Electrical conduction mechanism in $\text{La}_3\text{Ta}_{0.5}\text{Ga}_{5.3}\text{Al}_{0.2}\text{O}_{14}$ single crystals

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The electrical conduction mechanism in $\text{La}_3\text{Ta}_{0.5}\text{Ga}_{5.3}\text{Al}_{0.2}\text{O}_{14}$ (LTGA) single crystals was studied by nonstoichiometric defect formation during crystal growth. Since stoichiometric LTGA is not congruent, the single crystal grown from the stoichiometric melt was Ta-poor and Al-rich, where Al atoms were substituted not only in Ga sites but also in Ta sites. The population of the substitutional Al in Ta sites increased with increasing oxygen partial pressure during growth (growth- $p\text{O}_2$) in the range from 0.01 to 1 atm. Below 600 °C, substitutional Al atoms in Ta sites were ionized to yield holes, and thus the electrical conductivity of the LTGA crystal depended on temperature and the growth- $p\text{O}_2$. The dependence of the electrical conductivity on the growth- $p\text{O}_2$ decreased as temperature increased. The temperature rise increases ionic conductivity, for which the dominant carriers are oxygen defects formed by the anion Frenkel reaction. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4839955>]

I. INTRODUCTION

In order to reduce emissions of global warming greenhouse and pollutant gases, various automobile manufacturers are competing to develop new engines with improved combustion efficiency that can greatly contribute to reducing CO_2 , NO_x , and other gas emissions. Combustion pressure sensors installed in engine cylinders are becoming increasingly important for monitoring combustion conditions to control the ideal combustion in an engine.

Langatate ($\text{La}_3\text{Ta}_{0.5}\text{Ga}_{5.5}\text{O}_{14}$: LTG) is a Langanisite ($\text{La}_3\text{Ga}_5\text{SiO}_{14}$: LGS)-type crystal which has a $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ structure with the P321 space group. Since LGS-type crystals have a piezoelectric constant about 3 times higher than that of quartz and are stable over a wide temperature range, they are the most attractive piezoelectric materials for use at high temperatures.¹

LTG, which has the highest electrical resistivity among LGS type crystals,² is considered to be a candidate piezoelectric material for combustion pressure sensors used at high temperatures. Furthermore, it has been reported that Al-substituted langatate has higher resistivity than LTG. Takeda *et al.* reported that single crystal LTGA0.5 ($\text{La}_3\text{Ta}_{0.5}\text{Ga}_5\text{Al}_{0.5}\text{O}_{14}$) has one order of magnitude higher resistivity than LTG. They showed that the resistivity of the LTGA0.5 crystals was about $1\text{E}+8\ \Omega\text{cm}$ at 500 °C, and one of the LTG crystals had a resistivity of about $5\text{E}+6\ \Omega\text{cm}$.³ In contrast, Zhang *et al.* reported that the LTGA0.2 crystal resistivity was $2.2\text{E}+7\ \Omega\text{cm}$ and the LTG crystal resistivity was $1.5+7\ \Omega\text{cm}$,^{4,5} for which the ratio of the LTG resistivity to the LTGA resistivity is less than 1.5 times. As mentioned above, the resistivity values for LTGA and LTG vary in different studies. Therefore, it is important to study the electrical conduction mechanism in LTGA.

We previously investigated the electrical conduction mechanism in LTG from the standpoint of nonstoichiometric defects created during growth from the melt using the Kroger–Vink diagram.⁶ The purpose of the present study was to investigate the electrical conduction mechanism in LTGA in the same way as in the previous paper. LTGA single crystals were grown from the stoichiometric melt under various oxygen partial pressures, $p\text{O}_2$, and the electrical conductivity was measured in these specimens. Using the Kroger–Vink diagram, we discuss the conduction mechanism in LTGA single crystals grown from the stoichiometric melt based on substitutional Al ions in Ta sites originating holes below 600 °C; the conductivity became increasingly ionic due to the oxygen defects as the temperature increased.

II. EXPERIMENTAL

A. Growth of LTGA single crystal by the floating zone (FZ) method

High-purity (99.99%) powders of La_2O_3 , Ta_2O_5 , Ga_2O_3 , and Al_2O_3 were used to make a single phase LTGA feed rod. The mixed powder with the composition of $\text{La}_3\text{Ta}_{0.5}\text{Ga}_{5.3}\text{Al}_{0.2}\text{O}_{14}$ was sintered at 1420 °C for 10 h in air. After crushing and thorough mixing of the sintered sample, the powder was packed into a rubber tube and sealed after evacuation. The tube was isotropically pressed at $5.9 \times 10^7\ \text{N/m}^2$, whereby the powder was compacted into a rod. The rod was hung in a furnace using a Pt wire and sintered at 1420 °C for 10 h in air. X-ray diffraction analysis (Rigaku, Japan) of a feed rod confirmed only a single phase.

In order to avoid possible Ir contamination from the crucible, single crystals of LTGA were grown by the FZ method using the feed rod. An infrared convergence-type apparatus (Crystal System Corp.; FZ-T-2000-H-UD-PC) was employed for the FZ growth. A Z-oriented LTG single crystal was used as a seed. To avoid Ir contamination, Ir-free seed crystals made by the FZ method were used. The growth rate was about 3 mm/h and the molten zone length was 3–4 mm. The

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rotation rates of the feed rod and growing crystal were 25 rpm and 10 rpm, respectively, in opposite directions. During growth, the oxygen partial pressure (growth- pO_2) was held between 0.001 and 1 atm using an Ar/ O_2 gas mixture.

LTGA single crystals grown by the FZ method under growth- pO_2 from 0.001 to 1 atm are shown in Fig. 1. The grown crystals had a 5 mm diameter and 10–15 mm length. Preliminary electron probe micro-analysis (EPMA) results indicated that the composition of the crystals along the growth direction became constant (steady-state) beyond 4 mm from the growth-start position. Thus, to fabricate specimens for electrical conductivity and chemical composition measurements, single crystals were cut perpendicular to the Z-axis and 6 mm from the growth-start position; disk-shaped specimens with 1.5 mm thickness and 25 mm² cross-sectional area along the Z-plane were obtained.

B. Chemical composition measurement

The chemical compositions of the grown crystals and the feed rod were determined by EPMA with a wave dispersion system (JEOL JXA-8621MX). LaB_6 , GaAs, pure Ta, Al_2O_3 , and LaP_5O_{14} were used as the standard for La, Ga, Ta, Al, and O, respectively. In all measurements, the accelerating voltage was 15 kV, the specimen current was 20 nA, and the microprobe diameter was 2 μm . Measurements were carried out at 30 points along the radial direction at constant intervals. Since there was no obvious radial variation in composition, the average composition was determined for each specimen and feed rod.

C. Measurements of ionic transport number and electrical conductivity

The ionic transport number was measured for the LTGA single crystal by the electromotive force (emf) method. The ionic transport number, t_{ion} , is defined as the ratio of the measured open circuit voltage, V , to the complete ionic conductor voltage V_0 , i.e.,

$$t_{ion} = V/V_0. \quad (1)$$

Here, V_0 is expressed by the Nernst equation

$$V_0 = \frac{kT}{4q} \ln \frac{pO_2^I}{pO_2^{II}}, \quad (2)$$

where pO_2^I and pO_2^{II} are the oxygen partial pressures on opposite sides of the crystal, k is the Boltzmann's constant, T is the absolute temperature, and q is the elementary charge. In this experiment, pO_2^I and pO_2^{II} were fixed at 1 atm and Air (0.21 atm), respectively, and the open circuit voltage V was monitored with a digital voltmeter (HEWLETT PACKARD; 34401 A).

The electrical conductivity of the single crystal LTGA was measured by the DC two-terminal circuit method. Pt sputtering was carried out to form electrodes on both sides of the specimens. Electrical conductivity measurements were performed in the temperature range from 300 to 1000 °C with a 30 min holding time at each temperature under the same atmosphere as used for the crystal growth. The applied voltage across the sample was 100 V, and the current was measured by a pA meter (KEITHLEY; 6487).

III. EXPERIMENTAL RESULTS

A. Coloration and chemical composition of single crystal

Fig. 1 shows the LTGA single crystals grown by the FZ method for various growth- pO_2 values. The crystals grown under low growth- pO_2 were colorless and transparent. The color of the crystals grown under higher growth- pO_2 was light orange, similar to LTG single crystals,⁶ but the orange color of the LTGA crystal was lighter than that of the LTG crystal.

The chemical compositions of the single crystal and the feed rod as analyzed by EPMA are shown in Fig. 2. The feed rod was maintained to have the same composition of the raw materials. The La, Ga, and O concentrations of the single crystal and feed rod were thus approximately the same. The Ta concentration in the single crystals tended to be lower than that in the feed rod and decreased as the growth- pO_2 increased. In contrast, the Al concentration in the single crystals grown under the growth- pO_2 , in the range from 0.01 to 1 atm, tended to be higher than that in the feed rod and the Al concentration of single crystals increased as the growth- pO_2 increased.

Takeda *et al.* reported that the segregation coefficient of Al was greater than unity in LTGA0.5 grown by the Czochralski (CZ) method under 0.01 atm growth- pO_2 ,⁷ and Jung *et al.* reported that the segregation coefficient of Al was 0.99 in LTGA0.1 and 0.97 in LTGA0.3 grown by the micro-pulling-down method under 0.01 atm growth- pO_2 .⁸ In this result of the FZ method, the segregation coefficient of Al was a little lower than unity under 0.001 atm growth- pO_2 and higher than unity under growth- pO_2 in the range from 0.01 to 1 atm.

Although segregation depends on the growth method, composition and growth conditions used, the present results indicate that the composition of single crystal LTGA tends

FIG. 1. Single crystals of LTGA fabricated under growth- pO_2 in the range from 0.001 to 1 atm.

FIG. 2. Chemical compositions of single crystals and feed rods where pO_2 represents growth- pO_2 and feed rod fabricated pO_2 , respectively. Symbols are the experimental points and dotted lines are the linear approximation fits.

to deviate toward the Al-rich condition from the initial composition in the range from 0.01 to 1 atm.

In addition, XRD studies on CZ grown LTGA0.5 crystals by Takeda *et al.* show that Al atoms preferably substituted octahedral sites which Ta and Ga equally occupied in half.⁹ Therefore, it seems reasonable to suppose that Al atoms occupied not only Ga but also Ta sites in the octahedral sites.

B. Ionic transport number and electrical conductivity of single crystal LTGA

The ionic transport number of the LTGA single crystal with 0.01 atm growth- pO_2 is plotted as a function of temperature in Fig. 3. The LTGA conductivity is dominantly

FIG. 3. Ionic transport number as a function of temperature for LTGA single crystals with growth- $pO_2 = 0.01$ atm.

electronic below 600 °C and becomes increasing ionic as the temperature rises.

The electrical conductivity of single crystal LTGA is plotted as a function of growth- pO_2 and temperature in Fig. 4. The electrical conductivity increased with increasing growth- pO_2 , and the growth- pO_2 dependence of electrical conductivity declined with temperature. The ionic transport number measurement suggested that the growth- pO_2 dependence of electrical conductivity was strong below 600 °C when electronic conduction was predominant, and became weaker as the temperature became higher where ionic conduction is dominant.

The power index for the growth- pO_2 for the as-grown LTGA in the growth- pO_2 is shown in Fig. 5, and is seen to

FIG. 4. Electrical conductivity of single crystal LTGA as a function of growth- pO_2 . The symbols represent experimental points and the dotted lines are the power approximation fits.

FIG. 5. Power index of pO_2 for single crystal LTGA in the growth- pO_2 range from 0.001 to 1 atm.

decrease with temperature. The power index for LTGA was 0.23 at 300 °C, which is smaller than the value of 0.55 for LTG.⁶

Takeda *et al.* and Zhang *et al.* have reported that the electrical resistivity of LTGA was higher than that of LTG. Takeda *et al.* showed that the resistivity of the LTGA0.5 crystal was about $1E+8 \Omega \text{ cm}$ at 500 °C and that of the LTG crystal was about $5E+6 \Omega \text{ cm}$.³ In addition, Zhang *et al.* reported that the resistivity of the LTGA0.2 crystal was $2.2E+7 \Omega \text{ cm}$ and that of the LTG crystal was $1.5E+7 \Omega \text{ cm}$.⁵ In our study, the highest resistivity of LTGA was lower than that of LTG; the resistivity of LTGA0.2 with 0.001 atm growth- pO_2 was $6.7E+7 \Omega \text{ cm}$ and that of LTG with 0.005 atm growth- pO_2 was $2.2E+8 \Omega \text{ cm}$ at 500 °C.⁶ However, the resistivity of LTGA in our study was close to the reference data, while in contrast, the LTG in our study showed higher resistivity compared to the reference data.

IV. DISCUSSION

We consider the electronic carrier formation mechanism to be valid at temperatures below 600 °C. The electrical conductivity increases with growth- pO_2 and the conduction is electronic, and thus the carrier is a hole according to the Kroger-Vink diagram. Since the carriers are holes, the possible defect reaction is related to excess oxygen, metal vacancy, or substitution with lower valence element.

We noted in Sec. III A that Al atoms occupied not only Ga but also Ta sites in the octahedral sites. The quasi-chemical equation expressing the formation of a neutral substitutional Al in the Ta site ($Al_{Ta}^{\times}$) during growth due to the incorporation of oxygen at an oxygen lattice position is given by

where $O_O^{\times}$ is an oxygen atom at the respective site in the crystal lattice. The concentration of $O_O^{\times}$ is usually assumed

to be $[O_O^{\times}] \approx 1$. From the law of mass action and the $[O_O^{\times}] \approx 1$ approximation, the equilibrium constant ($K_{Al_{Ta}^{\times}}$) and free energy change ($\Delta G_{Al_{Ta}^{\times}}$) associated with the reaction (Eq. (3)) are given as

$$K_{Al_{Ta}^{\times}} = [Al_{Ta}^{\times}] (pO_2)^{-1/2}, \quad (4)$$

and

$$\Delta G_{Al_{Ta}^{\times}} = \Delta G_{Al_{Ta}^{\times}}^{\circ} + RT \ln K_{Al_{Ta}^{\times}}, \quad (5)$$

where pO_2 is the growth- pO_2 , R is the gas constant, and $\Delta G_{Al_{Ta}^{\times}}^{\circ}$ is the standard free energy difference of substitutional Al formation.

Since $\Delta G = 0$ at equilibrium, Eqs. (4) and (5) give the concentration of the neutral substitutional Al in the Ta site as

$$[Al_{Ta}^{\times}] = (pO_2)^{1/2} \exp\left(\frac{-\Delta G_{Al_{Ta}^{\times}}^{\circ}}{RT_S}\right), \quad (6)$$

where T_S is the solidification temperature of LTGA. Eq. (6) shows that the concentration of substitutional Al forming at the Ta lattice increases as the oxygen partial pressure increases. During crystal growth of LTGA via the FZ method, the temperature gradient in the crystal near the solid-liquid interface was very high such that the substitutional Al was frozen-in and remained at the measurement temperature.

Since the maximum valencies of Ta and Al are five and three, respectively, the maximum ionization of substitutional Al in Ta is doubly negative. When a neutral substitutional Al in Ta, $Al_{Ta}^{\times}$, is singly ionized to yield a hole, $h^{\bullet}$

where Al_{Ta}' is a negatively charged substitutional Al in Ta and $h^{\bullet}$ is a hole formed in the valence band. The substitutional Al concentration was fixed under a certain growth temperature and growth- pO_2 . Therefore, even if the substitutional Al was highly ionized and the respective ionized substitutional Al concentrations changed, the total concentration of these substitutional Al remained constant. The equilibrium constant ($K_{Al_{Ta}'}$) associated with Eq. (7) is given by

$$K_{Al_{Ta}'} = [Al_{Ta}'] p / [Al_{Ta}^{\times}], \quad (8)$$

where p is the hole concentration.

Electrical neutrality requires

$$[Al_{Ta}'] = p. \quad (9)$$

Combining Eq. (9) with Eqs. (6) and (8), the hole concentration, p , is proportional to the quarter power of the growth- pO_2

$$p = (K_{Al_{Ta}'})^{1/2} [Al_{Ta}^{\times}]^{1/2} \propto (pO_2)^{1/4}. \quad (10)$$

When the substitutional Al is doubly ionized and yields two holes at higher temperatures, the quasichemical reaction and hole concentration are given by

$$Al_{Ta}^{\times} \leftrightarrow Al_{Ta}^{\prime\prime} + 2h^{\bullet}, \quad (11)$$

$$p = \left(2K_{V_{Ta}^{\prime\prime}}\right)^{1/3} [Al_{Ta}^{\times}]^{1/3} \propto (pO_2)^{1/6}, \quad (12)$$

where $Al_{Ta}^{\prime\prime}$ is a secondary charged substitutional Al and $K_{V_{Ta}^{\prime\prime}}$ is the equilibrium constant.

From Eqs. (10) and (12), it should be noted that the power index for pO_2 for hole concentrations decreases with ionization of the substitutional Al as $1/4(0.25)$, $1/6(0.17)$. Comparing with the power index for pO_2 in electrical conductivity measurements, the dominant substitutional Al in Ta at each temperature is expected to be as shown in Table I below 600 °C where holes are the dominant carriers.

The power index decrease as $1/4(0.25)$, $1/6(0.17)$ is the same as an oxygen atom in a lattice position presented as

$$\frac{1}{2}O_2 \leftrightarrow O_i^{\times}, \quad (13)$$

$$O_i^{\times} \leftrightarrow O_i' + h^{\bullet} \left(\frac{1}{2}O_2 \leftrightarrow O_i' + h^{\bullet} \right), \quad (14)$$

$$p = \left(K_{O_i'}\right)^{1/2} (pO_2)^{1/4}, \quad (15)$$

$$O_i^{\times} \leftrightarrow O_i'' + h^{\bullet} \left(\frac{1}{2}O_2 \leftrightarrow O_i'' + 2h^{\bullet} \right), \quad (16)$$

$$p = \left(K_{O_i''}/4\right)^{1/3} (pO_2)^{1/6}, \quad (17)$$

where O_i' and O_i'' are singly and doubly charged interstitial oxygen ions, respectively, and $K_{O_i'}$ and $K_{O_i''}$ are equilibrium constants.

However, the EPMA results showed the trend that the Ta concentration decreased and the Al concentration increased in the LTGA single crystals as the growth- pO_2 increased. It should be noted that the predominant carrier is a hole attributed to not interstitial oxygen but substitutional Al in a Ta site.

Ionic transport number measurements indicated that the LTGA conductivity becomes increasingly ionic as the temperature rises above 600 °C. Fig. 6 shows the activation energy of the electrical conductivity obtained by the Arrhenius plot in the temperature range from 700 to 1000 °C for single crystal LTGA.

Since the activation energy for LTGA is 1.1–1.2 eV, which is close to that for oxygen vacancy diffusion in LGS (1.2 ± 0.2 eV) reported by Schulz *et al.*,¹⁰ this supports the case for oxygen defects (vacancy or interstitial oxygen) being the dominant carriers of ionic conduction as in the case of LTG in the previous paper.⁶

TABLE I. Power index of pO_2 for single crystal LTGA and dominant substitutional Al in Ta sites at each temperature.

Temperature (°C)	Power index of pO_2	Dominant substitutional Al in Ta
300	0.23	$Al_{Ta}^{\prime}$
400	0.21	$Al_{Ta}^{\prime}$
500	0.18	$Al_{Ta}^{\prime\prime}$
600	0.16	$Al_{Ta}^{\prime\prime}$

FIG. 6. Activation energy Ea of electrical conductivity obtained by an Arrhenius plot in the temperature range from 700 to 1000 °C for single crystal LTGA.

Oxygen defects are formed during the crystallization of LTGA, shown by the anion Frenkel reaction

V. CONCLUSIONS

The electrical conduction mechanism in single crystal LTGA was investigated from the standpoint of nonstoichiometric defects created during growth from the melt. Since the stoichiometric LTGA is not congruent, the single crystal grown from the stoichiometric melt was Ta-poor and Al-rich, where Al atoms were substituted not only in Ga sites but also in Ta sites. The ionic transport number and electrical conductivities were measured in the temperature range from 300 to 1000 °C. The ionic transport number showed that the LTGA conductivity is dominantly electronic below 600 °C and becomes increasing ionic as the temperature rises.

The dependence of the growth- pO_2 on conductivities was studied based on the Kroger-Vink diagram. The electrical conductivity of the LTGA single crystal depended on the growth- pO_2 , its power indices and composition change suggesting that hole conduction was predominant due to ionization of substitutional Al in Ta sites below 600 °C. The temperature rise increases ionic conductivity with the dominant carrier being oxygen defects formed by the anion Frenkel reaction. The activation energy in this case was 1.1–1.2 eV in the temperature range from 700 to 1000 °C, which supports oxygen vacancies being the dominant carrier.

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- ¹H. Fritze and H. L. Tuller, [Appl. Phys. Lett.](#) **78**, 976 (2001).
- ²J. Bohm, R. B. Heimann, M. Hengst, R. Roewer, and J. Schindler, [J. Cryst. Growth](#) **204**, 128 (1999).
- ³H. Takeda, S. Tanaka, H. Shimizu, T. Nishida, and T. Shiosaki, [Key Eng. Mater.](#) **320**, 239 (2006).
- ⁴S. Zhang, A. Yoshikawa, K. Kamada, E. Frantz, R. Xia, D. W. Snyder, T. Fukuda, and T. R. Shrout, [Solid State Commun.](#) **148**, 213 (2008).
- ⁵S. Zhang, Y. Zheng, H. Kong, J. Xin, E. Frantz, and T. R. Shrout, [J. Appl. Phys.](#) **105**, 114107 (2009).
- ⁶R. Yaokawa, S. Uda, and K. Aota, [J. Appl. Phys.](#) **108**, 064112 (2010).
- ⁷H. Takeda, S. Tanaka, T. Nishida, K. Uchiyama, and T. Shiosaki, [Trans. Mater. Res. Soc. Jpn.](#) **31**(1), 11 (2006).
- ⁸I. H. Jung, T. Fukuda, and K. H. Auh, [J. Electroceram.](#) **13**, 471 (2004).
- ⁹H. Takeda, J. Yamaura, T. Hoshina, and T. Tsurumi, [IOP Conf. Ser.: Mater. Sci. Eng.](#) **18**, 092020 (2011).
- ¹⁰M. Schulz, H. Fritze, H. L. Tuller, and H. Seh, [IEEE Trans. Ultrason. Ferroelectr. Freq. Control](#) **51**, 1381 (2004).