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Synthesis, structure and ionic conductivities of novel Li-ion conductor $A_3Li_xTa_{6-x}Zr_xSi_4O_{26}$ (A = Sr and Ba)

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ABSTRACT

The solid state oxide Li-ion conductors with high electrochemical stability as well as high ionic conductivity are needed for application to all-solid-state Li-ion battery. In this study, $A_3Li_xTa_{6-x}Zr_xSi_4O_{26}$ (A = Sr and Ba) as the candidate solid electrolytes stable against Li metal were synthesized by a conventional solid state reaction, and their structure and ionic conductivities were investigated. Both the compounds with A = Sr and Ba crystallize in hexagonal structure with space group $P\bar{6}2m$ in the same as $A_3Ta_6Si_4O_{26}$ does. MEM analysis, first principles calculation, and NMR spectroscopy showed that Li ions reside in interstitial sites. The sample with A = Ba exhibits higher ionic conductivity (e.g. 6.9×10^{-8} S cm^{-1} at 500 K in $x = 1.0$) than that with A = Sr (e.g. 3.2×10^{-8} S cm^{-1} at 500 K in $x = 1.0$). Ionic conductivity was enhanced with an increase of the substitution of Li and Zr. Further enhancement of ionic conductivity was derived by making deficiencies at A site cation. Consequently, $Ba_{2.75}Li_{1.5}Ta_5ZrSi_4O_{26}$ exhibits the highest total ionic conductivity of 4×10^{-7} S/cm at 500 K and the lowest activation energy of 0.72 eV. The consideration of the size of bottlenecks and nudged elastic band calculations suggest that Li ions diffuse in the A-site deficient layer perpendicular to the c-axis.

1. Introduction

The demand for battery with high energy density, high reliability and safety continues to increase [1]. Li metal anode, which is the most electropositive and has large capacity, is expected to meet the properties of high energy density. However, applying Li metal as anode with liquid electrolyte is difficult because dendritic growth of Li metal during discharge–charge cycles leads to explosion hazards [2]. All-solid-state Li ion battery using ceramic electrolytes is expected to have high energy density, reliability and safety by preventing dendritic growth of Li metal and getting rid of using flammable organic-based electrolytes. Indeed, Ohta et al. reported that an all-solid-state Li ion battery using Li metal and garnet-type $Li_{6.75}La_3Zr_{1.75}Nb_{0.25}O_{12}$ oxide as an anode and a solid state electrolyte, respectively, retained 98% of discharge capacity after the 100th cycle [3].

However, there are some difficulties when oxide solid state electrolytes are applied to all-solid-state-batteries, though they have the advantage of stability under ambient atmosphere with moisture over sulfide electrolytes [4]. One difficulty is high resistivity of electrolyte as well as the interface between electrolyte and electrodes. The other is the lack in electrochemical stability e.g. the reduction of electrolyte by Li containing anode [5]. Therefore, the oxide solid state electrolyte exhibiting both the high ionic conductivity and electrochemical stability is desired to be applied as all-solid-state battery.

There are some oxide electrolytes possessing high bulk conductivity at room temperature such as perovskite-type $La_{2/3-x}Li_{3x}Ti^{4+}O_3$ ($x \approx 0.1$) (1×10^{-3} S/cm) [6], $La_{0.29}Li_{0.04}Nb^{5+}O_3$ (4×10^{-5} S/cm) [7], LISICON-type $Li_{3.6}Ge_{0.6}V^{5+}{}_{0.4}O_4$ (4×10^{-5} S/cm) [8], NASICON-type $Li_{1.3}Ti^{4+}{}_{1.7}Al_{0.3}(PO_4)_3$ (7×10^{-4} S/cm) [9], and garnet-type $Li_7La_3Zr^{4+}{}_2O_{12}$ (5×10^{-4} S/cm) [10]. Most of these solid oxide electrolytes include transition metal ion with electron configuration of d^0. High ionic conductivity of those oxides is probably attributable to the flexibility of framework that originates from hybridization between filled 2p orbital of oxygen and empty d orbital of transition metal, so-called second-order Jahn–Teller (SOJT) effect [11]. The migration of Li ion in solid electrolytes causes local distortion of structural framework. The electrolytes containing SOJT active cation can accept such distortion and therefore exhibit high ionic conductivity.

The reduction of the electrolytes are commonly seen in Ti^{4+} containing oxides such as perovskite-type $La_{2/3-x}Li_{3x}TiO_3$ [6] and NASICON-type $Li_{1.3}Ti_{1.7}Al_{0.3}(PO_4)_3$ [9]. Nakayama et al. found that the electrochemical stability of electrolytes against Li metal depends on their composition and structure [12]. They showed that the electrolytes containing the

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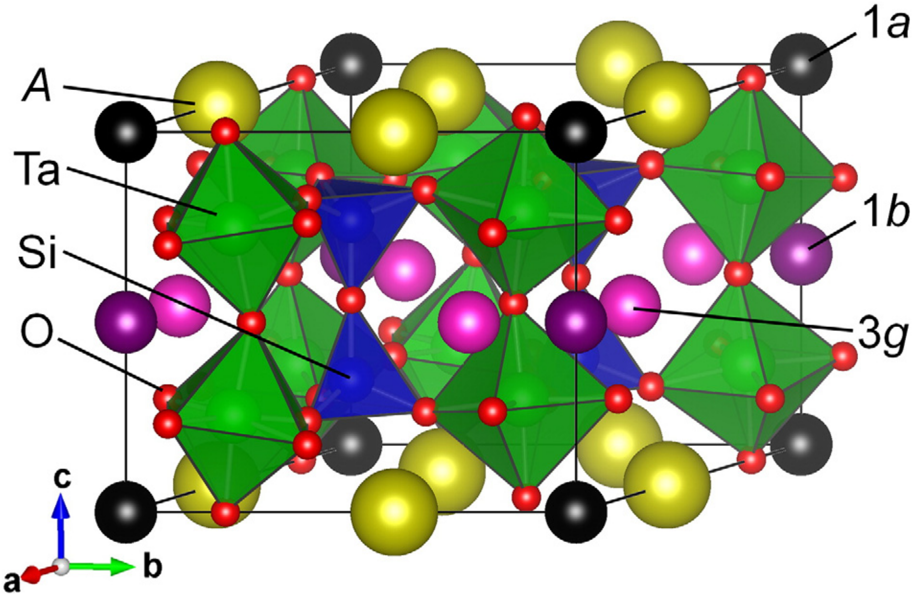

Fig. 1. Crystal structure of $A_3Ta_6Si_4O_{26}$ (A = Sr and Ba). 1a, 1b and 3g represent interstitial sites.

cations with high effective nuclear charge such as Ti^{4+}, Nb^{5+} and Sb^{5+} were unstable against Li metal. Furthermore, electrochemical stability of electrolytes is improved by increasing ionicity between ligands and cation. Their compositional criteria are in agreement with those in terms of electronegativity. The electronegativities [13] of Ti^{4+} and Sb^{5+} are greater than those of Ta^{5+} and Zr^{4+}, resulting in the lower energy level of empty d and s orbital (LUMO) of Ti^{4+} and Sb^{5+}, respectively, compared to the level of LUMO of Ta^{5+} and Zr^{4+}.

In this study, based on the concept above mentioned, we attempted to prepare novel solid state oxide electrolytes for all-solid-state battery. To improve electrochemical stability and ionic conductivity, Ta^{5+} and Zr^{4+} were selected as constituent ions forming framework because

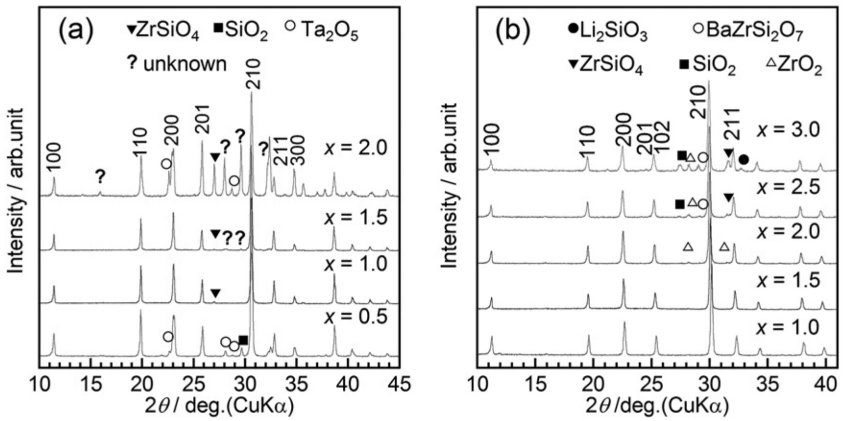

Fig. 2. X-ray diffraction patterns for $A_3Li_xTa_{6-x}Zr_xSi_4O_{26}$ at various x values. A = Sr and Ba for (a) and (b), respectively.

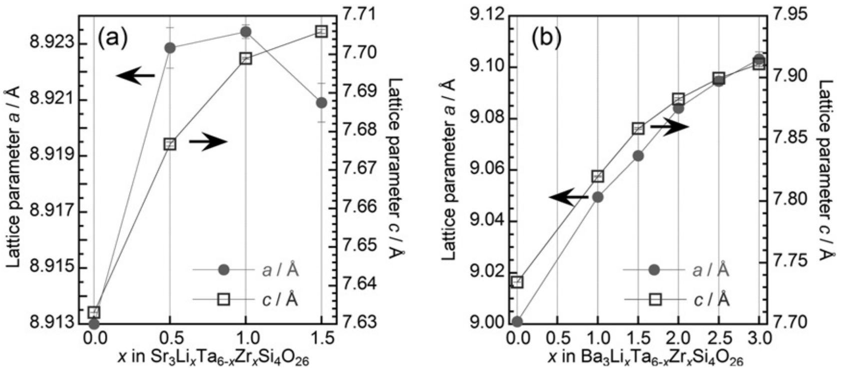

Fig. 3. Composition dependencies of lattice parameters for $A_3Li_xTa_{6-x}Zr_xSi_4O_{26}$ at various x values. A = Sr and Ba for (a) and (b), respectively.