Oxide ion conductivity in doped bismuth based mixed oxide with new structure

マクシミリアン, パーウェル クルチニー

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Name: Maksymilian Pawel Kluczny

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(新しい結晶構造を有するビスマス系複合酸化物の酸素イオン伝導性)

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Thesis Summary

Bismuth oxide based electrolytes have several disadvantages, which include instability in reducing atmospheres even at low temperatures, volatilization of bismuth at moderate temperatures, high reactivity, corrosion and poor mechanical strength. These properties are limiting the applicability of stabilized Bi_2O_3 in electrochemical devices despite many studies on bismuth oxide related materials. In this thesis, oxide-ion conductors based on bismuth oxychloride were mainly studied. By insertion of chlorine, which is expected to be more strongly bonded with Bi^{3+}, bismuth oxychloride is expected to be a fast oxide ion conductor with high stability. Additionally, oxide ion conductivity in mixed oxide of $Bi_2Ga_4O_9$ was also studied as a new structure oxide ion conductor.

In Chapter 2, oxide ion conductivity in Sillén-Aurivillius phase, bismuth niobium oxychloride (Bi_4NbO_8Cl) was studied. Although it is well-known that Bi base oxide shows high oxide ion conductivity within narrow p_{O2} range, it was found that Bi_4NbO_8Cl shows high and rather stable oxide ion conductivity over wide p_{O2} range (down to 10^{-19} atm) and doping Sr to Bi site in Bi_4NbO_8Cl is most effective for increasing oxide ion conductivity compared to all the examined dopants. The optimized oxide ion conductivity was achieved at x = 0.1 in $Bi_{4-x}Sr_xNbO_{8-\delta}Cl$. The predominant conducting species are oxide ion, as determined by AC impedance measurement, electromotive force (EMF) of gas concentration cell and the oxygen tracer oxygen diffusion measurement. Considering the activation energy of self-diffusion constant and grain conductivity, oxide ion may be mainly diffused along $[Bi2O2]^{2+}$ layer and the choline layer may interrupt the diffusion of oxide ion because of electrostatic repulsion. Oxide ion conductivity in $Bi_{4-x}Sr_xNbO_{8-\delta}Cl$ could be two dimensional, however, Cl^- layer in Sillén-Aurivillius phase may contribute the increased stability in reducing atmosphere. This study reveals that Bi_4NbO_8Cl is a new family of oxide ion conductor and the oxide ion conductivity in Sr doped sample is comparable with that in LSGM.

In Chapter 3, conductivity in Sillén phase based, lead bismuth oxychloride ($PbBiO_2Cl$) was also studied. From the detail study on doping various cation, it was found that a double doping of bismuth site with an alkaline earth and an isovalent cation simultaneously (Ca^{2+} and Ga^{3+}) is effective for increasing the electrical conductivity and stability. The optimized dopant was found to be 25mol% Ca and 10mol% Ga. While the oxide ion conductivity is similar to another recently reported material, $Ba_7Nb_4MoO_{20}$ (BNMO), EMF and DC-conductivity relaxation measurements suggests that oxide ion is not the major charge carrier, but more chlorine ion conductivity is recognized. The estimated oxide ion transport number is around 18% at 973 K. $PbBiO_2Cl$ appears to be a triple conductor of