Electronic Structure of Solid Electrolyte $Li_{6.5}La_3Zr_{1.5}Ta_{0.5}O_{12}$ Bulk Single Crystal Studied by Angle-resolved Photoemission Spectroscopy

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In recent years, as the use of secondary Li-ion batteries has expanded, the development of all-solid batteries using solid electrolytes has progressed to realize greater safety, wider thermal stability range, easier material handling. To understand their electronic properties and transport characteristics, the electronic structure is essentially important. However, there are few examples of experimental observations on solid electrolytes. In this study, we performed angle-resolved photoemission spectroscopy (ARPES) measurements on the lithium solid electrolytes $Li_{6.5}La_3Zr_{1.5}Ta_{0.5}O_{12}$ (LLZTO) [1] to investigate the valence band structure in relation to ionic conduction properties. Under sufficiently suppressed photon flux condition (3×10^{10} photons/s), we successfully observed valence band dispersions. From a comparison with density functional theory (DFT) calculation [2], we found qualitative similarities with the ARPES results. For example, the valence band width (~ 3 eV) of LLZTO is consistent with DFT predictions. On the other hand, the band gap observed in ARPES (3.5 eV) is smaller than that of DFT (4.5 eV), suggesting negligible correlation effects in garnet-type LLZTO. This contrasts with perovskite-type $Li_xLa_{(1-x)/3}NbO_3$ (LLNbO) and $Li_{3x}La_{2/3-x}TiO_3$ (LLTO), which exhibit a larger gap size in ARPES relative to DFT calculation [3]. Additionally, under high-flux photon irradiation condition (1×10^{12} photons/s), we observed anomalous spectral modulation over a 20-minute duration in LLZTO, characterized by a transfer of spectral weight to higher binding energies and a rigid peak energy shift. We will discuss these spectral modulations in relation to those observed in LLNbO and LLTO, where possible relation between spectral modulations and Li^+ dynamics has been expected, since the spectral modulations were not observed in the Li-free $La_{1/3}NbO_3$ [3].

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