three-fold axes, the movements of III are correlated with II. Based on the movements of these oxygen ions, oxygen ions I and III become more distant from the centre of A-site which are coincident with expansion of the site by the occupation of a large ion. On the other hand, oxygen II moves to the centre of A-site. When a large sized ion occupies A-site, the A-site expands to [100] and shrinks to [120]. The mechanism of piezoelectricity on langasite crystal structure was presented in previous papers [3,5,6] on which the piezoelectricity generated at [100] direction by dipole moment appeared from moving the centres of mass of positive and negative charges. The piezoelectric constant $|d_{11}|$ and electromechanical coupling factor k_{12} as a function of A_L/B_L increase lineally as the size

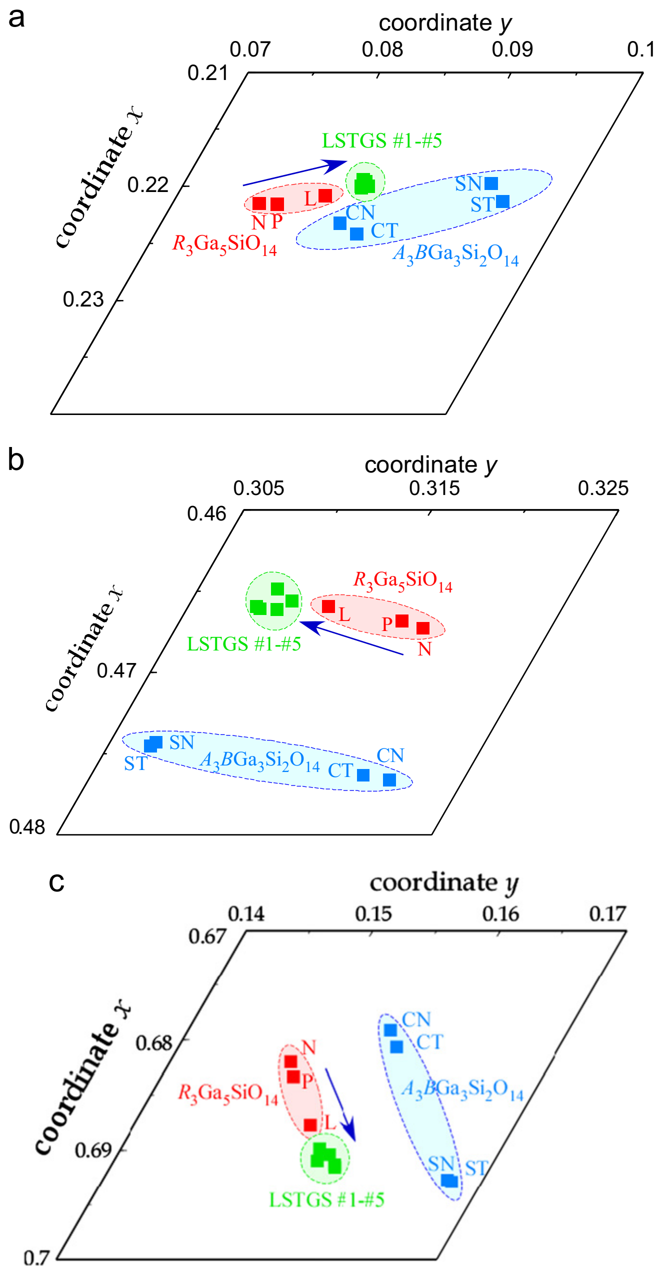

Fig. 4. The coordinates of three oxygen ions I (a), II (b), and III (c) on the five-element compounds with three-element compounds and four-element compounds.

of *A*-ion increases as shown in Fig. 2(a) [5,6,7]. In the case of the four-element compounds (SC)(TN)GS as shown in Fig. 4, the effects for *A*-site substitution of Sr for Ca on STGS/SNGS and CTGS/CNGS, and for *B*-site substitution of Ta for Nb on STGS/CTGS and SNGS/CNGS are discussed in this section. Movement of oxygen I, II and III of the four-element compounds are similar with those of three-element compound, so the *A*-site expands to [100] and shrinks to [120]. The $|d_{11}|$ and k_{12} of these compounds as a function of A_L/B_L are increased lineally same as three-element compounds as shown in Fig. 2(b). SNGS/STGS with large ionic radius in *A*-site shows large piezoelectric properties. In the case of the five-element compounds, the distribution of oxygen of this case appears in narrow area, because of five piece crystals obtained from the same single crystal. And the distribution of oxygen coordinates of five-element compounds locates nearer to three-element compounds than the four-element compounds, because the compositions of the five-element compounds are similar with those of three-element compounds as stated before.

As presented above, the five-element compounds locate near the three-element compounds, and moreover the five-element compounds locate on the extended direction of the enlarged ionic radius of *R*-ion on the three-element compounds which are indicated by arrows in Fig. 4(a)–(c). The piezoelectric properties are expected to be high $|d_{11}|$ and k_{12} based on the Fig. 2.

4. Conclusions

Five piece single crystals of the five-element compounds are obtained from a single crystal grown from $La_{3-x}Sr_x$-$Ta_yGa_{5-x+y}Si_{1+x-2y}O_{14}$ ($0 \le x \le 3$, $0 \le y \le 1$) composition with $x=1$ and $y=0.5$. The compositions are calculated from site occupancies obtained from X-ray single crystal analysis located near the $(La_2Sr)_A(Ta_{0.5}Ga_{0.5})_B(Ga_3)_C(GaSi)_DO_{14}$ composition. The differences of crystal structure between three-, four- and five-element compounds are comparing coordinate of oxygen ions. It was clarified that the coordinates of oxygen I, II and III on the five-element compounds locate on the extended line of *R*-ion in *A*-site of the three-element compounds, and the dielectric properties was expected to be large.

Acknowledgements

The author would like to thank to Dr. K. Kawasaki and Dr. J. Sato of TDK Co. for the presenting of single crystals, Professors Cheon Chae-Il and Kim Jeong-Seog of Hoseo University Korea for discussion of the contents. A part of his work was supported by JSPS KAKENHI Grant Nos. 13650738, and 22560673.

References

[1] T. Fukuda, K. Shimamura, T. Kohno, H. Takeda, M. Sato, New piezoelectric crystal langasite, Journal of the Japanese Association of Crystal Growth 22 (5) (1995) 358–363.

[2] K. Tsukada, M. Takeuchi, S. Tokumitsu, Y. Ohmura, K. Kawaguchi, Combustion pressure sensor, R&D Review of Toyota CRDL 28 (4) (1993) 49–57.

[3] T. Iwataki, H. Ohsato, K. Tanaka, H. Morikoshi, J. Sato, K. Kawasaki, Mechanism of the piezoelectricity of langasite based on the crystal structures, Journal of the European Ceramic Society 21 (2001) 1409–1412.

[4] J. Sato, H. Takeda, H. Morikoshi, K. Shimamura, P. Rudolph, T. Fukuda, Czochralski growth of $RE_3Ga_5SiO_{14}$ (RE=La, Pr, Nd) single crystals for the analysis of the influence of rare earth substitution on piezoelectricity, Journal of Crystal Growth 191 (1998) 746–753.

[5] N. Araki, H. Ohsato, K. Kakimoto, T. Kuribayashi, Y. Kudoh, H. Morikoshi, Origin of piezoelectricity for langasite $A_3Ga_5SiO_{12}$ (A=La and Nd) under high pressure, Journal of the European Ceramic Society 27 (2007) 4099–4102.

[6] H. Ohsato, Origin of piezoelectricity on langasite, in: S.D. Hutagalung (Ed.), Material Science and Technology, InTech, Croatia, 2012, pp. 15–40.

[7] H. Ohsato, T. Iwataki, H. Morikoshi, Crystal structure and piezoelectric properties of four component langasite $A_3BGa_3Si_2O_{14}$, Transactions on Electrical and Electronic Materials 13 (2012) 171–176.