Synthesis and characterization of $Ba_3MeGa_3Si_2O_{14}$ ($Me=Nb^{5+}$, Ta^{5+}) crystal

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New piezoelectric $Ba_3MeGa_3Si_2O_{14}$ (abbreviated as BNGS for $Me=Nb^{5+}$ and BTGS for $Me=Ta^{5+}$) crystals were synthesized by the Czochralski technique using raw materials with stoichiometric compositions. An analysis of growing process showed that the BTGS crystal congruently melts and that the BNGS one incongruently melts. The crystal structure of BNGS has been refined using single-crystal X-ray diffraction data with a precision corresponding to an R index of 0.027. The crystal structure is isostructural to that of $Ca_3Ga_2Ge_4O_{14}$, which has the trigonal space group $P321$ and Z = 1. The lattice parameters were a = 8.5114(5) and c = 5.1943(3) Å. The distribution of each cation was found to be ordered in each site. Some surface acoustic wave (SAW) properties of BTGS are reported.

Key words: site preference, oxides, crystal growth, x-ray diffraction, crystal structure

1. INTRODUCTION

Recent progress of electronic technology requires new piezoelectric crystals with the high thermal stability of frequency and large electromechanical coupling factors. For designing devices such as filters with a wide pass band while maintaining high stabilities and small insertion attenuation, the necessity has arisen in discovering new piezoelectric crystals having intermediate properties between those of quartz and lithium tantalate ($LiTaO_3$). $La_3Ga_5SiO_{14}$ (abbreviated as LGS) and $La_3Ta_{0.5}Ga_{5.5}O_{14}$ (LTG) are leading candidates to satisfy those requirements [1-3]. Very recently, for a use in wideband-code division multiple access (W-CDMA) station, surface acoustic wave (SAW) filters made of LGS wafers have intensively been mass-produced.

The LGS crystal has $Ca_3Ga_2Ge_4O_{14}$-type structure (space group $P321$) [4]. 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 being smaller than that of the C site. In the $Ca_3Ga_2Ge_4O_{14}$ 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. Therefore, the chemical formula of $Ca_3Ga_2Ge_4O_{14}$ can be represented as $(Ca_3)^{3c}(Ga_1)^{1a}(Ga_1Ge_2)^{3f}(Ge_2)^{2d}O_{14}$ with the Wyckoff-site notation superscripted. Due to the existence of these many cation sites, a large number of $Ca_3Ga_2Ge_4O_{14}$-type compounds have been synthesized by isovalent and/or aliovalent substitution [5,6].

In refs.[7,8], ionic size preferences of cation site in the $Ca_3Ga_2Ge_4O_{14}$-type structure are reported as follows:

$$A = Na^+, Sr^{2+}, La^{3+} \quad (c.a. \ 1.22\text{Å})$$
$$B = Ga^{3+}, Sn^{4+}, Nb^{5+}, Ta^{5+} \quad (c.a. \ 0.65\text{Å})$$
$$C = Ga^{3+}, Ge^{4+} \quad (c.a. \ 0.43\text{Å})$$
$$D = Si^{4+}, Ge^{4+}, Al^{3+} \quad (c.a. \ 0.33\text{Å})$$

Based on the above data, one of the authors synthesized $Sr_3TaGa_3Si_2O_{14}$ single crystals [9]. The electro mechanical coupling factor of this crystal is comparable to that of LTG. It has been reported [8] that an increase lattice parameter a leads to an increase of the piezoelectric modulus $|d_{11}|$ of $Ca_3Ga_2Ge_4O_{14}$-type crystals (see figure
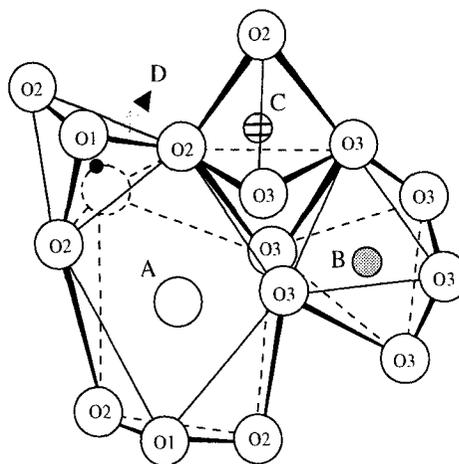

Fig. 1 Schematic coordination polyhedra of oxygen atoms around cationic atoms in $A_3BC_3D_2O_{14}$-type structure. Open circle ( ), coarse dot circle ( ), fine dot circle (◉), hatched circle (‒) and solid circle (●) represent oxygen atoms, the eight-(A), six-(B), four-(C) and smaller four-coordination (D) sites, respectively.
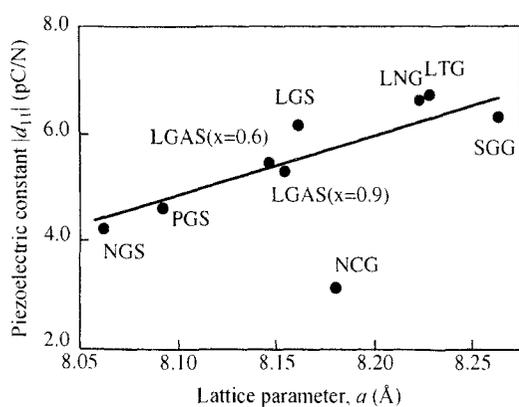
2). This report gave us a hint as to how to produce materials superior to LGS, and LTG. The simple way is possibly the substitution by larger cations of Sr^{2+} in Sr$_3$TaGa$_3$Si$_2$O$_{14}$. Hence, for the further development of new compounds, we synthesized strontium niobium(tantalum) gallium silicate Ba$_3$MeGa$_3$Si$_2$O$_{14}$ (abbreviated as BNGS for Me=Nb^{5+} and BTGS for Me=Ta^{5+}) crystal. No details of the crystal growth and structure analysis of these compounds were found. No description of the piezoelectric properties of BNGS and BTGS has been also published until now.

In this paper, we report the synthesis of BNGS and BTGS by solid state reaction, and the growth of crystals by the Cz technique. The distribution of substituted cations in the crystal structure and some piezoelectric properties are also described.

2. EXPERIMENTAL PROCEDURE
2.1 Sample preparation

The $A_3BC_3D_2O_{14}$ phase formation was studied in various mixtures by the solid state reaction technique. Starting materials were prepared by mixing 99.99 % pure oxide and carbonates powders at stoichiometric composition and pressed as pellet-like. Polycrystals with $A_3BC_3D_2O_{14}$-type structure were synthesized using a resistance furnace with SiC heating elements. The temperature used for synthesis ranged from 1200-1300 °C depending on the starting material. The holding time for reacting kept at 2-30 hours. For the resulted crystals the phases were identified by the powder X-ray diffraction (XRD) method. Single crystals were grown by a conventional RF-heating Cz technique using an iridium crucible (50 mm in diameter and height). The growth atmosphere was a mixture of Ar gas. The pulling rate and the rotation rate were 1.0 mm/h and 10 rpm, respectively. It may be worth nothing that <001> and <100> LTG or sintered rods were used as seed crystals

in this study.

2.2 Structure refinement

Single crystals cut from the grown boule was ground to a sphere and used for the structure analysis. The single crystal discharged at 296 K was mounted on a Rigaku image-plate detector system diffractometer with graphite-monochromated Mo K radiation. Detailed information of the data collection and refinement are summarized in Table I. Intensities were corrected for Lorentz, polarization and absorption factors using the Rigaku programs *Rapid*. The crystal structure was refined using the full-matrix least-squares program *SHELXL-93* [10].

2.3. SAW measurement

Their thickness and width were about 1mm and 20mm, respectively. A surface of the crystal was polished to optically flat, and lapping treatment was used for another side. Al IDTs were fabricated on polished surface of the crystals by photolithography process. A pair of IDTs was used for filter measurement. The IDTs were placed on the crystals at 22.5° intervals of azimuthal angle, and the dependence of SAW characteristics on propagation direction was examined. The S-parameters of the IDTs were measured with a network analyzer (Advantest R3762AH), and the radiation admittance and filter characteristics were obtained. From these characteristics, the SAW velocity v, coupling coefficient k^2 were calculated.

3. RESULTS AND DISSCUSSION
3.1 Growth phenomena

The synthesized BNGS and BTGS powders consisted of the Ca$_3$Ga$_2$Ge$_4$O$_{14}$-type phase. The BNGS and BTGS melted at ~1220 and ~1350°C, respectively. The solidification behavior of both compounds depended on

Fig.3 Piezoelectric modulus $|d_{11}|$ versus the lattice parameter, a, in $A_3BC_3D_2O_{14}$-type crystals. After Takeda [7].

LGS	La$_3$Ga$_5$SiO$_{14}$	PGS	Pr$_3$Ga$_5$SiO$_{14}$
NGS	Nd$_3$Ga$_5$SiO$_{14}$	LNG	La$_3$Nb$_{0.5}$Ga$_{5.5}$O$_{14}$
LTG	La$_3$Ta$_{0.5}$Ga$_{5.5}$O$_{14}$	LGAS	La$_3$Ga$_{5-x}$Al$_x$SiO$_{14}$
SGG	Sr$_3$Ga$_2$Ge$_4$O$_{14}$	NCG	Na$_2$CaGe$_6$O$_{14}$

Table 1 Crystal Data and Intensity Collection for Ba$_3$NbGa$_3$Si$_2$O$_{14}$

Color	Colorless
Diameter of specimen (mm)	0.140
Crystal system	Trigonal
Space group	$P321$ (No.150)
Lattice parameters	$a = 8.5114(5)$ Å
	$c = 5.1943(3)$ Å
Volume (Å^3)	325.88
Formula weight	944.27
Calculated density (g/cm^3)	5.066
Radiation	Mo Kα
	($\lambda = 0.71069$ Å)
Monochromator	Graphite (002)
μ (Mo Kα) (mm^{-1})	16.13
Maximum 2θ (°)	55
No. of reflections measured	3126
No. of independent reflections	499
No. of used reflections [F^2 ≥ 3σ(F^2)]	302
R	0.027
R$_w$	0.058
Goodness of fit	1.016

Table II Atomic parameters of $Ba_3NbGa_5Si_2O_{14}$ with estimated standard deviations in parentheses.

Site		x	y	z	B
Ba	3e	0.43168(1)	0	0	0.0071(3)
Nb	1a	0	0	0	0.0061(5)
Ga	3f	0.7449(2)	0	1/2	0.0026(9)
Si	2d	1/3	2/3	0.4799(9)	0.0051(4)
O1	2d	1/3	2/3	0.795(2)	0.007(2)
O2	6g	0.475(1)	0.2986(9)	0.646(1)	0.007(1)
O3	6g	0.2169(9)	0.107(1)	0.225(1)	0.009(1)

Table III Selected Interatomic Distances (Å) for $Ba_3NbGa_5Si_2O_{14}$ with estimated standard deviations in parentheses.

	Nb octahedron				Si tetrahedron				Ga tetrahedron		
Nb - O3	×6	1.982(8)		Si - O1	×1	1.636(12)		Ga - O2	×2	1.877(8)
O3 - O3	×6	2.769(12)		- O2	×3	1.643(8)		- O3	×2	1.823(7)
- O3'	×3	2.822(10)		(Si-O)av		1.641		(Ga-O)av		1.850
- O3"	×3	2.849(10)		O1 - O2	×3	2.742(12)		O2 - O2'	×1	3.011(10)
(O-O)av		2.802		O2 - O2'	×3	2.609(11)		- O3	×2	2.946(11)
				(O-O)av		2.676		O2' - O3	×2	2.926(11)
								O3 - O3'	×1	3.282(9)
								(O-O)av		3.006

	Ba polyhedron										
Ba - O1	×2	2.740(4)		O1 - O2	×2	3.954(7)		O2 - O3	×2	3.359(11)
- O2	×2	2.730(8)		- O2'	×4	3.271(12)		- O2'	×1	2.609(14)
- O2'	×2	3.006(7)		- O3	×2	3.317(8)		- O3'	×1	3.599(11)
- O3	×2	2.684(8)						- O2"	×1	4.501(10)
(Ba-O)av		2.790						O3 - O3'	×1	2.822(10)
								(O-O)av		3.420

the holding time for reacting. The authors found that the solidified aggregates mainly consisted of glass phase after the powders obtained by reacting at 2 hours melted The crystalline phase was obtained from the solidified melts using the powder by reacting at 30 hours. There was no difference in the powder XRD profiles of both powders. These solidification phenomena are under investigation. Hence, the powders obtained by reacting at 30 hours were used for crystal growth.

In BNGS, the boule grown from melts with a stoichiometric composition was opaque and had large amounts of Ba_2SiO_4 and $BaGa_2O_4$ as the impurity phases. Although the Cz growth of BNGS was performed using <001> and <100> LTG as a seed, the same results were obtained. In BTGS, the obtained crystal was colorless transparent and had no crack and bubble. All peaks on X-ray diffraction patterns were identified to be those of BTGS and no peaks of a second phase were found. The growth process showed that the BTGS crystal congruently melts, and that BNGS incongruently melt. Since BNGS phase was already observed in the initial part of the boule, it was suggested that BNGS is not a peritectic compound such as $La_3M^{4+}Ga_5O_{14}$ (M=Ti, Zr, Hf) [11] and show the melting behavior such as $LiTaO_3$[12]. The bulk crystal for piezoelectric measurement was obtained only in BTGS.

3.2 Structural feature

In both BNGS and BTGS, samples with the size enough for the single crystal X-ray diffraction method were prepared. We describe the structure feature of BNGS only because that of BTGS is very similar to BNGS. The positional and isotropic thermal parameters of BNGS are summarized in Table II. Selected

interatomic distances are listed in Table III.

The distribution of Nb, Ga and Si was examined by the common site-multiplicity refinement, assuming that the octahedral (1a) and two tetrahedral (2d and 3f) sites were occupied by Nb and Ga atoms and by Ga and Si ones, respectively. The distribution model that Ta and Si atoms partially occupy two tetrahedral and octahedral sites, respectively, produced larger R value (>0.10). The model that each site was fully occupied by each metal produced minimum R value (see table I). Therefore, the distribution of all metals determined finally was $(Ba_3)^{3e}(Nb)^{1a}(Ga_3)^{3f}(Si_2)^{2d}O_{14}$, with the Wyckoff-site notation superscripted.

The Ba atoms are coordinated to eight O atoms, at distance 2.684-3.006 Å, forming a distorted cubic antiprism. The coordination around Nb is close to a regular octahedron. The average Nb-O distance (1.982 Å) is shorter than those in $Ca_3NbGa_3Si_2O_{14}$ (1.992 Å) [13] and the estimated Nb^{VI}-O distance (2.002 Å) [14]. The mean Ga-O distance (1.850 Å) is similar to that (1.847 Å) in $Ca_3NbGa_3Si_2O_{14}$, and the mean Si-O distance (1.641 Å) is longer than the corresponding one (1.628 Å). The difference (0.213 Å) in A site bond length between BNGS and $Ca_3NbGa_3Si_2O_{14}$ is smaller than that in ionic radii (0.30 Å). This result suggests that Ba^{2+} ion is too large to enter into A site. This suggestion agreed with ionic size preference of cation site in the $Ca_3Ga_2Ge_4O_{14}$-type structure reported in ref [7,8].

A calculation of empirical bond valences [15] from the structural data, using the distribution of atoms determined by the refinement, gives a bond-valence sum of +4.95 for Nb for at 1a site in BNGS. The similar value is also observed in $Sr_3TaGa_3Si_2O_{14}$[9], that for Ta at the same site is +5.16. In $La_3Nb_{0.5}Ga_5O_{14}$[16] and

$Ca_3NbGa_3Si_2O_{14}$[13] with the same structure; the bond–valence sums for Nb at $1a$ site are +4.75 and +4.82, respectively. Therefore, it was suggested that the $1a$ site prefers a higher valence atom by the incorporation of atoms with larger ionic radii (Ca^{2+}; r^{VIII} = 1.12 Å, La^{3+}; 1.16 Å, Sr^{2+}; 1.26 Å ; Ba^{2+}, 1.42 Å [14]) into the decahedral site.

3.3 SAW properties

The SAW properties of BTGS crystal were characterized. Figure 3 shows the frequency response of a SAW filter with IDTs λ=0.1(mm) utilized X-axis propagation of SAW on a BTGS Y-cut crystal without matching circuit. The propagation direction dependence of SAW velocity measured was also obtained. The angular dependence of velocity of BTGS was very similar to that of isomorphs LGS[17,18] and LTG[3,19]. The maximum velocity obtained on BTGS Y-cut crystal was 2870 m/s. The maximum k^2 values in Y-cut BTGS wafer was about 0.43% at X-axis propagation. This value is larger than those of LGS (0.38%[17] and 0.35%[18]), and is comparable to that of LTG (0.39%[19] and 0.44%[3]). For the BTGS crystal, a large reduction (40%) of the Ga_2O_3 amount against LGS and LTG are expected. The piezoelectric device made of BTGS crystal enables the use of a lower amount of expensive gallium oxide as the raw material. Therefore, we can say that the BTGS crystal is the preferable piezoelectric materials with the $Ca_3Ga_2Ge_4O_{14}$-type structure for both bulk- and surface-acoustic wave devices.
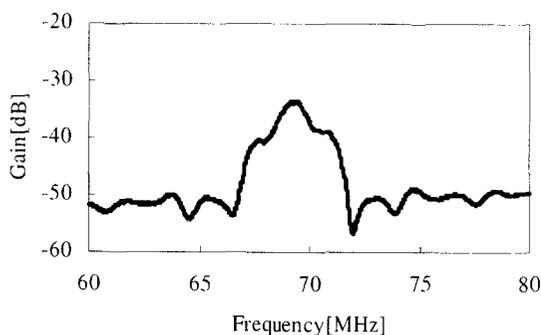

Figure 3 The filter characteristic $Ba_3TaGa_3Si_2O_{14}$ Y-cut crystal wafer at X-axis propagation.

4. SUMMARY

Piezoelectric BNGS and BTGS single crystals were grown by the Czochralski technique. The results of single-crystal X-ray structure analysis indicated that each metal occupies its respective crystallographic site in an ordered way. Using the BTGS crystals, SAW filters were prepared and Their properties were determined. The BTGS crystal is superior to LGS, which is currently the mass-produced material, with respect to piezoelectric properties.

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