

## Electronic state analysis of $\text{Li}_{3+x}\text{V}_{1-x}\text{Si}_x\text{O}_4$

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Currently, organic solvents are used in lithium-ion batteries as an electrolyte. However, attempts to use a solid electrolyte are proceeding from the viewpoint of safety and durability. The promising solid electrolytes are oxide and sulfide systems. This time we adopted a highly safe oxide system (LISICON), whose ion conductivity is maximized at  $x = 0.4$  to  $0.6$  [1, 2]. This may be because the interstitial lithium increases then the lithium forms a dimer. In this study, we clarified the influence of the ionic conductivity by investigating the electronic state of lithium.

$\text{LiOH}\cdot\text{H}_2\text{O}$ ,  $\text{V}_2\text{O}_5$ ,  $\text{SiO}_2$  (Aldrich) were used as a starting material for the sample preparation. First, the starting materials were weighed, pulverized in a mortar, and fired at  $850^\circ\text{C}$  for 5 hours. Thereafter, the sample was crushed again in a mortar and fired under the same condition as the first time. The finished sample was finely pulverized by grinding with a mortar and then used for measurements.

The photoelectron spectroscopy (PES) experiment was performed at the linearly polarized soft x-ray beamline BL-7 of SR center, Ritsumeikan University, using a hemispherical electron energy analyzer, SCIENTA SES2002. The measurements were performed at room temperature under ultrahigh vacuum of  $\sim 1 \times 10^{-7}$  Pa. The X-ray diffraction (XRD) experiment was performed at Ritsumeikan University. The radiation source was  $\text{Cu K}\alpha$  ( $\lambda = 0.15418$  nm).

Figure 1 shows the XRD results for each composition. From Fig. 1, it can be seen that the structures around  $22\text{-}25^\circ$  and  $33\text{-}35^\circ$  change in the case of  $x = 0.1, 0.3, 0.5$  and  $x = 0.7, 0.9$ . So it can be seen that the crystal structure is divided into two types within the range of  $x = 0.1$  to  $0.9$ . From the XRD results, we found that the samples with  $x = 0.1, 0.3, 0.5$  have the same crystal structures as  $\text{Li}_2\text{Zn}[\text{GeO}_4]$  and the samples with  $x = 0.7, 0.9$  have the same crystal structure as  $\text{Li}_4\text{SiO}_4$ .

Figure 2 shows the PES results for each composition. The  $\text{Li } 1s$  peaks around the binding energies of  $55$  eV and  $60$  eV were observed for all the samples. The previous work indicated that the impurity  $\text{Li}$  peak appears around  $55$  eV [3]. Therefore, it can be considered that the intrinsic peak for  $\text{Li}_{3+x}\text{V}_{1-x}\text{Si}_x\text{O}_4$  appears around  $60$  eV. Although the XRD results indicates the same crystal structures for  $x = 0.1, 0.3, 0.5$ , their  $\text{Li } 1s$

binding energies are different. Likewise, the same change was seen for  $x = 0.7, 0.9$ .

In this study, we have succeeded in producing LISICON, and performed XRD and PES measurements. Experimental results revealed that there was a change in the electronic states within the same crystal structure.

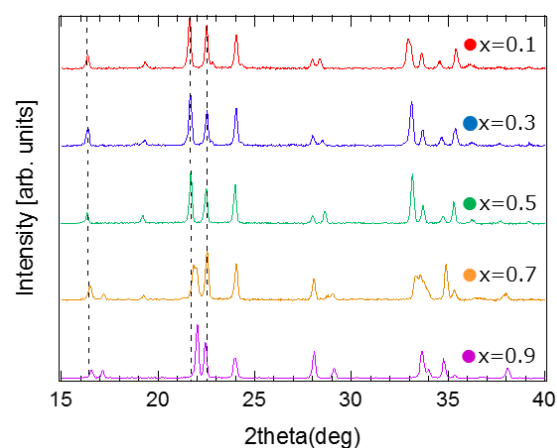


Fig. 1 Results of XRD.

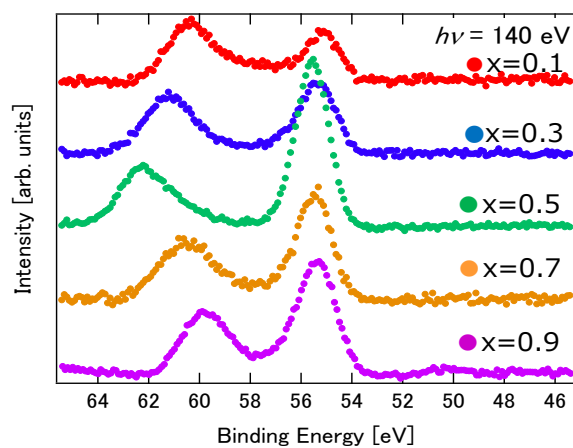


Fig. 2 Results of PES.

### References

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