

Ionic conduction of lithium in B-site substituted perovskite related compounds, $(\text{Li}_{0.1}\text{La}_{0.3})\text{M}_x\text{Nb}_{1-x}\text{O}_3$ (M=Zr, Ti, Ta)

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A-site deficient perovskites are promising materials for solid electrolyte of solid-state lithium secondary batteries. Several works have been focused on the ionic conductivity and crystal structure of the compounds expressed by general formula $\text{La}_{2/3-x}\text{Li}_x\text{Nb}_2\text{O}_6$ [1-4], and these materials show the ionic conductivity of Li about 10^{-5} S/cm at 298K. In order to improve the ionic conductivity, we synthesized three perovskite compounds with different substitution cations in B-site, $(\text{Li}_{0.1}\text{La}_{0.3})_y\text{M}_x\text{Nb}_{1-x}\text{O}_3$ (M=Zr⁴⁺, Ti⁴⁺, Ta⁵⁺; y is arranged by considering electrical neutrality requirement) and investigated the relationship between crystal structure and the lithium ionic conductivity in view of the classical ionic crystal model.

It was assumed that this perovskite belongs to classical ionic crystal which is composed of ionic bonds between cations and anions. Therefore the variation of potential energy through the ion conduction can be calculated by the combination of Coulombic potential and Born repulsive potential. The results of calculation indicates that ionic conductivity is expected to increase under following two conditions, (i) smaller average charge of B-site cations and (ii) larger unit cell.

B-site substitution samples were synthesized by conventional solid state reaction. Stoichiometric amount of starting reagents, Li_2CO_3 , La_2O_3 , Nb_2O_5 , ZrO_2 , TiO_2 , and Ta_2O_5 were mixed and heated up to 1250deg.C for more than 24h. The samples were characterized by powder XRD technique for determination of lattice parameters and by impedance measurement for the ionic conductivity.

From the powder XRD patterns, the only perovskite phase of $(\text{Li}_{0.1}\text{La}_{0.3})_y\text{Zr}_x\text{NbO}_3$ was observed in the composition range from $x=0$ to $x=0.05$. Similarly the single phase regions were determined as $x\leq 0.075$ for Ti substitution and $x\leq 0.0625$ for Ta substitution, respectively. The cell volume of samples substituted for B-site cations changed linearly with increasing the composition x (Fig.1). The partial substitution of Zr^{4+} for Nb^{5+} caused an increase of the cell volume, while that of Ti^{4+} caused a decrease. In the case Ta^{5+} substitution, no marked change in the cell volume was observed. Comparing ionic radius[5] of doped ions, Zr^{4+} (0.72Å), Ti^{4+} (0.605 Å), and Ta^{5+} (0.64 Å) with that of host ion, Nb^{5+} (0.64 Å), the change of cell volume reflect radius of the doped ion.

Fig.2 shows ionic conductivity of lithium for the samples $(\text{Li}_{0.1}\text{La}_{0.3})_y\text{M}_x\text{Nb}_{1-x}\text{O}_3$ with M=Nb, Zr, Ti, Ta. From the results, ascending the substitution amount of B-site, the ionic conductivity monotonously decreased. The activation energy of Zr and Ti substitution samples increased in that order, while activation energy of Ta substitution samples showed no marked change with original one, $\text{Li}_{0.1}\text{La}_{0.3}\text{NbO}_3$.

In view of classical ion crystal model, the ionic conductivity for Zr substitution would increase, since

lattice parameter is larger, and the average charge of B-site cation is smaller than pristine material, $\text{Li}_{0.1}\text{La}_{0.3}\text{NbO}_3$. However the results of ionic conductivity exhibit evidently decreasing. This disagreement indicates that there is an additional factor affecting the ionic conductivity. We suggest three possible explanations, (1) local distortion introduced by cation substitution, (2) the change of B-O bond covalency, and (3) formation of short-range ordering with B-site substitution.

References

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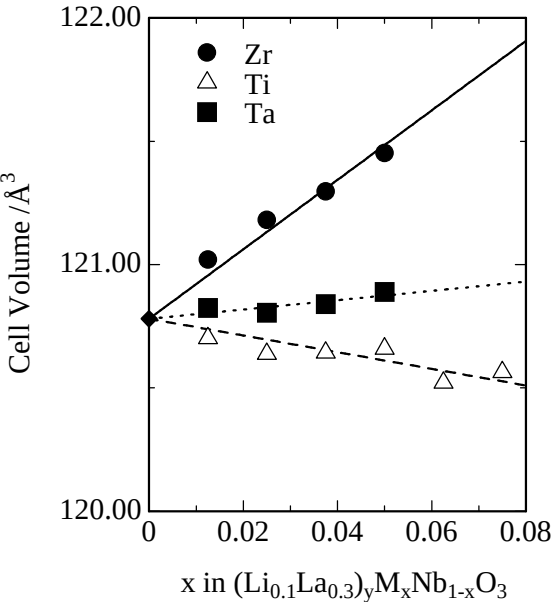


Fig.1 Variations of the cell volume with B-site substitution in $(\text{Li}_{0.1}\text{La}_{0.3})_y\text{M}_x\text{Nb}_{1-x}\text{O}_3$.

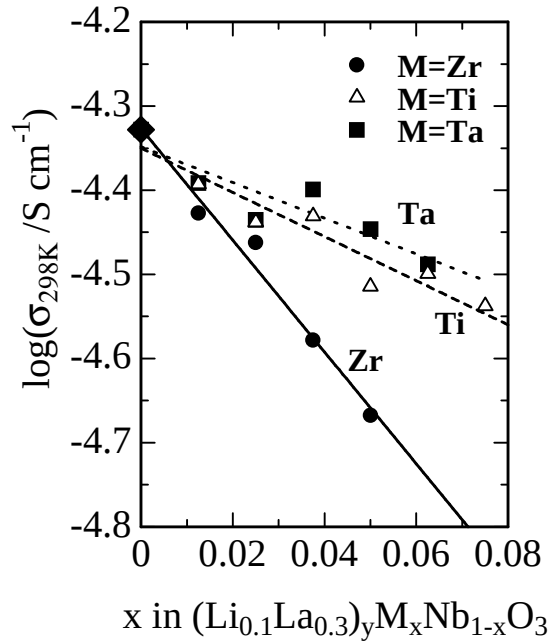


Fig.2 The variation of the ionic conductivity at 298K with composition x for the perovskite $(\text{Li}_{0.1}\text{La}_{0.3})_y\text{M}_x\text{Nb}_{1-x}\text{O}_3$.