Synthesis of Perovskite-Type $\text{Li}_x(\text{W}_{1-y}\text{Nb}_y)\text{O}_3$ Single Crystals and Their Lithium Ion Conductivity

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ペロブスカイト型 $\text{Li}_x(\text{W}_{1-y}\text{Nb}_y)\text{O}_3$ 単結晶の合成とリチウムイオン伝導性

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We synthesized single crystals of perovskite-type new compounds in the system $\text{Li}_x(\text{W}_{1-y}\text{Nb}_y)\text{O}_3$ ($x \sim 0.4$, $0 \leq y < 0.15$) by electrolysis of fused salt. Their lithium ion conductivity was measured by a dc method using electron-blocking electrodes. A sample ($x = 0.4$, $y = 0.06$) showed conductivity of $1.0(1) \times 10^{-7} \text{ S/cm}$ along [100] at room temperature.

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1. Introduction

Lithium ionic conductors have been a subject of interest not only because of their application to solid lithium batteries and chemical sensors, but also from a fundamental point of view in relation to ionic transportation inside of the solid state. Among many lithium ionic conductors, $(\text{La}_{2/3-x}\text{Li}_x)\text{TiO}_3$ has been especially interesting because of its high ionic conductivity as much as 10^{-3} S/cm at room temperature.¹⁾ The structure of this compound and its modified materials are perovskite-type, in which lithium ion and its vacancy are located at its A-site, and the mechanism of ionic transportation is considered as hopping of lithium via vacancy. The influence of lanthanum ion occupying the same A-site was also studied. As such lanthanum ions may close the pass way of lithium ion, the ionic conduction is often discussed on a percolation model. Harada et al. studied the effect of lanthanum ordering and found that the ordering of lanthanum reduced the ionic conductivity.^{2),3)} Therefore, it is worth while investigating materials, especially in a single crystal form, based on a similar ReO_3 type framework containing nothing at the A-site other than lithium and its vacancy, in order to obtain better Li conductors as well as to understand the detailed conduction mechanism of lithium in this class of compounds. However, such a study employing a single crystal sample is very few.⁴⁾

Lithium-tungsten bronze Li_xWO_3 is a perovskite-type compound whose A-site is occupied only by lithium ion and its vacancy. The single crystal of this material can be obtained by electrolysis of fused salt of mixture of Li_2WO_4 and WO_3 . However, Li_xWO_3 itself cannot be a solid electrolyte, because it has high electronic conductivity more than 10^3 S/cm , and cannot be used as a solid electrolyte. On the other hand, it has been reported that partial substitution of tungsten by niobium or tantalum reduces the electronic conductivity of sodium-tungsten bronzes. In this short paper, we report the synthesis of single crystal niobium doped lithium-tungsten bronzes $\text{Li}_x(\text{W}_{1-y}\text{Nb}_y)\text{O}_3$ and preliminary results of ionic conductivity measurements by a dc method using electron-blocking electrodes.

2. Experimental

The synthesis of niobium doped lithium-tungsten bronze was carried out after the synthesis of sodium-tungsten bronzes reported by Weller et al.⁵⁾ and Shank.⁶⁾ About 10 mg of a mixture of Li_2WO_4 , WO_3 , and Nb_2O_5 was set into a

30 ml alumina-silica porcelain crucible. The crucible placed in a quartz tube was heated using an infrared imaging furnace to the temperature 50°C higher than the melting point of the relevant mixture shown in a phase diagram by Mellor,⁷⁾ to melt the mixture completely. After cooling the melt to temperature 10°C higher than the melting point (i.e., 755°C when $\text{Li} : \text{W} : \text{Nb} = 100 : 95 : 5$), it was electrolyzed using a chromel wire working electrode and a carbon rod counter electrode at a constant current between 0.5 and 20 mA for 6 h, to deposit crystals of $\text{Li}_x(\text{W}_{1-y}\text{Nb}_y)\text{O}_3$ on the chromel cathode. The polarization at the counter electrode was monitored by a Pt wire reference electrode. The temperature of the electrolysis bath was controlled within $\pm 1^\circ\text{C}$ using a thermocouple near the working electrode. Nitrogen was streamed in the quartz tube to protect the resultant bronze compound from oxidation. After electrolysis, the electrodes were pulled up from the fused salt and cooled down to room temperature. The compound deposited on the cathode was washed by 10% K_2CO_3 aq. solution and then by 50% HF aq. solution if needed.

The structure of compound was studied by 4-axis X-ray diffraction (Rigaku, AFC7R, with graphite monochromated $\text{Mo K}\alpha$ radiation) and powder X-ray diffraction (Rigaku, Rint2100S, with graphite monochromated $\text{Cu K}\alpha$ radiation). The composition was determined by inductively coupled plasma (ICP) spectroscopy (SPS4000, Seiko Instruments). Before ICP measurement, the compounds were dissolved by following process; compound was mixed with K_2CO_3 and KNO_3 , and kept at 500°C for 1 h. After cooling the resultant matter, it was added in water. Excess K_2CO_3 was neutralized by nitric acid. Then a diluted HF solution was added to dissolve compound completely. Oxygen content was determined thermo-gravimetrically.

Ionic conductivity was measured by a dc two-electrode technique using a pair of electron-blocking electrodes composed of metallic lithium and a porous polyethylene (PE) film impregnated with 1 mol/dm^3 LiClO_4 /propylene carbonate (PC) (=electron-blocking layer). Thus the setup is represented as

$\text{Li} | (\text{LiClO}_4/\text{PC}, \text{PE}) | \text{sample} | (\text{LiClO}_4/\text{PC}, \text{PE}) | \text{Li}$
[Cell I]

A single crystal sample was polished with $1 \mu\text{m}$ diamond slurry. The face of crystal was determined by Laue pattern. A constant dc voltage was applied between two lithium electrodes and the transient current was measured. Construc-

tion of the cell and conductivity measurements were all carried out in an Ar-filled dry box. Electronic conductivity was also measured by dc-method, using gold paste as electrodes.

3. Results and discussion

The deposit at the cathode was a purple-black agglomerate of crystals, which was so loose that it could be easily separated into small individual cubic crystals, typically, 1 mm on a side. Figure 1 shows a photograph of a crystal. They showed the Laue pattern characteristic of a single crystal. When we carried out the electrolysis using a seed crystal and small current, a larger single crystal (about 5 mm on a side) was obtained. In the present study, the ratio of lithium to the other metallic elements in the bath was fixed at 1, and the ratio of niobium to tungsten was varied. Table 1 shows the composition of fused salt and the composition and structure of resultant compounds. Lithium content x was about 0.4 independently of the niobium content. Niobium content y of the compounds was higher than that of fused salt, and they were in a single cubic perovskite-type phase in the range of $y < 0.15$. The lattice parameter of the compounds is almost independent of the niobium content in this composition range. Table 2 summarizes the crystallographic parameters of $\text{Li}_{0.40}(\text{W}_{0.94}\text{Nb}_{0.06})\text{O}_3$ obtained by the 4-axis X-ray diffraction. In refinement we scattered niobium at random over the tungsten sites. Lithium was fixed at the

6b site, though the structure ($Im\bar{3}$) has another possible lithium site ($2a$), because a neutron diffraction study on isostructural $\text{Li}_{0.36}\text{WO}_3$ has shown such a preferential occupation.⁸⁾ The tilting of WO_6 octahedra was about 4.2° in the niobium-doped compounds and was smaller than that of about 11° in the $\text{Li}_{0.36}\text{WO}_3$. We also obtained the tantalum doped lithium-tungsten bronzes by similar method. In the case, the single phase region of perovskite-type structure was in the range of $0 \leq x < 0.07$.

Figure 2 shows the transient currents after application of various levels of voltage to Cell I where the sample is $\text{Li}_{0.40}(\text{W}_{0.94}\text{Nb}_{0.06})\text{O}_3$. The current passes along the $[100]$ direction of the sample. Saturated values of current, as-

Table 2. Structural Parameters of $\text{Li}_{0.40}(\text{W}_{0.94}\text{Nb}_{0.06})\text{O}_3$. Isotropic Atomic Displacement Parameter B_{iso} of Lithium was Fixed at 0.028 nm^2 , which was Obtained by Wiseman and Dickens.⁸⁾ ($R = 6.1\%$, Space Group: $Im\bar{3}$, $a = 0.74590(4) \text{ nm}$)

Species	g	x	y	z	$B_{\text{iso}} / \text{nm}^2$
Li	0.53	0.000	0.500	0.000	0.028
W	0.94	0.250	0.250	0.250	0.002(1)
Nb	0.06	0.250	0.250	0.250	0.002(1)
O	1	0.236(2)	0.262(2)	0.000	0.019(3)

Fig. 1. Photograph of single crystal $\text{Li}_{0.40}(\text{W}_{0.94}\text{Nb}_{0.06})\text{O}_3$ obtained by fused salt electrolysis.

Fig. 2. Transient current of $\text{Li}_{0.40}(\text{W}_{0.94}\text{Nb}_{0.06})\text{O}_3$ at room temperature after voltage was applied using dc two-electrode technique.

Table 1. Composition and Structure of the Niobium Doped Lithium-Tungsten Bronzes Obtained by Fused Salt Electrolysis. x and y in the Table Represent Lithium Content ($x = \text{Li}/(\text{Nb} + \text{W})$) and Niobium Content ($y = \text{Nb}/(\text{Nb} + \text{W})$), respectively

Melt Composition		Crystal Composition		Structure	
x	y	x	y	Symmetry	Lattice Parameter / nm
1.00	0.00	0.288(7)	-	cubic ($Im\bar{3}$)	$a = 0.74632(8)$
1.00	0.025	0.379(2)	0.065(1)	cubic ($Im\bar{3}$)	$a = 0.74636(8)$
1.00	0.050	0.387(17)	0.129(6)	cubic ($Im\bar{3}$)	$a = 0.74643(20)$
1.00	0.100	0.311(2)	0.277(2)	unknown	-

Fig. 3. Ionic current of $\text{Li}_{0.40}(\text{W}_{0.94}\text{Nb}_{0.06})\text{O}_3$ at room temperature as a function of applied dc-voltage.

sumable as ionic current, are plotted in Fig. 3 as a function of applied voltages. The plot is linear and the ionic conductivity of the sample calculated from the slope is $1.0(1) \times 10^{-7} \text{ S/cm}$. We confirmed that the resistance due to other resistive components in the circuit such as PE film, PE/sample and PE/Li interfaces etc. was negligible as compared to the sample resistance. Ionic conductivity of $1.0(1) \times 10^{-7} \text{ S/cm}$ is comparable with $8.2 \times 10^{-8} \text{ S/cm}$, the estimated conductivity of Li_xWO_3 , which is calculated from its reported diffusion coefficient.⁹⁾ However, it is much smaller than 10^{-3} S/cm of $(\text{La}_{2/3-x}\text{Li}_{1/3})\text{TiO}_3$. This is probably because the bottleneck between the A-sites in $\text{Li}_{0.40}(\text{W}_{0.94}\text{Nb}_{0.06})\text{O}_3$ is far narrower; the shorter O-O distance at the bottleneck is 0.352 nm, whereas that of $(\text{La}_{2/3-x}\text{Li}_{1/3})\text{TiO}_3$ is 0.387 nm.¹⁾ It is known that lithium conductivity in ReO_3 type frameworks depends strongly on their lattice parameter, because the barrier energy is very sensitive to the bottleneck size.¹⁰⁻¹³⁾ The electronic conductivity of this compound was 1.85 S/cm . Thus the transport number of lithium ion was 5.4×10^{-8} .

Since tungsten takes a mixed valence state of W^{6+} and W^{5+} , $\text{Li}_x(\text{W}_{1-y}\text{Nb}_y)\text{O}_3$ is a mixed conductor in which electronic conduction is far superior, if $x > y$. However, compounds in this system are expected to turn to an ionic conductor or lithium-conductive solid electrolyte, when lithium is extracted, electrochemically or chemically, to a level $x = y$ at which tungsten reaches the fully oxidized state. We tried to extract excess lithium according to following reaction:

A compound $\text{Li}_x(\text{W}_{1-y}\text{Nb}_y)\text{O}_3$ was put in a Pyrex glass tube. After the tube was evacuated, Br_2 was introduced. The temperature of the tube was kept at 200°C for 4–6 h. The pres-

sure of Br_2 gas was about 0.2 MPa. Reaction (1) is considered to cease proceeding when the lithium content x reaches y . However, ICP analysis showed that almost no lithium was contained in the resultant solid matter, while a considerable amount of bromine was detected by X-ray Photoelectron Spectroscopy (XPS) analysis. It is, therefore, thought that the following reaction, instead of Eq. (1), occurred when the compound was oxidized by Br_2 :

It is important to find adequate oxidizer and condition to obtain the compound in expectation, although they have not found yet.

4. Conclusion

We synthesized single crystal of niobium doped lithium-tungsten bronze by fused salt electrolysis. The single phase of perovskite-type cubic compound was obtained when niobium content y was less than 0.15. Ionic conductivity of single crystal was obtained from dc two-electrode technique using electron-blocking electrodes. Ionic conductivity along $[100]$ was $1.0(1) \times 10^{-7} \text{ S/cm}$, and the size of bottleneck has probably important affects on ionic conductivity. In this synthesis, it is reported to introduce another cation like Na and La at A-site, and it is interesting to study the affects of another cation.

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