# XANES studies of boron doped in $Li_2MnSiO_4$ cathode materials for lithium-ion batteries

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Rechargeable Li-ion batteries with a high energy density and more environmental benignity are in great demand, especially in the electric vehicles. Thus, novel electrode materials with high capacity have been widely investigated. $Li_2MnSiO_4$ has been expected as a promising cathode material with a high theoretical capacity of 333 mAh/g. However, $Li_2MnSiO_4$ exhibits a lower rate performance because of its low electric conductivity ($5\times10^{-16}$ S/cm) and low diffusivity of lithium [1]. Boron doping is reported to be useful to improve the electric conductivity of oxide materials [2]. In the present study, boron-doped $Li_2MnSiO_4$ ($Li_2MnSi_{1-x}B_xO_4$, $B_x$-$Li_2MnSiO_4$) was prepared by a sol-gel method and characterized by the crystal structure and coordination state of boron in the $Li_2MnSiO_4$ using XRD and B-K edge XANES.

Powders of $Li_2MnSi_{1-x}B_xO_4$ and $B_x$-$Li_2MnSiO_4$ ($x$ = 0, 0.03, 0.05, 0.10, 0.30, 0.50) were prepared by a sol-gel method. First, $Si(OC_2H_5)_4$, $C_6H_{10}O_4$, $Mn(NO_3)_2\cdot6H_2O$, $CH_3COOLi$, and $B(OH)_3$ were dissolved in an aqueous ethanol solution with a stirring. After further stirring for 24 h, the obtained suspension was kept at 80 $^oC$ to remove an excess solvent. The resulting wet gel was dried in vacuum at 50 $^oC$ overnight, followed by being ground. Finally, the dried gel powder was heated at 700 $^oC$ for 12 h under an Ar gas flow. The crystal structure for the sample powders was characterized using an XRD instrument (RIGAKU, RINT2200). B-K edge XANES spectra for $Li_2MnSi_{1-x}B_xO_4$ and $B_x$-$Li_2MnSiO_4$ were measured at BL-2 of SR Center of Ritsumeikan University. The spectra were recorded in the total electron yield (TEY) mode.

Results from XRD show that all synthesized materials are orthorhombic $Li_2MnSiO_4$. The orthorhombic structure consists of hexagonal close-packed array of oxide ions with all cations in corner-sharing tetrahedra of $O_4$ [3]. Figure 1 shows the

B-K edge XANES spectra of $Li_2MnSi_{1-x}B_xO_4$. A peak at 194 eV is attributed to four-fold boron. It shows that boron had the fourfold coordinated state in $Li_2MnSi_{1-x}B_xO_4$. Figure 2 shows the B K-edge XANES spectra of $B_x$-$Li_2MnSiO_4$. A peak at 192 eV is attributed to the threefold boron. A peak at 194 eV was observed in all samples ($x$ = 0.03 ~ 0.5). It shows that boron had a fourfold coordinated state in $B_x$-$Li_2MnSiO_4$. However, for high boron concentration of $x$ = 0.5, some threefold boron related impurities were formed.

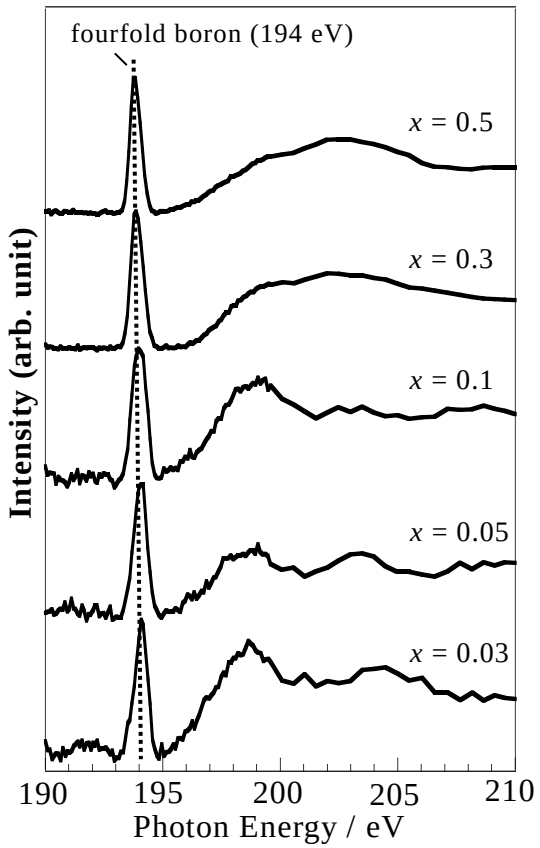


Fig.1. B K-edge XANES spectra of $Li_2MnSi_{1-x}B_xO_4$.

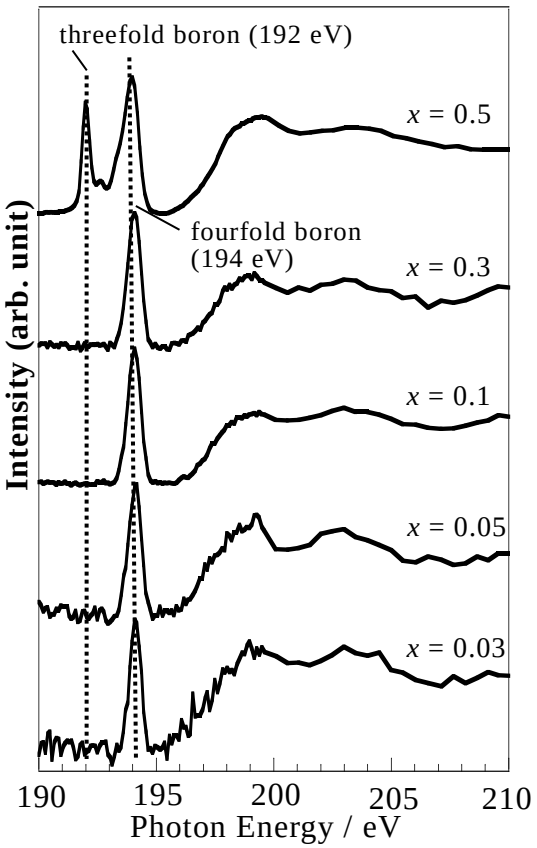


Fig.2. B K-edge XANES spectra of $B_x$-$Li_2MnSiO_4$.


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