

The effect of growth atmosphere and Ir contamination on electric properties of $\text{La}_3\text{Ta}_{0.5}\text{Ga}_{5.5}\text{O}_{14}$ single crystal grown by the floating zone and Czochralski method

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Abstract The influence of growth atmosphere and Ir contamination on electrical resistivity of langatate ($\text{La}_3\text{Ta}_{0.5}\text{Ga}_{5.5}\text{O}_{14}$; LTG) was studied. LTG single crystals were grown via the Czochralski method under different oxygen partial pressures with Ir contamination from the Ir crucible. In addition, LTG crystals were grown by the floating zone method and they were not contaminated by Ir. The electrical resistivity and ionic transport number of these crystals were measured in the temperature range 300–1000°C. The conduction mechanism of LTG changed at about 720°C. At $T < 720^\circ\text{C}$, electronic conduction was dominant, and the resistivity was affected by growth atmosphere as well as Ir contamination. In contrast, at $T > 720^\circ\text{C}$, ionic conduction was dominant, and the resistivity was affected only by Ir contamination. In both temperature regions, Ir contamination decreased the resistivity by an order of magnitude.

Keywords Langatate · Piezoelectric material · Electrical resistivity · High temperature · Defect

1 Introduction

$\text{La}_3\text{Ga}_5\text{SiO}_{14}$ (LGS), $\text{La}_3\text{Ta}_{0.5}\text{Ga}_{5.5}\text{O}_{14}$ (LTG) and $\text{La}_3\text{Nb}_{0.5}\text{Ga}_{5.5}\text{O}_{14}$ (LNG) belong to the same acentric

crystal class (32) as quartz. These LGS-type crystals attract great interest as new candidate materials for piezoelectric applications because they have the following distinct advantages: (i) their piezoelectric constants are about three times larger than that of quartz and thus they are expected to have a high electromechanical coupling coefficient, (ii) they have no phase transitions up to their melting points, and (iii) large single crystals can be grown by the Czochralski (CZ) and vertical Bridgman (VB) methods. Thus, LGS-type crystals have been regarded as the most promising materials for bulk acoustic wave (BAW) and surface acoustic wave (SAW) devices operating at near-room temperature to elevated temperatures. Hornsteiner et al. reported the usages of LGS-type crystals comparing with other piezoelectric materials such as quartz, LiNbO_3 and $\text{Li}_2\text{B}_4\text{O}_7$ [1]. In fact, LGS has been utilized for several years now as a piezoelectric substrate material for SAW filters, which have been employed in the base stations of third-generation mobile communication systems [2]. One other promising application of these materials is a wireless temperature or pressure sensor operating at high temperatures. Among LGS-type crystals, LTG may be the most suitable material for high-temperature applications because its resistivity is an order of magnitude higher than that of LGS [3] and its piezoelectric constant is stable in a wide temperature range [4]. The phase relationships around LGS and LTG in both ternary system and growth of these single-crystals have been reported by the present authors [5–8].

High-temperature sensor applications require higher electrical resistivity of LGS or LTG from the standpoint of the electric loss and resolution of the sensor. Bamba *et al.* successfully improved the resistivity of the LGS in the temperature range from room temperature to 450°C by growth in inert gas atmospheres [9]. They reported that

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LGS crystals grown or annealed in inert gas atmosphere, had higher resistivity than those grown in oxygen-containing atmospheres. Seh and Tuller investigated the conduction mechanism of undoped, Sr-doped and Nb-doped LGS in the temperature range 700–1000°C using the Brouwer defect model [10, 11]. Under an oxygen partial pressure from 1 to 10^{-5} atm, the resistivity of undoped LGS was not affected by oxygen partial pressure, and ionic conduction was dominant. The resistivities of Sr- and Nb-doped LGS were smaller than that of undoped LGS, and electronic conduction was dominant, because Sr and Nb acted as acceptor and donor in the crystal, respectively. Seh and Tuller showed that even a small amount of impurity could decrease the resistivity of LGS when the impurity acted as acceptor or donor. On the other hand, Takeda *et al.* positively utilized impurity doping to improve the resistivity of LGS and LTG, and reported recently that Al-substituted LGAS ($\text{La}_3\text{Ga}_{5-x}\text{Al}_x\text{SiO}_{14}$; $x=0.9$) and LTGA ($\text{La}_3\text{Ta}_{0.5}\text{Ga}_{5.5-x}\text{Al}_x\text{O}_{14}$; $x=0.5$) crystals had a significantly higher resistivity than the pure materials [4]. As mentioned above, the resistivity and conduction mechanism of LGS and LTG are affected by the impurity or oxygen partial pressure.

LTG single crystals have been grown in the industry by the CZ method using Ir crucibles because of the high melting temperature ($\sim 1500^\circ\text{C}$) of LTG. The crystals grown in this manner contain Ir. A quantitative analysis of the amount of Ir in the crystal, for example, through inductively coupled plasma mass spectrometry (ICP-MS), is very difficult because Ir is not soluble in any solvent. However, the coloration of these crystals strongly indicated the presence of Ir contamination. Dubovik *et al.* reported that a LGS crystal grown by the CZ method using a Rh crucible and a Rh-doped LGS crystal showed the same absorption pattern [12]. This pointed to Rh contamination in the crystal originating from the crucible. Similarly, in the case of LTG growth using an Ir crucible, Ir would presumably be incorporated into the crystal, and hence, may affect the resistivity of LTG. Investigation of the influence of Ir contamination on electrical resistivity is important for industrial production.

The present study investigates the influence of growth atmosphere and Ir contamination on the electrical resistivity of LTG. In order to grow LTG single crystals free of Ir contamination, we first performed floating zone (FZ) growth because the FZ method does not use an Ir crucible. LTG single crystals with Ir contamination were grown by the CZ method using an Ir crucible. These CZ-grown crystals were manufactured in Fomos Materials Company Limited. In both methods, growth was performed under various oxygen partial pressures. Electrical resistivity and ionic transport number of these crystals were measured.

2 Experimental procedure

2.1 Preparation of feed rod and growth of LTG by the FZ method

High-purity (99.99%) powders of La_2O_3 , Ga_2O_3 and Ta_2O_5 were used to make a feed rod for FZ growth. A total of about 100 g of the powders were weighed to an accuracy of ± 0.0005 g, and a thoroughly mixed powder with stoichiometric composition was prepared. The powder was sintered at 1450°C for 10 h in air. After crushing and thorough mixing of the sintered sample, about 7 g of the powder was packed into a rubber tube and sealed after evacuation. The tube was pressed at 5.9×10^7 N/m², whereby the powder was compacted into a rod. The rod was drilled at one end and hung using a Pt wire in a furnace and sintered at 1450°C for 10 h in air. Finally, a feed rod, 5.5 mm in diameter and 60 mm in length, was obtained, having a theoretical density of more than 80%. X-ray diffraction analysis (Rigaku, Japan) of the feed rod showed only the single phase LTG.

An infrared convergence-type apparatus (Crystal System Corp.; FZ-T-2000-H-UD-PC) was employed for the FZ growth. In this apparatus, four ellipsoidal mirrors were used to focus infrared radiation from 350 W halogen bulbs onto the sample. X-oriented LTG single crystal was used as a seed. The growth rate was set to 3–5 mm/h. The rotation rates of the feed rod and grown crystal were fixed to 25 rpm and 10 rpm, respectively, in opposite directions. During growth, the oxygen partial pressure was maintained at 1 and 10^{-6} atm using an Ar/O₂ gas mixture. Details of the growth conditions are tabulated in Table 1.

2.2 Measurement of electrical resistivity and ionic transport number

Electrical properties of the crystals grown under various oxygen partial pressures by the FZ method as well as those grown by the CZ method using an Ir crucible were measured. All of the crystals grown were cut into disks

Table 1 Growth conditions used in FZ growth.

Conditions	
Composition of feed rod	Stoichiometric
Dimension of feed rod	ϕ ; 5 mm, length; 60 mm
Seed crystal	X-oriented LTG
Rotation	Crystal; 10 rpm (left), feed; 25 rpm (right)
Growth rate	3–5 mm/h
Zone dimension	ϕ ; 4–5 mm, length; 5–6 mm
Growth atmosphere	P_{O_2} ; 1, 10^{-6} atm
Crystal dimension	ϕ ; 5 mm, length; 10–30 mm

along their X-axes, and were 1.5–2.0 mm in thickness and $\sim 20^\circ\text{C mm}^2$ in cross-sectional area along the X-plane. A Pt paste was painted on both sides of the disk as the electrodes and it was dried at 200°C for 30 min.

Electrical resistivity measurements were performed in air by a two-terminal circuit. The measurement temperature was increased from 300°C to 1000°C in increments of about 25°C and the sample was maintained for 30 min at each temperature. The applied voltage across the sample was set to 10 V and the current was measured by a nano-amperemeter (ADVANTEST; R8240). The electrical resistivity of the samples was calculated from the measured current value.

The ionic transport number was measured by the electromotive force (emf) method. Figure 1 schematizes the apparatus. The ionic transport number, t_{ion} , is given by the ratio of the measured open circuit voltage, V , and the thermo-dynamic voltage, V_0 , i.e.,

$$t_{\text{ion}} = \frac{V}{V_0}, \quad (1)$$

where V_0 is expressed by the Nernst equation [13],

$$V_0 = \frac{kT}{4q} \ln \frac{P_{\text{O}_2}^I}{P_{\text{O}_2}^{II}}, \quad (2)$$

and where $P_{\text{O}_2}^I$ and $P_{\text{O}_2}^{II}$ represent 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, $P_{\text{O}_2}^I$ and $P_{\text{O}_2}^{II}$ were fixed to 0.5 and 0.2 atm, respectively, and the open circuit voltage, V , was monitored with a digital voltmeter (HEWLETT PACKARD; 34401A). Since both $P_{\text{O}_2}^I$ and $P_{\text{O}_2}^{II}$ were close to atmospheric pressure which was the same pressure condition as that used in the electrical resistivity measurement, we could use the resistivity and ionic transport number together to discuss the conductivity mechanism of LTG.

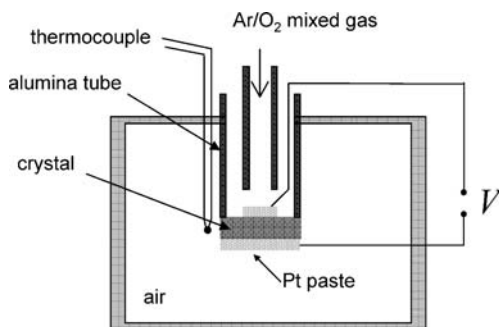


Fig. 1 Schematic representation of O_2 , Pt: LTG; Pt, O_2 cell used in the measurement of ionic transport number

3 Results and discussion

3.1 Growth of LTG single crystals by the FZ method

Growth was performed in four steps: seeding, necking, growth of body part, and separation of crystal from feed rod. In the case of LTG growth, the necking process was important for stable growth. When the growth rate was faster than 3.5 mm/h, a cellular structure was formed in the crystal and induced crucial cracks during growth. Thus, a growth rate of 3.0 mm/h or slower is recommended for LTG growth by the FZ method. LTG crystals grown at 3 mm/h under oxygen partial pressures of 1 atm and 10^{-6} atm are shown in Fig. 2.

3.1.1 Effect of large temperature gradient on FZ growth

The crystals grown were almost round although LTG has a strong tendency to form facets parallel or perpendicular to the growth orientation. This was due to the large temperature gradients in FZ growth. After the separation process, cracks were initiated at the separated boundary and propagated to the center of the crystal. The large temperature gradient also induced thermal stress in the crystal.

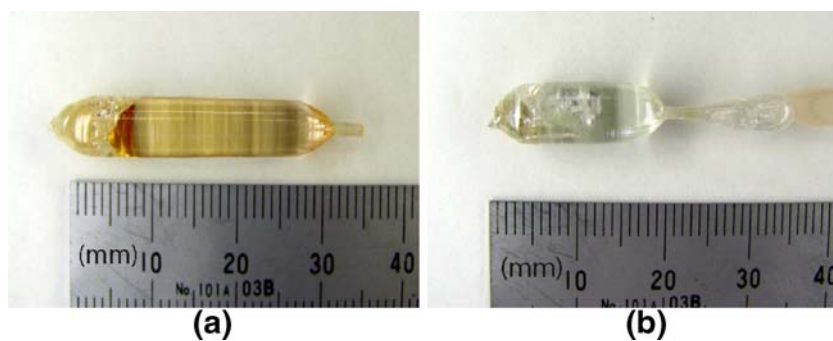
3.1.2 Shape of growth interface

The shape of the growth interface varied with growth atmosphere. Figure 3(a) and (b) show the growth interface during growth under an oxygen partial pressure of 1 atm and 10^{-6} atm, respectively. Under 1 atm, the interface was concave toward the melt, while under 10^{-6} atm, it was almost flat. This difference could be explained by the difference in crystal coloration. The color of the crystal grown under 1 atm of oxygen partial pressure was light yellow and the crystal grown under lower oxygen partial pressures became colorless and transparent as shown in Fig. 2. The colored crystal grown under 1 atm strongly absorbed infrared radiation, and thus, the temperature inside the crystal was higher than that inside the transparent crystal grown under 10^{-6} atm. This temperature difference influenced the heat transfer through the crystal, resulting in a concave interface.

3.1.3 Coloration of grown crystals

As mentioned above, grown crystal became colorless and transparent with decrement of oxygen partial pressure during growth. These discoloration trends were similar to those observed in the case of the LTG crystal grown by the CZ method using an Ir crucible although the strength of coloration in the FZ growth was much weaker than that in the CZ method. The coloration in the FZ method might be

Fig. 2 LTG crystals grown at 3 mm/h using *X*-oriented LTG seed crystals under (a) 1 atm, (b) 10^{-6} atm of oxygen partial pressure



due to the seed crystal used for growth. These seed crystals were grown by the CZ method using an Ir crucible and thus contained Ir. Thus, the growing crystal might have been contaminated by Ir. However, even if this were the case, the crystal grown by the FZ method would contain much smaller amount of Ir than the one grown by the CZ method.

3.1.4 Comparison of background impurity of grown crystal between FZ method and CZ method

We prepared LTG crystals using FZ and CZ method which have different Ir concentration. Before discussing the electrical property of these crystals based on the difference of Ir concentration (see Section 3.2), we need to compare the concentration of background impurity of these crystals. It was noticed that the same source materials of 99.99% purity (La_2O_3 : Deqing Xing Bang Rare Earth New Materials Co. Ltd., Ga_2O_3 : Shandong Aluminum Industry Co. LTD, China, Ta_2O_5 : F&X ELECTRO-MATERIALS LIMITED, JIANGMEN) were used in FZ and CZ growth. Thus if segregation of impurities in both growth was the same, background impurities concentration would be the same in these crystals. The length of the crystal grown by FZ method was about 10 mm from the seed which was not much longer than the zone length (6 mm). Also, the initial part of the crystal used for the measurement which was grown by CZ method consumed less than 10 percent of the

total melt. Since both crystals subjected to the measurement corresponded to very early stage of solidification in which segregation of impurities was not so different, we assumed that concentration of background impurities were almost the same in both crystals. Thus, we were able to compare the electrical properties of LTG with or without Ir contamination.

3.2 Effects of growth atmosphere and Ir contamination on electrical properties of LTG

The electrical resistivities of LTG crystals grown by the FZ and CZ methods under various oxygen partial pressures were measured. In this study only the first run with thermal treatment was evaluated because the temperature increased up to 1000°C in air during the measurement (see Section 2.2) and the effect of growth atmosphere on electric resistivity would be different than the second run. The FZ method yielded crystals with little amount of Ir contamination as previously mentioned, while the CZ method resulted in a significant amount of Ir in the crystal. Thus, we will refer to the crystal grown by the FZ and CZ methods as ‘Ir-free-LTG’ and ‘Ir-LTG’, respectively, hereafter. The results of both measurements were plotted as a function of temperature (see Fig. 4). The electrical resistivities of every crystal evidently varied at about 720°C . Similar changes of electrical resistivity near 700°C were observed in LGS [14].

Fig. 3 Growth interface of the LTG crystal under an oxygen partial pressure of (a) 1 atm and (b) 0.2 atm

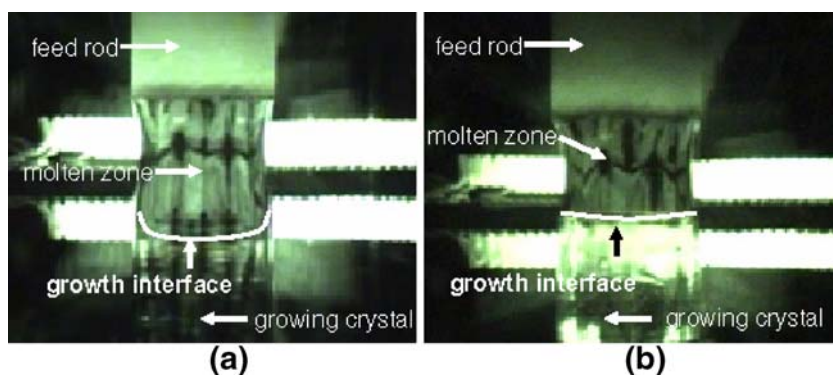
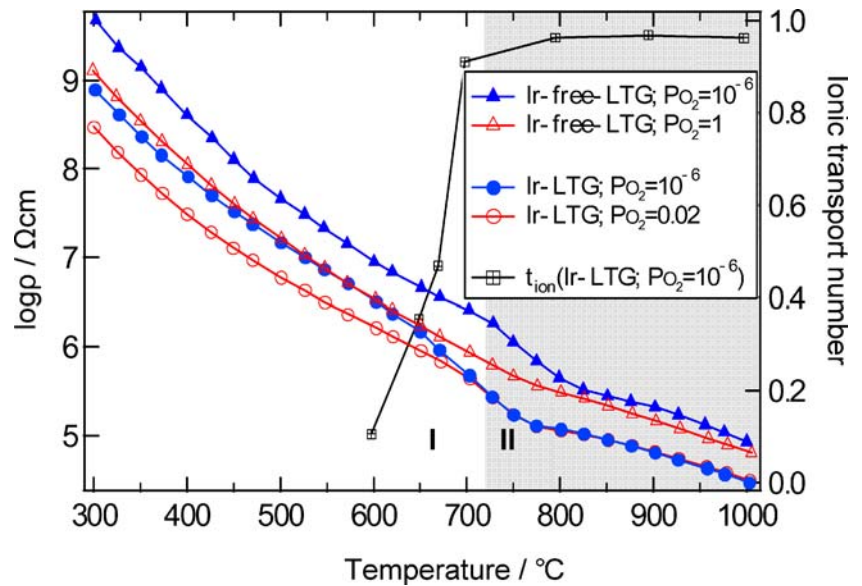


Fig. 4 Electrical resistivity and ionic transport number of LTG crystals grown by the FZ and CZ methods under various oxygen partial pressures



They seem to show a change of dominant conduction mechanism between electronic and ionic rather than a change in one conducting type (electronic or ionic). In order to confirm this, the ionic transport number of one LTG crystal (Ir-LTG; $P_{O_2}=10^{-6}$) was measured as a function of temperature which was also demonstrated in Fig. 4. The ionic transport number also showed a dramatic change at about 720°C. It was less than unity below 720°C, which indicated that electronic conduction was dominant. In contrast, it was approximately unity above 720°C, which showed that ionic conduction was dominant. This results led us to conclude that the conduction mechanism of all LTG crystals varied from electronic to ionic conduction at 720°C. The conduction mechanism of LTG will be discussed in two separate regions, namely region I ($T < 720^\circ\text{C}$) and region II ($T > 720^\circ\text{C}$).

3.2.1 Region I ($T < 720^\circ\text{C}$)

In region I, the resistivity of LTG depends on both the growth atmosphere and Ir contamination. The ionic transport number showed the electronic conduction mechanism, thus the total electrical conductivity in region I is represented by the equation

$$\sigma_{\text{total}} \approx q_e c_e \mu_e + q_h c_h \mu_h, \tag{3}$$

where q_j is the charge, c_j is the concentration and μ_j is the mobility of an electron ($j=e$) and hole ($j=h$). Since q_j is a constant, the difference in electrical conductivity between the crystals (see Fig. 5(a)) should be explained by the difference in carrier concentration and carrier mobility between an electron and hole. However, the mobility of electrons and holes in LTG are not known. In this paper, we

assume that the two are not so different and focus on the difference in carrier concentration.

In Ir-free-LTG, higher oxygen partial pressures during growth gave higher electronic conductivities. This showed that holes were generated by oxidation via Eq. (4) and became the dominant carrier in these crystals.



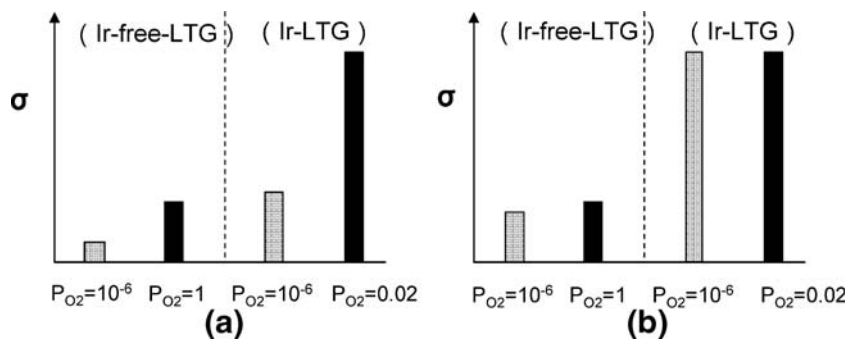
where O_2 is oxygen gas, $O_i^{\prime\prime}$ is an interstitial oxygen atom, and h^\bullet is a hole. Since the mobility of an interstitial oxygen together with a hole in the RHS in Eq. 4 was much smaller than that of a hole, the electronic conduction was not affected by interstitial oxygens.

Ir-LTG had a higher electronic conductivity than Ir-free-LTG. This showed that Ir contributed to generation of electronic carriers by acting as a donor or acceptor. On the basis of the ionic radii of Ir^{3+} and Ir^{4+} , it can be said that the Ir ion is most likely to occupy the octahedral site of LTG, which is occupied by Ga^{3+} and Ta^{5+} in a pure LTG crystal. If an Ir^{3+} ion substituted Ga^{3+} in the octahedral site and was then oxidized to Ir^{4+} , a compensating carrier would be generated via



where $\text{Ir}_{\text{Ga}^{3+}}^{\times}$ and $\text{Ir}_{\text{Ga}^{3+}}^{\bullet}$ are Ir^{3+} and Ir^{4+} substituting Ga^{3+} , respectively, and e^{\prime} is an electron. Considering the recombination of hole and electron, p-type conductivity (Eq. 4) could decrease with increasing Ir content. In the case of Ir-LTG crystal, however, Ir content seemed to be large enough to counteract p-type conductivity and consequently grown crystal would show n-type conductivity. In these crystals electric conductivity would be higher than

Fig. 5 Magnitude relationship of electrical conductivity at the temperature range of (a) 300–500°C in region I and (b) 800–1000°C in region II



that in Ir-free-LTG. The growth under higher oxygen partial pressures would promote oxidation of Ir via Eq. 5 and generate more electrons in the growing crystal. This is the case for the Ir-LTG crystal; the experimental results are consistent with the above assumption.

3.2.2 Region II ($T > 720^\circ\text{C}$)

The conductivity of oxides showing completely ionic conduction is usually independent of oxygen partial pressure [15]. As shown in Fig. 5(b), the conductivity of Ir-free-LTG and Ir-LTG crystals in region II met this condition, while the conductivity of these crystals in region I depended on oxygen partial pressure as shown in Fig. 5(a). This conductivity dependence on oxygen partial pressure, then, suggested the change of the conduction mechanism from electronic (region I) to ionic (region II) at 720°C. Ionic conductivity can be interpreted by a defect model, i.e., a Brouwer diagram, which illustrates the equilibrium relationship between oxygen partial pressure and carrier concentration. We will discuss the electrical conductivity in region II using a Brouwer diagram.

The impurity concentration of Ir-free-LTG was so low that the generation of dominant carriers was concluded to be an intrinsic property of LTG. Figure 6(a) shows the Brouwer diagram corresponding to these crystals. The region where LTG possibly shows ionic conduction is dominated by oxygen vacancies ($V_O^{\bullet\bullet}$) and interstitial oxygens ($O_i^{\prime\prime}$) and pairs of these carriers, known as anti-Frenkel disorders, are generated according to Eq. 6,



and

$$[V_O^{\bullet\bullet}] = [O_i^{\prime\prime}] = K_F^{1/2}, \tag{7}$$

where O_O^{\times} is an oxygen ion in its normal site. The concentration of these carriers was determined by equilibrium constant K_F , as shown in Eq. 7, and depended only on temperature, T.

The conductivity of Ir-LTG was much higher than that of Ir-free-LTG. This indicated that the dominant carriers in Ir-LTG were induced by Ir. Since the oxidation state of Ir is influenced by the oxygen partial pressure, we draw the Brouwer diagram corresponding to the Ir-LTG taking into account the change of oxidation number of Ir as shown in Fig. 6(b). In this diagram a region where LTG possibly shows ionic conduction is dominated by Ir^{4+} ($\text{Ir}_{Ga^{3+}}^{\bullet}$) ions

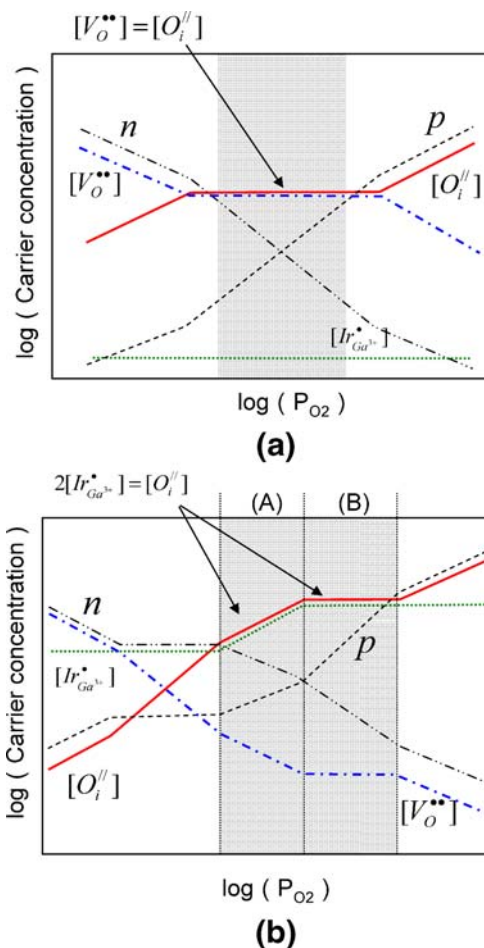
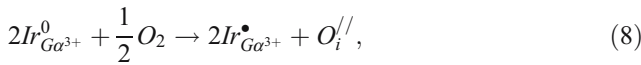


Fig. 6 Schematic Brouwer diagram corresponding to (a) Ir-free-LTG by the FZ method and (b) Ir-LTG grown by the CZ method. In region (A) of diagram (b), oxidation number of Ir changed from +3 to +4 according to Eq. (8)

and interstitial oxygen ($O_i^{//}$). These carriers were generated according via Eq. 8:



and

$$[Ir_{Ga^{3+}}^\bullet] = 2[O_i^{//}], \tag{9}$$

In Fig. 6(b), the region of ionic conduction consists of regions (A) and (B). Region (A) corresponds to the early stage of Eq. 8, where conductivity depended on the oxygen partial pressure, while region (B) corresponds to the latter stage of Eq. 8, where conductivity is independent of the oxygen partial pressure. In both regions, the concentration of dominant carriers was determined by $[Ir_{Ga^{3+}}^\bullet]$, i.e., the concentration of Ir^{4+} in the LTG crystal, as shown in Eq. 9. Here again, the experimental observation that the electrical conductivities of Ir-LTG were almost equal leads to the following conclusions: (i) In CZ growth, the concentration of Ir contamination in the LTG crystal grown was almost the same regardless of the oxygen partial pressure. The oxidation number of Ir was different depending on the growth atmosphere, which reflected the difference of electronic conductivity in region I. However, (ii) during resistivity measurements, these crystals were annealed in air

Table 2 Activation energy of conduction.

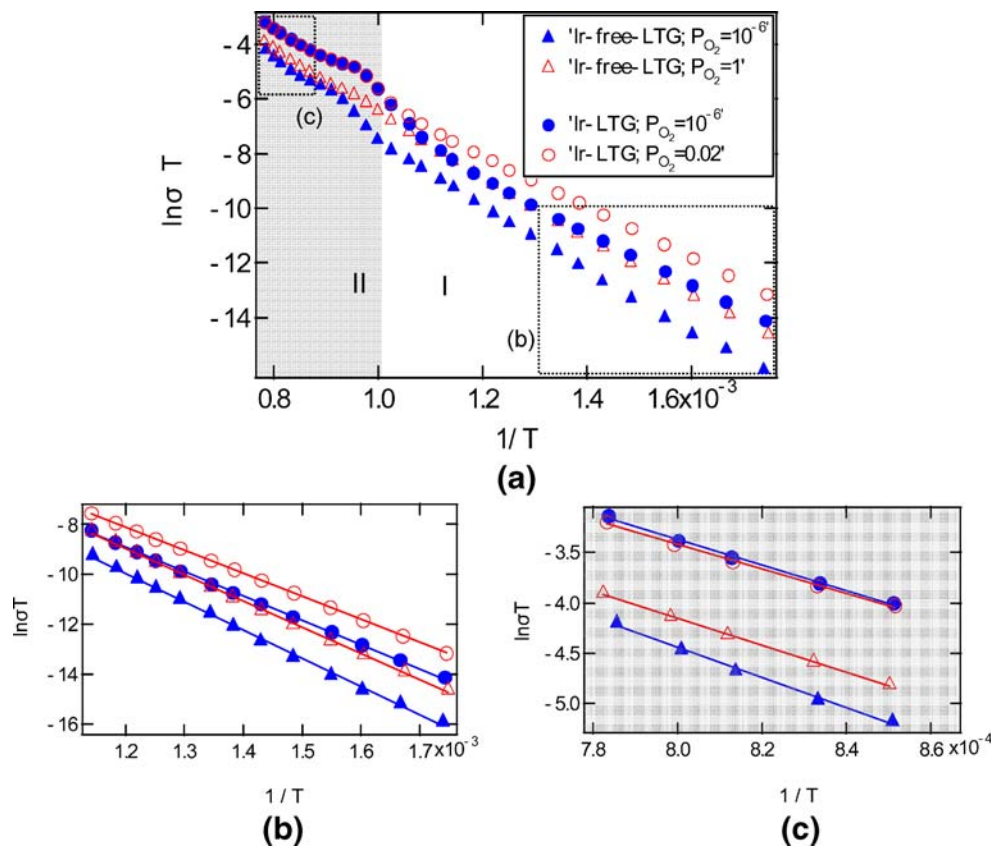
Crystal	Region I	Region II
Ir-free-LTG, $P_{O_2}=1$	0.91 eV	1.15 eV
Ir-free-LTG, $P_{O_2}=10^{-6}$	0.98 eV	1.29 eV
Ir-LTG, $P_{O_2}=0.02$	0.80 eV	1.04 eV
Ir-LTG, $P_{O_2}=10^{-6}$	0.84 eV	1.09 eV

in the high temperature region II, and the equilibrium concentration of Ir^{4+} was determined by the surrounding atmosphere. Thus, the difference in carrier concentration observed in region I disappeared in region II.

3.2.3 Activation energy of conduction

Dominant carriers of Ir-free-LTG changed from h^\bullet (Eq. 4) to $O_i^{//}$ (Eq. 6) while these of Ir-LTG changed from e' (Eq. 5) to $Ir_{Ga^{3+}}^\bullet$ and $O_i^{//}$ (Eq. 8). Existence of these transitions was also supported by the activation energy of electric conduction. Assuming that the transport process of electrical carriers in LTG is the hopping mechanism, which is similar to the jumping transport process of ionic carriers, the activation energy of conduction is best evaluated by an Arrhenius plot of σT vs. $1/T$, as shown in Fig. 7. The

Fig. 7 (a) Arrhenius plot of σT vs. $1/T$ of LTG crystals and a magnified view of this plot in region I (b) and region II (c)



calculated activation energy values in regions I and II are tabulated in Table 2. The activation energy of each crystal differed by 0.2 eV or more between regions I and II, which suggested the difference in conduction mechanism between regions I (electronic conduction) and II (ionic conduction).

The activation energy always holds two contributions: the generation of carriers and the migration of carriers. They are related to the concentration and mobility of carriers. To explain the transition at 720°C, we need to differentiate the activation energy into these two factors and determine them independently by a hole measurement in addition to a detailed analysis of the dependence of conductivity on oxygen partial pressure.

4 Conclusions

In this study, we investigated the influence of growth atmosphere and Ir contamination on the electrical resistivity of LTG. To prepare an LTG single crystal free of Ir contamination, we first performed FZ growth under various oxygen pressures. The electrical resistivity and ionic transport number of LTG single crystals with and without Ir contamination were measured. The conduction mechanism of LTG clearly changed at about 720°C. In the region $T < 720^\circ\text{C}$, electronic conduction was dominant, and the resistivity was affected by growth atmosphere and Ir contamination. In contrast, in the region $T > 720^\circ\text{C}$, ionic conduction was dominant, and the resistivity was only affected by Ir contamination. In both regions, Ir contamination decreased the resistivity by an order of magnitude. This is important for industrial production of LTG. In order

to grow higher-resistivity LTG, the use of Ir crucibles should be avoided in CZ growth and platinum crucible should be used instead with caution at high temperature.

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