Oxygen Vacancies in Fast Ion Conducting Lithium-Garnets

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Replacing today's liquid electrolyte Li-batteries by all solid state batteries is highly desirable to avoid safety and durability issues. The garnet $Li_7La_3Zr_2O_{12}$ (LLZO) has received a lot of attention as solid electrolyte with significant Li conductivity at room temperature in air. A typical strategy for stabilizing the fast conducting cubic phase(s) and avoiding the tetragonal phase is to add donor dopants such as Al^{3+}, Ga^{3+} or Nb^{5+}, Ta^{5+}, thus reducing Li stoichiometry. A big challenge in preparation of highly conductive LLZO ceramics is the preparation process. Relatively high temperatures are necessary but possible Li-loss requires attention to finally produce the desired LLZO composition. In most of today's research, only optimizing the cation compositions is attempted for improving the conductive properties of LLZO, while oxygen anion stoichiometry is considered to be fixed at exactly 12 oxygen atoms per formula unit. In this contribution we show clear evidence that in contrary to this assumption, oxide anion defects do indeed exist in LLZO. Consequently their contribution as donor dopant to the total defect chemistry of LLZO and the lattice related implications of oxygen vacancies require attention.

Oxygen isotope exchange and subsequent SIMS 3D profiling is used as technique to investigate oxygen anion defects. Several different compositions including single crystals and polycrystals of Al, Ga, and Nb doped LLZO were investigated. Mobile oxygen vacancies were found in all investigated samples. Surprisingly, very high oxygen diffusion coefficients up to ~10^{-11} cm/s were measured at temperatures of 350°C. This temperature was chosen because LLZO remains unchanged compared to room temperature until 350°C according to thermogravimetry measurements. The impact of oxygen vacancies on the Li^+ stoichiometry at room temperature as well as the effects on the crystal structure is discussed.