Crystal growth and characterization of Li$_x$La$_{1-x}$/3NbO$_3$ using Czochralski method

Shuya MINEGISHI$^1$, Takuya HOSHINA$^1$, Takaaki TSURUMI$^1$, Kheirreddine LEBBOU$^2$ and Hiroaki TAKEDA$^{1,3}$

1School of Materials and Chemical Technology, Tokyo Institute of Technology, Meguro, Tokyo 152-8552, Japan
2Institut Lumière Matière, UMR5306 CNRS, Université de Lyon 1, 69622 Villeurbanne Cedex, France
3Graduate School of Science and Engineering, Saitama University, 255 Shimo-Okubo, Sakura-ku, Saitama 338-8570, Japan

Single crystals of Li$_x$La$_{1-x}$/3NbO$_3$ were grown in air using Czochralski method from La-poor melt. The lithium-ion conductivity of the crystals was measured. The length and maximum diameter of the boule grown were 23 and 20 mm, respectively. The boule contained no inclusions but was covered with a very thin polycrystalline film of LaNbO$_4$ and LiNbO$_3$ in its upper region. The composition of the crystals grown was estimated to be $x = 0.15$ and the starting melt composition was $x = 0.20$. The ionic conductivity of the crystal was anisotropic with $\sigma_{[100]} = 2.8 \times 10^{-2} \text{ S cm}^{-1}$ and $\sigma_{[001]} = 9.7 \times 10^{-2} \text{ S cm}^{-1}$ at 306 K. The activation energy, $E_a$ of these conductivities was almost the same in the range of 0.28–0.29 eV. Further, we discussed the anisotropic lithium-ion conductivity of the crystal.

Key-words : Lithium-ion conductivity, Crystal growth, Perovskite, Niobate, Anisotropy

1. Introduction

Currently, various electronic devices such as notebook computers and smart phones are ubiquitous. Hence, lithium-ion batteries (LIBs) are primarily used to satisfy the demand for smaller and higher-capacity batteries because of their high energy density. Although liquid electrolytes have been used conventionally in LIBs, LIBs demonstrate certain drawbacks, such as electrolyte leakage and fire. All solid-state LIBs are expected to solve these problems and offer significant advantages, such as thermal stability and large potential windows to enable the use of high-voltage cathode materials and/or metallic lithium anodes.\(^1\)-\(^3\) In particular, sulfide solid electrolytes are expected to be used in next-generation LIBs because of their high ionic conductivity, $\sigma$, of $10^{-2} \text{ S cm}^{-1}$, which is higher than those of oxides.\(^4\) However, sulfide solid electrolytes react with the moisture in the atmosphere and produce hydrogen sulfide gas. Therefore, oxide solid electrolytes, such as perovskite structures (e.g. La$_2$/3 TiO$_3$ (LLTO)\(^5\)-\(^10\), Li$_x$La$_{1-x}$/3NbO$_3$ (LLNbO)\(^1\)-\(^6\)) and garnet electrolytes (e.g. Li$_3$LaZr$_2$O$_7$\(^1\)-\(^8\)) are promising candidates because of their high chemical stability and high $\sigma$.

In recent years, significant effort has been made to grow single crystals of oxide solid electrolytes for evaluating the intrinsic lithium-ion conductivity without the effect of grain boundaries in ceramic polycrystalline state.\(^19\)-\(^24\) The growth methods include the floating zone,\(^19\) Bridgman,\(^20\)-\(^21\) and traveling solvent floating zone methods.\(^22\)-\(^24\) Another bulk growth method is the Czochralski (Cz) method, which is a conventional method used to produce Si ingots. Compared to the other methods, the advantages of the Cz method are as follows:

1. the growth of bulk crystals is reproducibly performed,
2. the crystal grown is free from mechanical stress because the crystal is not in contact with the crucible, and
3. growth orientation can be selected arbitrarily.

To the best of our knowledge, few reports regarding the crystal growth of oxide solid electrolytes by the Cz method exist in literature. An optimized growth condition of the Cz method promotes the production of substrates for the solid electrolyte of LIBs.

In this study, we selected LLNbO as an oxide electrolyte example. LLNbO can be used as a solid electrolyte for all solid-state LIBs as its ionic conductivity is larger than $1 \times 10^{-2} \text{ S cm}^{-1}$\(^1\)-\(^3\),\(^10\) comparable to LLTO.\(^5\)-\(^11\) It is difficult to reduce the valence of Nb in LLNbO at high temperatures and in low oxygen partial pressures compared with the Ti in LLTO. Moreover, a platinum crucible

\(^{†}\) Corresponding author: H. Takeda; E-mail: htakeda@ceram.titech.ac.jp, takeda@apc.saitama-u.ac.jp

\(^{‡}\) Preface for this article: [DOI] http://doi.org/10.2109/jcersj2.128.P8-1

©2020 The Ceramic Society of Japan
can be used because the melting temperature of the LLNbO is lower than 1400 °C. Use of a platinum crucible enables to apply high oxygen partial pressures in the growth atmosphere. This prevents the volatilization of Li and reduction of Nb. A conventional crystal structure of LLNbO is shown in Fig. 1. Here, La ions and vacancies at A-sites in the perovskite $ABO_3$ structure of the parent $La_{1/3}NbO_3$ are ordered within alternate (001) planes and doubles the parameter $c$ of the cubic perovskite type cell. Li$^+$ ions are substituted for the occupied and vacant sites of La in the La-occupied layers. Anisotropic lithium-ion conduction along [100] and [100] has been reported previously. However, the activation energy of lithium-ion conductivity activation along [100] and [100] has not been discussed.

In this study, LLNbO single crystals were grown using the Cz method. The starting material composition was optimized to grow inclusion-free crystals. After determining the lithium-ion conductivity and its activation energy, we discuss anisotropic lithium-ion conductivity in LLNbO crystal from the site percolation perspective.

2. Experimental

$Li_2CO_3$ and $Nb_2O_5$ powders with 99.95% purity and $La_2O_3$ powder with 99.9% purity were used as starting materials. First, we synthesized the $LiNbO_3$ phase using $Li_2CO_3$ and $Nb_2O_5$ to prevent the volatilization of Li. The $Li_2CO_3$ and $Nb_2O_5$ powders were mixed using a wet ball-mill and then dried and calcined in air at 950 °C for 5 h. The calcined powders were pulverized and mixed with the $La_2O_3$ and $Nb_2O_5$ powders to obtain the composition with $Li_xLa_{(1-x)/3}NbO_3$ ($LLNbO_{100x}$ for $x = 0.10$ and 0.20: $LLNbO_{10}$ and $LLNbO_{20}$). The mixed powder was calcined in air at 1200 °C for 20 h. The calcined powders were charged into platinum or iridium crucibles (50 mm in diameter and height). We attempted to grow these single crystals using the conventional RF-heating Cz method. The seeds were $LLNbO_{10}$ and $LLNbO_{20}$ ceramic bars for each growth process. The pulling rate and rotation rate were 1.0–1.5 mm/h and 10 rpm, respectively. The phases of the as-grown crystals were identified by powder X-ray diffraction (XRD). Based on the results of this experiment and those in recent studies, we selected the $LLNbO_{20}$ composition for further crystal growth.

We determined the optimum composition around $LLNbO_{20}$ for bulk crystal growth by the Cz method through the following process. The powders of the composition with $LLNbO_{20} + yLa_2O_3$ [$y = −0.007, −0.004, 0$ ($LLNbO_{20}$, 0.004)] were prepared, as demonstrated in Fig. 2 and Table 1. The calcined powders were placed in a

![Schematic of crystal structure of $Li_xLa_{(1-x)/3}NbO_3$.](image1)

![Ternary plot of the $Li_2O$-$La_2O_3$-$Nb_2O_3$ system and (b) its enlarged figure around $LLNbO_{20}$.](image2)

**Table 1.** Starting melt composition, $La_2O_3$ mole shift from $LLNbO_{20}$, and melting solidification experiment results

| Composition no. | $Li_2O$ (mol%) | $Nb_2O_5$ (mol%) | $La_2O_3$ (mol%) | $LLNbO_{20} + yLa_2O_3$ | Secondary phases in the solidified melts |
|----------------|----------------|-----------------|-----------------|------------------------|---------------------------------------|
| 1              | 13.56          | 67.81           | 18.63           | 0.004                  | $LaNbO_4$, $LiNbO_3$                   |
| 2              | 13.64          | 68.18           | 18.18           | 0                      | $LaNbO_4$, $LiNbO_3$                   |
| 3              | 13.71          | 68.56           | 17.73           | −0.004                 | $LiNbO_4$, $LiNbO_3$                   |
| 4              | 13.76          | 68.81           | 17.43           | −0.007                 | $LiNbO_4$, $LiNbO_3$                   |
platinum crucible and further fired in air at 1300 °C for 2 h and cooled in a furnace at a rate of 2 °C/min. The powders were molten and solidified through this process. In this study, this series of steps is called the melting solidification experiment. The composition of the resulting solidified compounds was analyzed by electron microprobe analysis (EPMA) and the compounds were pulverized. Subsequently, we identified their crystalline phases using powder XRD analysis.

Based on the results of the melting solidification experiment, LL NbO20 + γLa2O3 with y = —0.004 single crystals were grown using the Cz method. The raw materials, mixing and calcining process, and growth conditions were the same as aforementioned. The growth atmosphere was an air gas flow of 10⁻³ m³/min. The seed was an LL NbO20 ceramic bar. The phase of the as-grown crystals was identified by powder XRD and their density was measured using the Archimedes method with distilled water at room temperature (296 K). The crystals grown were cut along [100] and [001] using a backscattering Laue XRD and a wire saw. After polishing and sputtering Au on the crystal surfaces, samples with (100) and (001) planes were fabricated. The lithium-ion conductivity was measured using an ac complex impedance method using an HP4194A impedance/gain phase analyzer over the frequency range of 40–110 MHz. The temperature range was 306–403 K. The measurements were performed in air. We plotted the values of the imaginary part of the impedance against the real part. The data exhibited a straight line at low frequencies and a distorted semicircle at higher frequencies. The resistance was recorded as the value of Z’ at the intersection between the Z’ axis and the extrapolation of the semicircle or the linear portion of the plot.

3. Results and discussion

The calcined LL NbO10 and LL NbO20 powders before crystal growth were composed solely of perovskite LL NbO phase. After the crystals were grown using the Cz method with the LL NbO10 and LL NbO20 powders as starting materials, all the boules grown were white and opaque. The powder XRD analysis of the pulverized boules exhibited them to be a mixture of LL NbO and LaNbO₄. It has been reported that the melting point of LaNbO₄ (1620 °C) is higher than that of LL NbO (1300–1400 °C). Therefore, it was assumed that LaNbO₄ precipitated first and then, the LL NbO phase was solidified during the growth process. Furthermore, the powder XRD analysis showed that the amount of LaNbO₄ in the boule grown from the LL NbO20 melt was smaller than that from the LL NbO10 melt. It was assumed that the precipitation of LaNbO₄ could be prevented by reducing the amount of La₂O₃ in the starting material composition. Therefore, for determination of the optimal composition, the melting solidification experiment was conducted using powders with the composition LL NbO20 + γLa₂O₃.

Then, all solidified compounds with the composition LL NbO20 + γLa₂O₃ comprised the perovskite LL NbO phase primarily and contained phases of small impurity amounts as shown in Table 1. The impurity phases were LaNbO₄ and LiNbO₃ in the LL NbO20 + γLa₂O₃ samples with y = 0.004 and 0. The LL NbO20 + γLa₂O₃ samples with y = —0.004 and —0.007 contained LiNbO₃ and LiNb₂O₅. The melting point of LiNbO₃ and peritectic point of LiNbO₂ were less than 1300 °C. It was assumed that these two phases occurred because the cooling rate was higher than that of the Cz method. Moreover, the powder XRD analysis showed that the LL NbO20 + γLa₂O₃ sample with y = —0.004 had the lowest volume of impurity phases. We attempted to grow perovskite LL NbO20 single crystals using the starting material with the composition LL NbO20 + γLa₂O₃ with y = —0.004.

Figure 3 shows the as-grown LL NbO20 crystal boule fabricated by the Cz method; the maximum diameter was 20 mm and the length was 23 mm. The upper region of the LL NbO20 crystal was opaque while the lower half was transparent and yellow. The upper regions comprised the rim and other parts. The thickness of the rim was less than 300 μm. Using EPMA and powder XRD analysis, as shown in Fig. 4(a), it was discovered that the rim contained LaNbO₄ and LiNbO₂ as impurity phases analogous with the melting solidification experiment results. However, the volume of the impurity phases was approximately
density was 5.042 g cm$^{-3}$. The activation energy of lithium-ion conductivity of the LLNbO20 single crystal was 0.29 and 0.28 eV, respectively. These values are lower than those of the LLNbO single crystal (0.34 eV$^{20,23}$) and polycrystalline materials (0.36 eV$^{11}$). The activation energy of lithium-ion conductivity of LLNbO single crystals is isotropic, with $E_a[100]/E_a[001] = 1.03$, and it is similar to that of (1.06) in the LLTO single crystal.$^{19}$ In the LLTO-based oxides, Inaguma et al.$^{28}$ reported that the ratios of lithium to vacancy concentration and site percolation are predominant factors in lithium-ion conductivity. In terms of site percolation, $\sigma$ obeys the following relation:$^{29}$

$$\sigma \propto (n - n_c)^{\mu},$$

where $n$ is the sum of lithium and vacancy concentrations and $n_c$ is the threshold. When $n_c = 0.3$ and $\mu = 2$, the variety of lithium-ion conductivities in the LLTO-based oxide are detailed in.$^{26}$ $n_c = 0.3$ was applied for a simple cubic lattice and the exponent $\mu = 2$ implied three-dimensional conduction. If the conduction occurred two-dimensionally, then $\mu$ must be 4/3. In terms of site percolation, the deference of $\mu$ could produce an anisotropic lithium-ion conductivity because the activation energy of the lithium-ion conductivity was isotropic. It was assumed that the longitudinal and lateral migrations of the lithium ion were three and two-dimensional, respectively.

---

**Figure 5.** Crystal substrates with (100) and (001) planes cut from the crystal shown in Fig. 3.

**Figure 6.** (a) Impedance plots and (b) Arrhenius plots of lithium-ion conductivity for LLNbO20 single crystal at 298 K. Filled circles and plain rhombi represent data along [100] (//a) and [001] (//c), respectively.
4. Conclusion

In this study, we synthesized an LLNbO single crystal in air using the Cz method. The starting material was a Lapoor composition. The crystals grown were inclusion-free and yellow. The Li concentration (x = 0.15) in the crystals was lower than that in the starting materials (x = 0.20) because the segregation coefficient k_Li was less than 1 in the LLNbO perovskite structure from the molten to the crystal phase. The ionic conductivity of the LLNbO single crystals was anisotropic with $\sigma_{[100]} / \sigma_{[001]} = 2.9$ for $x = 0.15$. The anisotropic conductivity was explained using percolation theory. Because $\sigma_{[100]} = 2.8 \times 10^{-4} \text{ S cm}^{-1}$, and the crystal was easily grown using the Cz method, the LLNbO crystal can be used as a substrate for the solid electrolyte of LIBs.

Acknowledgment This work was supported by JSPS KAKENHI—Grant Numbers 16H02394 and 19H05515.

References

1) P. Knauth, *Solid State Ionics*, 180, 911–916 (2009).
2) J. G. Kim, B. Son, S. Mukherjee, N. Schuppert, A. Bates, O. Kwon, M. Jong Choi, H. Y. Chung and S. Park, *J. Power Sources*, 282, 299–322 (2015).
3) K. Kataoka, H. Nagata and J. Akimoto, *Sci. Rep.*, 8, 9965 (2018).
4) Y. Kato, S. Hori, T. Saito, K. Suzuki, M. Hirayama, A. Mitsui, M. Yonemura, H. Iba and R. Kanno, *Nat. Energy*, 1, 16030 (2016).
5) L. Latie, G. Villeneuve, D. Conte and G. Le Flem, *J. Solid State Chem.*, 51, 293–299 (1984).
6) S. Stramare, V. Thangadurai and W. Weppner, *Chem. Mater.*, 15, 3974–3990 (2003).
7) M. Itoh, Y. Inaguma, W. Jung, L. Che and T. Nakamura, *Solid State Ionics*, 70, 203–207 (1994).
8) Y. Inaguma, Y. Matsui, Y. Shan, M. Itoh and T. Nakamura, *Solid State Commun.*, 86, 689–693 (1993).
9) Y. Inaguma, Y. Matsui, Y.-J. Shan, M. Itoh and T. Nakamura, *Solid State Ionics*, 79, 91–97 (1995).
10) Y. Inaguma, J. Yu, Y. Shan, M. Itoh and T. Nakamura, *J. Electrochem. Soc.*, 142, L8–L11 (1995).
11) Y. Kawakami, H. Ikuta and M. Wakihara, *J. Solid State Electr.*, 2, 206–210 (1998).
12) A. Belous, E. Pashkova, O. Gavrilenko, O. V’yunov and L. Kovalenko, *Ionics*, 9, 21–27 (2003).
13) S. Garcia-Martín, J. M. Rojo, H. Tsukamoto, E. Morán and M. A. Alario-Franco, *Solid State Ionics*, 116, 11–18 (1999).
14) M. Nakayama, K. Imaki, H. Ikuta, Y. Uchimoto and M. Wakihara, *J. Phys. Chem. B*, 106, 6437–6441 (2002).
15) M. Nakayama, H. Ikuta, Y. Uchimoto and M. Wakihara, *Appl. Phys. Lett.*, 84, 4227–4229 (2004).
16) M. Nakayama, M. Wakihara, Y. Kobayashi and H. Miyashiro, *J. Phys. Chem. B*, 109, 14648–14653 (2005).
17) R. Murugan, V. Thangadurai and W. Weppner, *Angew. Chem. Int. Edit.*, 46, 7778–7781 (2007).
18) J. Awaka, N. Kijima, H. Hayakawa and J. Akimoto, *J. Solid State Chem.*, 182, 2046–2052 (2009).
19) Y. Inaguma, J. Yu, T. Katsumata and M. Itoh, *J. Ceram. Soc. Jpn.*, 105, 548–550 (1997).
20) Y. Fujiwara, K. Hoshikawa and K. Kohama, *J. Cryst. Growth*, 433, 48–53 (2016).
21) Y. Fujiwara, T. Taishi, K. Hoshikawa, K. Kohama and H. Iba, *Jpn. J. Appl. Phys.*, 55, 090306 (2016).
22) Y. Maruyama, S. Minamimure, C. Kobayashi, M. Nagao, S. Watauchi and I. Tanaka, *R. Soc. Open Sci.*, 5, 181445 (2018).
23) M. S. Ali, N. Sato, I. Fukasawa, Y. Maruyama, M. Nagao, S. Watauchi and I. Tanaka, *Cryst. Growth Des.*, 19, 6291–6295 (2019).
24) K. Kataoka and J. Akimoto, *J. Ceram. Soc. Jpn.*, 127, 521–526 (2019).
25) E. P. Savchenko, N. A. Dodina and E. K. Keler, in “Chemistry of high temperature materials”, Ed. by N. A. Toporov, Consultants Bureau, New York (1969) pp. 108–113.
26) P. N. Iyer and A. J. Smith, *Acta Crystallogr.*, 23, 740–746 (1967).
27) I. Tanaka, R. Yoshihara, C. Nakazawa, M. Nagao and S. Watauchi, *J. Cryst. Growth*, 507, 251–254 (2019).
28) Y. Inaguma and M. Itoh, *Solid State Ionics*, 86–88, 257–260 (1996).
29) D. Stauffer, A. Aharony, “Introduction to PERCOLATION THEORY” (1994).