Investigating $\text{H}^+$/Li$^+$ exchange in cubic LLZO garnets: Spatially resolved H-determination using LIBS

S. Smetaczek$^1$, V. Zeller$^1$, D. Rettenwander$^2$, S. Ganschow$^3$, S. Berendts$^4$, J. Fleig$^1$ and A. Limbeck$^1$

$^1$Institute of Chemical Technologies and Analytics, TU Wien, Vienna, Austria
$^2$Institute for Chemistry and Technology of Materials, TU Graz, Graz, Austria
$^3$Leibniz-Institut für Kristallzüchtung, Berlin, Germany
$^4$Institute of Chemistry, TU Berlin, Berlin, Germany

*Mailing Address: stefan.smetaczek@tuwien.ac.at

ABSTRACT

With next generations battery concepts such as aqueous Li-O$_2$ cells in mind, stability in aqueous/moisture environment is a critical material property for solid electrolytes. Cubic Li$_7$La$_3$Zr$_2$O$_{12}$ (LLZO) garnets show many promising characteristics for application in future Li-ion batteries, like suitable Li-ion conductivity and stability against metallic Li, however, they are known to exhibit $\text{H}^+$/Li$^+$ exchange in contact with water [1, 2]. Despite a lot of research focusing on that topic, many aspects such as the extent and rate of the proton-exchange is still an unsettled matter [3]. In order to truly understand this phenomenon as well as its impact on possible applications of LLZO, detailed information about the exact H-uptake is necessary.

In this work, we present a method for the spatially resolved H-determination within LLZO garnets. Laser induced breakdown spectroscopy (LIBS) was used to conduct depth-profiling experiments on various LLZO samples, including poly- as well as single crystals. $\text{H}^+$/Li$^+$ exchange caused by immersion in different aqueous media like distilled water and diluted hydrochloric acid was investigated, confirming significant H-uptake during treatment with protic solvents.

Keywords: LLZO, garnet, $\text{H}^+$/Li$^+$ exchange, stability, LIBS, depth-profiling, single crystal

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