

論文 / 著書情報
Article / Book Information

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論文要旨

THESIS SUMMARY

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野) : Doctor of (理学)

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要旨 (英文 800 語程度)

Thesis Summary (approx.800 English Words)

Lithium ion conductors have attracted much attention for use as solid electrolytes in all-solid-state batteries. Among the solid electrolyte materials proposed, lithium containing oxides are potential candidates due to their high ionic conductivity and chemical stability over a wide range of operation temperature. However, discovering novel materials is still necessary to satisfy the strict demands for the electrochemical devices. Therefore, new lithium ion conducting oxide based materials were searched based on crystal structures. Perovskite and pyrochlore structures were selected since they could provide wide range of solid solutions with various compositions both in stoichiometric and non-stoichiometric systems.

The lithium containing double oxides, Li-Sr-Ta-*M*-O system (*M* = Al, Ga) with the perovskite structure, were synthesized by conventional solid-state reaction. The stoichiometric systems were investigated based on the composition of $(\text{Li}_x\text{Sr}_{1-x})(\text{M}_{(1-x)/2}\text{Ta}_{(1+x)/2})\text{O}_3$ (*M* = Al, Ga) in the *x* range from 0 to 0.5. The Ga-substituted system showed higher conductivities than those of Al-substituted system. It could be due to larger ionic radius of Ga than Al; comparatively larger bottleneck size was provided by an increase in the *B*-O bond length. On the basis of the Ga-substituted system, the non-stoichiometric compositions were examined by introducing vacancies into *A*-site instead of Sr with composition of $(\text{Li}_x\text{Sr}_{1-x-y}\square_y)(\text{Ga}_{[(1-x)/2]-y}\text{Ta}_{[(1+x)/2]+y})\text{O}_3$. This composition was examined for $0 \leq y \leq 0.20$ with the *x* values of 0.2 and 0.25. Changes in lattice parameters associated with vacancy insertion indicated the formation of solid solutions in non-stoichiometric composition. The highest conductivity, $1.85 \times 10^{-3} \text{ S cm}^{-1}$ at 250 °C, was obtained for $(\text{Li}_{0.25}\text{Sr}_{0.625}\square_{0.125})(\text{Ga}_{0.25}\text{Ta}_{0.75})\text{O}_3$ (*x* = 0.25, *y* = 0.125). The increase in conductivity resulting from the introduction of vacancies was attributed to the increase in the total number of Li ions and vacancies at the *A*-sites. The presence of vacancies in conjunction with lithium ions at the *A*-sites confirmed by neutron Rietveld analysis of the $(\text{Li}_{0.25}\text{Sr}_{0.625}\square_{0.125})(\text{Ga}_{0.25}\text{Ta}_{0.75})\text{O}_3$ suggests that lithium diffusion proceeds according to the vacancy mechanism.

The unexplored pyrochlore structure materials as lithium ion conductor were investigated. The pyrochlore-type oxy-fluorides, $A_2A'B_2\text{O}_6\text{F}$, have been interested since Li and Sr could be introduced into *A* and *A'*-sites and the appearance of F at 8*b* site decreases the columbic interaction than that of general oxides pyrochlore. Therefore, $\text{LiSrB}_2\text{O}_6\text{F}$ (*B* = Nb⁺⁵ or Ta⁺⁵) and their solid solutions have been investigated. Furthermore, extra Li was introduced at interstitial site in the lattice by doping lower oxidation state cation Zr⁺⁴ at the *B*-site, $\text{Li}_{1.1}\text{SrB}_{1.9}\text{Zr}_{0.1}\text{O}_6\text{F}$, as the non-stoichiometric composition. The Sr and F defected composition, $\text{LiSr}_{0.9}\text{B}_2\text{O}_6\text{F}_{0.8}$, was also synthesized. The lattice parameter for Ta compound is smaller than the Nb compound in all compositions because of the larger electronegativity difference between Ta and O, which contracted the *B*-O bond length. As a result, the Nb compounds showed higher conductivities. The conductivities of both Nb and Ta compounds increased with the introduction of interstitial Li ions and vacancies. The highest conductivity at 300 °C was observed for the vacancies introduced composition of $\text{LiSr}_{0.9}\text{B}_2\text{O}_6\text{F}_{0.8}$; Nb and Ta compounds showed $8.21 \times 10^{-6} \text{ S cm}^{-1}$ and $6.38 \times 10^{-6} \text{ S cm}^{-1}$.

cm^{-1} , respectively. The structures of the pyrochlore compounds were analyzed using synchrotron X-ray diffraction data. There are two networks of $[\text{B}_2\text{O}_6]^{+2}$ and $[(\text{Li},\text{Sr})\text{F}]^{+2}$ unit. The larger $B\text{--O}$ bond length in the Nb compounds is responsible for expansion of the hexagonal tunnels, which makes higher conductivities than that of Ta compounds. In addition, changes in the $B\text{--O--}B$ bond angle revealed that the vacancies at A - and F-sites also enlarged the hexagonal tunnels. In addition, the existence of Sr and F atoms in the hexagonal tunnels could be an obstacle for lithium migration pathway. These structural characterizations revealed that controlling the concentration of vacancies at A - and F-sites is more effective to enhance the conductivities of the pyrochlore type materials rather than the introduction of interstitial Li ions.

The new lithium ion conductors with perovskite and pyrochlore structures have been discovered in both stoichiometric and non-stoichiometric compositions. Understanding of the relationship among the Li vacancy concentration, interstitial Li, bottleneck size and the conductivity could provide the indication for designing novel lithium conductors.

備考：論文要旨は、和文 2000 字と英文 300 語を 1 部ずつ提出するか、もしくは英文 800 語を 1 部提出してください。
Note：Thesis Summary should be submitted in either a copy of 2000 Japanese Characters and 300 Words (English) or 1 copy of 800 Words (English).

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