Relationship between lithium content and ionic conductivity in the $\text{Li}_{5+2x}\text{La}_3\text{Nb}_{2-x}\text{Sc}_x\text{O}_{12}$ system

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ABSTRACT

The Al-free cubic garnet-like $\text{Li}_{5+2x}\text{La}_3\text{Nb}_{2-x}\text{Sc}_x\text{O}_{12}$ series with $x = 0\text{--}0.75$ was successfully synthesized by solid state reaction. Final sintering at 1150 °C for 12 h in a magnesia crucible with the mother powder method resulted in stoichiometric single phases that corresponded to each nominal composition. The relationship between the lithium content and ionic conductivity was investigated for each composition. The conductivity of the samples showed a positive dependency on the Li content and the optimum Li content for Li conduction was 6.25–6.5 in the formula unit. The highest bulk conductivity of $3.70 \times 10^{-4} \text{ S cm}^{-1}$ was observed for $x = 0.625$ at 25 °C and that for $x = 0.75$ at 50 °C was $6.05 \times 10^{-4} \text{ S cm}^{-1}$.

Key words:

Scandia-doped $\text{Li}_5\text{La}_3\text{Nb}_2\text{O}_{12}$

Garnet-like lithium ion conductor

$\text{Li}_{5+2x}\text{La}_3\text{Nb}_{2-x}\text{Sc}_x\text{O}_{12}$

Fast lithium-ion conductor

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1. Introduction

Cubic garnet-like lithium complex oxides, $\text{Li}_5\text{La}_3\text{M}_2\text{O}_{12}$ ($\text{M}=\text{Nb}$ and Ta), were first reported during investigation of the $\text{La}_2\text{O}_3\text{-Li}_2\text{O-M}_2\text{O}_5$ system [1,2]. Hyooma and Hayashi reported that these compounds have a three-dimensional cubic framework structure consisting of La, Nb(Ta), and O, where the lithium atoms occupy two different interstices in the framework [1]. In 2003, Thangadurai *et al.* investigated the electrical properties of these compounds as lithium ion conductors [3]. The bulk conductivity of both samples was around $10^{-6} \text{ S cm}^{-1}$ at 25°C and the activation energies were 0.43 eV (Nb) and 0.56 eV (Ta), which are comparable with other common lithium ion conductors. In addition, there was a noteworthy property for application as a lithium ion solid electrolyte in that these systems exhibited high stability against reaction with lithium metal. However, to increase the ionic conductivity, an increase of the lithium content in the garnet-like structure was required. Much research has been focused on improvement of the ionic conductivity of the $\text{Li}_5\text{La}_3\text{M}_2\text{O}_{12}$ ($\text{M}=\text{Nb}$ and Ta) system by the replacement of La^{3+} ions with divalent cations such as Ba^{2+} , Sr^{2+} and Ca^{2+} [4], or the replacement of $\text{Nb}^{5+}/\text{Ta}^{5+}$ with quadrivalent cations such as Sn^{4+} [5] and Zr^{4+} [6]. We can trace the process of the development in the recent review by Thangadurai *et al.* [7].

Among these new systems, cubic $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZ) was reported by Murugan *et al.* to exhibit a high bulk conductivity of *ca.* $5 \times 10^{-4} \text{ S cm}^{-1}$ at 25°C [6]. This material has attracted much attention from researchers because of its high stability with lithium metal and its high lithium ion conductivity. It has become more obvious that the thermodynamically stable phase of stoichiometric $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ is a poor ionically conductive tetragonal phase at room temperature [8] and the high ionically conductive cubic phase is stable only above 650°C , where the disorder of Li ions is realized in the structure [9,10]. The highly conductive cubic LLZ room temperature phase is not stoichiometric $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$, but an alumina stabilized garnet-like phase such as $(\text{Li}_{7-3x}\text{Al}_x)\text{La}_3\text{Zr}_2\text{O}_{12}$, where elemental Al originates from the aluminum crucible used for high temperature sintering [10]. Rangasamy *et al.* reported that at least 0.204 mole of Al is required to stabilize the cubic garnet-like phase [11].

Triggered by the discovery of LLZ, studies on the solid solution between $\text{Li}_5\text{La}_3\text{M}_2\text{O}_{12}$ ($\text{M}=\text{Nb}$ and Ta) and $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ have been ongoing. Ohta *et al.* reported a high ionic conductivity of $8.0 \times 10^{-4} \text{ S cm}^{-1}$ at 25°C for $\text{Li}_{6.75}\text{La}_3\text{Nb}_{0.25}\text{Zr}_{1.75}\text{O}_{12}$ [12], and Wang and Lai reported $\text{Li}_{6.7}\text{La}_3\text{Zr}_{1.7}\text{Ta}_{0.3}\text{O}_{12}$ with a high ionic conductivity of $9.6 \times 10^{-4} \text{ S cm}^{-1}$ at 25°C [13].

Trials with the substitution of trivalent cations such as Y^{3+} into the Nb^{5+} site was reported by Narayanan *et al.* [14] in an attempt to optimize the Li content in the

garnet-structure using the nominal $\text{Li}_{5+2x}\text{La}_3\text{Nb}_{2-x}\text{Y}_x\text{O}_{12}$ composition. Consequently, they reported that the highest conductivity of $2.7 \times 10^{-4} \text{ S cm}^{-1}$ at 25°C was observed for the $\text{Li}_{6.5}\text{La}_3\text{Nb}_{1.25}\text{Y}_{0.75}\text{O}_{12}$ composition. However, there was no mention of yttrium compositions richer than $x = 0.75$. An unknown trace phase appeared in the $x = 0.75$ sample, which implied that the solubility limit of Y^{3+} ions was around this composition. Thangadurai and Weppner also attempted the partial substitution of In^{3+} for Nb^{5+} ($\text{Li}_{5.5}\text{La}_3\text{Nb}_{1.75}\text{In}_{0.25}\text{O}_{12}$) and reported an improvement of conductivity to $1.8 \times 10^{-4} \text{ S cm}^{-1}$ at 50°C [15].

In the present paper, the relationship between the chemical composition (lithium content) and ionic conductivity of $\text{Li}_{5+2x}\text{La}_3\text{Nb}_{2-x}\text{Sc}_x\text{O}_{12}$ was investigated. The amount of lithium ions is considered to be a key factor in the lithium ion conductivity of the garnet-like phase. The ion radius of Sc^{3+} (88.5 pm) in 6-coordination is closer to that of Nb^{5+} (78 pm) than that of Y^{3+} (104 pm) or In^{3+} (94 pm), so that a wider solid solution region than that for Y^{3+} substitution in $\text{Li}_5\text{La}_3\text{Nb}_2\text{O}_{12}$ is expected to be formed. Thus, our aim is the synthesis of $\text{Li}_7\text{La}_3\text{NbScO}_{12}$, analogous with LLZ. The ionic radii values used here are taken from the table of crystal radii in an octahedron by Shannon and Prewitt [16]. In most of the papers that report on the synthesis of garnet-like lithium ion conductors, an aluminum crucible has been used as a container for the high temperature sintering, so that some degree of Al contamination from the crucible is unavoidable. The stabilization of highly conductive cubic LLZ is an example of the positive effect caused by the substitution of Al^{3+} ions into Li^+ ion sites; however, the uncontrolled inclusion of Al from an alumina crucible is unsuitable for the study of the relation between various properties and Li content, because the actual Li content could be different from the nominal composition. In the case of the $\text{Li}_{5+2x}\text{La}_3\text{Nb}_{2-x}\text{Y}_x\text{O}_{12}$ system reported by Narayanan *et al.*, Al contamination from the alumina crucible was qualitatively detected using ^{27}Al magic-angle spinning nuclear magnetic resonance spectroscopy (MAS NMR) [14]. Although the authors reported that the small amount of Al contamination (no quantitative analysis result was shown) had little influence on the conductivity, we consider that some effect on the composition and electrical properties cannot be denied. For sample preparation in the present work, a magnesia crucible was used as a reaction container to synthesize Al-free pure phases because the oxides of elements included in $\text{Li}_{5+2x}\text{La}_3\text{Nb}_{2-x}\text{Sc}_x\text{O}_{12}$ do not easily form compounds with MgO . Therefore, the relationship between the lithium content and the bulk ionic conductivity can be discussed without the inclusion of Al in the structure or the grain boundaries.

2. Experimental

Compounds with the nominal composition $\text{Li}_{5+2x}\text{La}_3\text{Nb}_{2-x}\text{Sc}_x\text{O}_{12}$ were prepared by solid-state reaction using stoichiometric amounts of $\text{LiOH}\cdot\text{H}_2\text{O}$ (Kanto Chemical), $\text{La}(\text{OH})_3$ (Aldrich), Nb_2O_5 (Wako), and Sc_2O_3 (Rare Metallic). 10 mol% excess $\text{LiOH}\cdot\text{H}_2\text{O}$ was added to compensate for Li evaporation during synthesis at high temperature. The powders were ball-milled in hexane, pressed into pellets, and then heated in air at 750 °C for 12 h on a gold sheet. The powders obtained after the first heat treatment were again ball-milled in hexane, isostatically pressed into pellets (12 mm diameter and 3–4 mm thick), covered with the mother powder in a magnesia crucible and then sintered at 1150 °C in air for 12 h.

The phases of the sintered samples were determined by powder X-ray diffraction (XRD; Rigaku RINT 2500) analysis with Cu K α radiation. Si was added to samples as a reference for angle correction of the XRD measurement. The software TOPAS 4.2 (Bruker AXS) was employed for Rietveld refinements. The densities of pellets are calculated from diameter, thickness, and weight of obtained pellets. Theoretical densities of pellets are calculated from the cell parameters from the XRD measurement. Elemental analysis for Li, La, Nb, Sc and Mg in the sintered samples was performed using Inductivity Coupled Plasma Optical Emission Spectroscopy (ICP-OES; Agilent Technologies ICP-OES 710). The samples were dissolved in a mixed solution of hydrochloric acid and nitric acid (3:1 volume ratio) and diluted to 1-5 ppm before ICP-OES measurement.

The electrical conductivity of the sintered samples (*ca.* 10 mm diameter and 3-4 mm thick) with sputtered gold electrodes was measured using a frequency response analyzer (Solartron 1260) in the frequency range of 0.1 Hz to 1 MHz and in the temperature range of 25 to 200 °C. The bias voltage was set at 10 mV and Z-plot software was employed for data analysis.

3. Results and discussion

Figure 1 shows powder XRD patterns of $\text{Li}_{5+2x}\text{La}_3\text{Nb}_{2-x}\text{Sc}_x\text{O}_{12}$ sintered at 1150 °C for 12 h along with the cubic garnet phase $\text{Li}_5\text{La}_3\text{Nb}_2\text{O}_{12}$ (LLN) from the database ICSD #68251. Almost all diffraction peaks of the samples from $x=0.0$ to 0.75 can be assigned to the cubic garnet-like structure, while some impurity peaks that mostly correspond to LiNbO_3 and LiScO_2 were observed only for the $x = 1.0$ sample, although a small amount of LiScO_2 was also present in the $x = 0.75$ sample.

The variation of lattice constant obtained from the powder XRD patterns is plotted in Figure 2 as a function of the Sc content. The lattice constant increased linearly with the Sc content from 1.2786(4) nm ($x = 0$) up to 1.2844(6) nm ($x = 0.75$), which reflects the substitution of larger Sc^{3+} ions (88.5 pm) for Nb^{5+} ions (78 pm). For $x = 1.0$, the lattice constant deviated from Vegard's law and was similar to that for $x = 0.75$. These results indicate that the solid solution of $\text{Li}_{5+2x}\text{La}_3\text{Nb}_{2-x}\text{Sc}_x\text{O}_{12}$ is formed in the range of $x = 0$ to 0.75, *i.e.*, between a lithium content of 5.0 and 6.5 per formula unit. Trials to expand the solubility region above $x = 0.75$ were unsuccessful; impurity phases such as LiNbO_3 and LiScO_2 increased with the Sc ratio. The single phase $\text{Li}_7\text{La}_3\text{NbScO}_{12}$ could not be synthesized under the present synthesis conditions.

In order to confirm that Sc^{3+} ion is substituting for Nb^{5+} ion in the 16a site, the Rietveld refinement was done as Sc^{3+} ion can be substituted for 24d(Li^+ site), 96h(Li^+ site), and 16a(Nb^{5+} site) in a space group *Ia3-d*. The results showed that all of Sc^{3+} ions almost exist in 16a site, and only a few Sc^{3+} ions exist in 96h site. The results of Rietveld refinements for $x=0.25$ and 0.625 are shown in Figures S1 and S2 in supplementary information.

The elemental contents of the samples were analyzed using ICP-OES and the results are summarized in Table I, where the ratios are normalized with respect to the Nb content. The measured atomic ratio of Li/La/Nb/Sc approximately coincides with that of the formula unit $\text{Li}_{5+2x}\text{La}_3\text{Nb}_{2-x}\text{Sc}_x\text{O}_{12}$, except for the sample of $x = 1.0$, where the objective $\text{Li}_7\text{La}_3\text{NbScO}_{12}$ material was not formed due to excessive Li evaporation and the formation of impurity phases. No Mg was detected in any of the samples, which confirmed that the MgO crucible was an effective reaction vessel for the high temperature synthesis of this system. The La content was slightly higher than that of the starting mixture for all the samples, and this may be due to the experimental uncertainty of ICP-OES measurements. The garnets are not so easily dissolved in acid and some interference by each element sometimes occurs. However, the distinct tendency was obtained when the composition of the samples was changed. In total consideration of the results from XRD measurements, we believe that the compositions of the sintered

samples, except for $x=1.0$, are consistent with the nominal formula of $\text{Li}_{5+2x}\text{La}_3\text{Nb}_{2-x}\text{Sc}_x\text{O}_{12}$.

The relative densities of the sintered samples (12 mm diameter and 3–4 mm thick before sintering) were within 92–95% except for $x = 0$ (80%) and 1.0 (85%). However, for $x = 0$ ($\text{Li}_5\text{La}_3\text{Nb}_2\text{O}_{12}$), a dense sintered pellet could not be obtained under the synthesis conditions. Therefore, some liquid phase containing Li and Sc may be formed during reaction to accelerate sintering.

Impedance measurements of the samples were conducted using a $\text{Au}/\text{Li}_{5+2x}\text{La}_3\text{Nb}_{2-x}\text{Sc}_x\text{O}_{12}/\text{Au}$ blocking cell in the frequency range from 0.1 Hz to 1 MHz. Figure 3 shows typical impedance profiles for $\text{Li}_{6.25}\text{La}_3\text{Nb}_{1.375}\text{Sc}_{0.625}\text{O}_{12}$ at various temperatures. Similar profiles were observed for all samples, which are shown in Figures S3 - S8 in supplementary information. The impedance plots were fitted on the bases of equivalent circuit which consists of a series circuit with a bulk resistance and a parallel combination of grain boundary resistance and capacitance. The intercepts of the semicircle on the real axis at high frequency was attributed to the bulk resistance, and that at low frequency side was attributed to the total resistance of bulk and grain boundary. The resistance of the bulk and grain boundary became smaller with increasing temperature, especially the contribution of the grain boundary resistance.

The temperature dependence of the bulk conductivity for $\text{Li}_{5+2x}\text{La}_3\text{Nb}_{2-x}\text{Sc}_x\text{O}_{12}$ is shown in Figure 4 and the composition dependence at 25 and 50 °C is shown in Figure 5. All conductivities shown here were measured in a heating direction, and the values of conductivity in the cooling direction also showed no large difference. The activation energies calculated from the linear part of the Arrhenius plot between 50 and 200 °C are listed in Table II along with the conductivities at 25 and 50 °C.

The bulk conductivities of the samples were increased by the substitution of Sc into Nb sites. The highest conductivity of $3.70 \times 10^{-4} \text{ S cm}^{-1}$ was observed for $x = 0.625$ at 25 °C and that for $x = 0.75$ at 50 °C was $6.05 \times 10^{-4} \text{ S cm}^{-1}$. The temperature dependence (Figure 4) appears divided into low temperature (<50 °C) and high temperature (>50 °C) regions. The conductivity of $\text{Li}_6\text{La}_3\text{Nb}_{1.5}\text{Sc}_{0.5}\text{O}_{12}$ measured from -10 °C to 25 °C was a linear gradient (see inset of Figure 4), which indicates that some extrinsic conductive mechanism may be involved due to the inclusion of defects in the structure [17]. The estimated conductivity for $x = 0.625$ at 25 °C extrapolated from the high temperature linear region is around $1.4 \times 10^{-4} \text{ S cm}^{-1}$. Therefore, to determine the relationship between the lithium content in $\text{Li}_{5+2x}\text{La}_3\text{Nb}_{2-x}\text{Sc}_x\text{O}_{12}$ and the lithium ion conductivity, a comparison of data from temperatures greater than 50 °C is required. The conductivity at 50 °C in Figure 5 increases with the Sc content (Li content) and is

highest for $x = 0.75$, or 6.5Li in the nominal formula (6.47Li by ICP measurement). The activation energy for conduction does not have a significant compositional dependence (0.36–0.40 eV in $0.25 \leq x \leq 0.75$), but the conductivity does show a positive dependence on the lithium content, which indicates that the mobility of Li ion does not change, but the number of mobile Li ions does increase. The conductivity of the garnet-like lithium ion conductors generally increases with the lithium content in the structure due to the increase in the occupational disorder of excess lithium at 96h interstitial sites (*Ia3-d*) [18]. The conduction of Li ions in the $\text{Li}_{5+2x}\text{La}_3\text{Nb}_{2-x}\text{Sc}_x\text{O}_{12}$ system may also be explained by a similar mechanism, where Li ions migrate through the tetrahedral 24d and 96h sites [19].

The bulk conductivity of ca. $3.5 \times 10^{-4} \text{ S cm}^{-1}$ at 25 °C for the $\text{Li}_{5+2x}\text{La}_3\text{Nb}_{2-x}\text{Sc}_x\text{O}_{12}$ system of $x = 0.625$ is relatively high and comparable to well-known garnet-like high lithium ion conductors. For example, the bulk conductivity of the famous $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ reported by Murugan *et al.* was estimated to be $5.11 \times 10^{-4} \text{ S cm}^{-1}$ at 25 °C from impedance plots [6]. The highest bulk conductivity found in solid solution systems with $\text{Li}_5\text{La}_3\text{M}_2\text{O}_{12}$ (M=Nb and Ta) was $8 \times 10^{-4} \text{ S cm}^{-1}$ at $x = 1.75$ in $\text{Li}_{5+x}\text{La}_3\text{Nb}_{2-x}\text{Zr}_x\text{O}_{12}$ [12], $9.6 \times 10^{-4} \text{ S cm}^{-1}$ at $x = 1.8$ in $\text{Li}_{5+x}\text{La}_3\text{Ta}_{2-x}\text{Zr}_x\text{O}_{12}$ [13], and $2.7 \times 10^{-4} \text{ S cm}^{-1}$ at $x = 0.75$ in $\text{Li}_{5+2x}\text{La}_3\text{Nb}_{2-x}\text{Y}_x\text{O}_{12}$ [14]. However, the solubility limit of Sc at Nb sites is around $x = 0.75$ in $\text{Li}_{5+2x}\text{La}_3\text{Nb}_{2-x}\text{Sc}_x\text{O}_{12}$. If a single phase with a higher Li content could be obtained, then higher conductivity may be realized. For example, the high temperature form of Al-free cubic $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$, although unstable at room temperature, is expected to have a lithium ion conductivity of $1.71 \times 10^{-3} \text{ S cm}^{-1}$ at 25 °C from extrapolation [10].

The bulk conductivity of Sc-free $\text{Li}_5\text{La}_3\text{Nb}_2\text{O}_{12}$ in the present study is $1.73 \times 10^{-4} \text{ S cm}^{-1}$ at 25 °C, which is much higher than that reported in the literature. Thangadurai *et al.* reported a value of around $10^{-6} \text{ S cm}^{-1}$ as the bulk conductivity [3], and a value of $4.4 \times 10^{-5} \text{ S cm}^{-1}$ (50 °C) when reporting the effect of sintering on the conductivity [15]. Samples were prepared at 900–1000 °C and higher conductivities were obtained with higher sintering temperatures. The samples in our study were sintered at 1150 °C, which is higher than that used by Thangadurai and Weppner [15]. Wang and Lai reported the relationship between the conductivity and Li content in the $\text{Li}_{5+x}\text{La}_3\text{Ta}_{2-x}\text{Zr}_x\text{O}_{12}$ system [13], where a high bulk conductivity of $1.6 \times 10^{-4} \text{ S cm}^{-1}$ was reported for $\text{Li}_5\text{La}_3\text{Ta}_2\text{O}_{12}$ prepared at a high temperature of 1230 °C. Thus, the sintering temperature may be significantly correlated with the lithium distribution in the samples, and consequently the ionic conductivity.

4. Conclusion

Al-free cubic garnet-type $\text{Li}_{5+2x}\text{La}_3\text{Nb}_{2-x}\text{Sc}_x\text{O}_{12}$ with $x = 0\text{--}0.75$ was successfully synthesized by high temperature solid state reaction with the mother powder bed method in a magnesia crucible. The conductivity of the samples was dependent on the Li content and the optimum Li content ratio in the formula unit for Li conduction was 6.25–6.5. The highest conductivity of $3.70 \times 10^{-4} \text{ S cm}^{-1}$ was observed for $x = 0.625$ at 25 °C and that for $x = 0.75$ at 50 °C was $6.05 \times 10^{-4} \text{ S cm}^{-1}$.

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Appendix

Supplementary data associated with this article can be found, in the online version, at doi:xxxxxxxxx.

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Figure Captions

Figure 1. XRD patterns of $\text{Li}_{5+2x}\text{La}_3\text{Nb}_{2-x}\text{Sc}_x\text{O}_{12}$. The symbols denote impurity phases; $\bullet$: Si (reference for angle correction), $\square$: lithium niobium oxides, $\circ$: LiScO_2 , $\blacksquare$: unknown peak.

Figure 2. Lattice parameter of $\text{Li}_{5+2x}\text{La}_3\text{Nb}_{2-x}\text{Sc}_x\text{O}_{12}$ as a function of the Sc content. The lines indicate the data trends.

Figure 3. Impedance profiles of $\text{Li}_{6.25}\text{La}_3\text{Nb}_{1.375}\text{Sc}_{0.625}\text{O}_{12}$ (10.2 mm diameter and 3.6 mm thick) measured at $\bullet$: 25 °C, $\square$: 50 °C, $\circ$: 90 °C and $\times$: 140 °C. The inset shows the close-up.

Figure 4. Arrhenius plot for the bulk conductivity of $\text{Li}_{5+2x}\text{La}_3\text{Nb}_{2-x}\text{Sc}_x\text{O}_{12}$, $\diamond$: $x = 0$, $\blacklozenge$: $x = 0.25$, $\square$: $x = 0.5$, $\times$: $x = 0.625$, $\circ$: $x = 0.75$, $\blacksquare$: $x = 1.0$. Inset shows the conductivity of $\text{Li}_6\text{La}_3\text{Nb}_{1.5}\text{Sc}_{0.5}\text{O}_{12}$ measured from -10 °C to 50 °C.

Figure 5. Bulk conductivity vs. Li content in $\text{Li}_{5+2x}\text{La}_3\text{Nb}_{2-x}\text{Sc}_x\text{O}_{12}$, measured at $\circ$: 25 °C and $\square$: 50 °C.

Table

Table I Li content of sintered samples measured by ICP-OES

x in $\text{Li}_{5+2x}\text{La}_3\text{Nb}_{2-x}\text{Sc}_x\text{O}_{12}$		0	0.25	0.5	0.625	0.75	1
Li content (theoretical)		5.0	5.5	6.0	6.25	6.5	7.0
ICP results	Li	4.99	5.53	6.14	6.33	6.47	6.61
	La	3.25	3.25	3.28	3.32	3.17	3.02
	Nb	2.00	1.75	1.50	1.375	1.25	1.00
	Sc	n.d.	0.25	0.54	0.67	0.86	1.02
	Mg	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

The ratios are normalized with respect to the Nb content. N.D: no detection

Table II Conductivity and activation energy of $\text{Li}_{5+2x}\text{La}_3\text{Nb}_{2-x}\text{Sc}_x\text{O}_{12}$

x in $\text{Li}_{5+2x}\text{La}_3\text{Nb}_{2-x}\text{Sc}_x\text{O}_{12}$		0	0.25	0.5	0.625	0.75	1
Conductivity ($\times 10^{-4} \text{ S cm}^{-1}$)	bulk (25°C)	1.73	3.14	3.55	3.70	3.19	1.42
	total (25°C)	0.22	0.52	1.02	1.38	1.26	0.68
	bulk (50°C)	2.81	3.86	4.77	5.30	6.05	2.88
	total (50°C)	0.71	1.97	3.46	3.76	5.16	1.95
Activation energy (bulk) (eV)		0.45	0.40	0.40	0.36	0.39	0.40

Fig. 1. XRD patterns of $\text{Li}_{5+2x}\text{La}_3\text{Nb}_{2-x}\text{Sc}_x\text{O}_{12}$. The symbols denote impurity phases; ●: Si (reference for angle correction), □: lithium niobium oxides, ○: LiScO_2 , ■: unknown peak.

Fig. 2. Lattice parameter of $\text{Li}_{5+2x}\text{La}_3\text{Nb}_{2-x}\text{Sc}_x\text{O}_{12}$ as a function of the Sc content. The lines indicate the data trends.

Fig. 3. Impedance profiles of $\text{Li}_{6.25}\text{La}_3\text{Nb}_{1.375}\text{Sc}_{0.625}\text{O}_{12}$ (10.2 mm diameter and 3.1 mm thick) measured at $\bullet$: 25 °C, $\square$: 50 °C, $\circ$: 90 °C and $\times$: 140 °C. The inset shows the close-up.

Fig. 4. Arrhenius plot for the bulk conductivity of $\text{Li}_{5+2x}\text{La}_3\text{Nb}_{2-x}\text{Sc}_x\text{O}_{12}$, $\diamond$: $x = 0$, $\blacklozenge$: $x = 0.25$, $\square$: $x = 0.5$, $\times$: $x = 0.625$, $\circ$: $x = 0.75$, $\blacksquare$: $x = 1.0$. Inset shows the conductivity of $\text{Li}_6\text{La}_3\text{Nb}_{1.5}\text{Sc}_{0.5}\text{O}_{12}$ measured from -10 °C to 80 °C.

Fig. 5. Bulk conductivity vs. Li content in $\text{Li}_{5+2x}\text{La}_3\text{Nb}_{2-x}\text{Sc}_x\text{O}_{12}$, measured at $\circ$: 25 °C and $\square$: 50 °C.