

Synthesis of Coarse-grained Garnet-type Li-ion Conductor $\text{Li}_{7-3x}(\text{Al}/\text{Ga})_x\text{La}_3\text{Zr}_2\text{O}_{12}$ and its Li-ion Dynamics

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Li-stuffed oxide garnets containing more than three Li cations per formula unit attract huge interest as they show a high Li-ion conductivity making them ideal candidates to design all-solid-state Li-ion batteries [1, 2]. Among this group, the garnet of nominal composition $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) is one of the most promising materials. Pure LLZO has a tetragonal structure and shows conductivities of approximately $10^{-6} \text{ S cm}^{-1}$ [3]. The incorporation of certain cations such as Al^{3+} [3, 4], Fe^{3+} [5] or Ga^{3+} [6] stabilizes the cubic LLZO phase, which crystallizes in the space group $Ia-3d$ with $a_0 \approx 12.97 \text{ \AA}$. The cubic form shows a high ion conductivity in the order of $10^{-4} \text{ S cm}^{-1}$ [3, 7].

Long-range ion dynamics as well as electrochemical properties of LLZO are influenced by the size and the morphology of the garnet crystals and their grain boundaries. Therefore, large grains and dense samples are needed to improve the total Li-ion conductivity. The grain size of LLZO prepared by conventional solid state synthesis is influenced by several parameters such as particle size of the reagent, Li content and sintering temperature [7]. We improved existing preparation routes and developed a method for the synthesis of dense LLZO samples with grain sizes of up to several hundreds of micrometres (see Figure 1a). So far, the samples have been investigated by Li NMR spectroscopy and give rise for fast Li-ion dynamics (see Figure 1b).

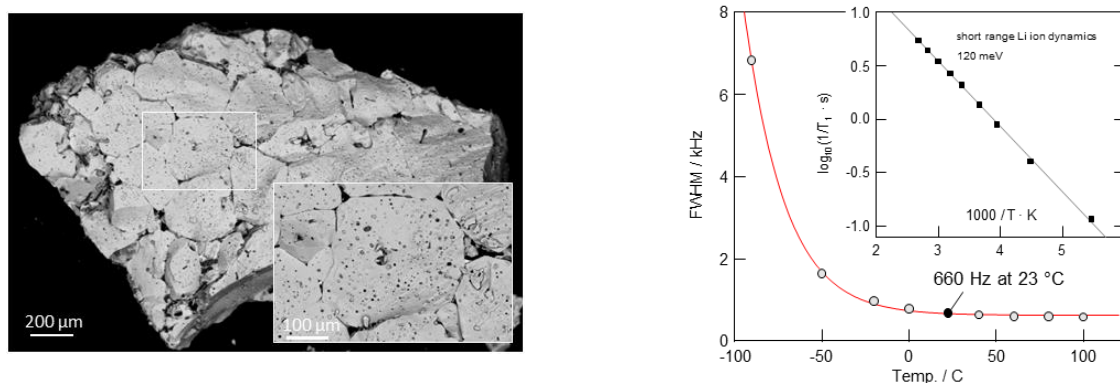


Figure 1a (left): SEM Image of $\text{Li}_{6.4}\text{Ga}_{0.2}\text{La}_3\text{Zr}_2\text{O}_{12}$; Figure 1b (right): ^7Li NMR line widths and preliminary diffusion-induced spin-lattice relaxation rates of $\text{Li}_{6.4}\text{Ga}_{0.2}\text{La}_3\text{Zr}_2\text{O}_{12}$ indicating very fast Li ion dynamics

References

- [1] Cussen, E.J.; *J. Mat. Chem.* **2010**, *20*, 5167-5173.
- [2] Thangadurai, V.; Narayanan, S.; Pinzaru, D.; *Chem. Soc. Rev.* **2014**, *43*, 4714-4727
- [3] Buschmann, H.; Dölle, J.; Berendts, S.; Kuhn, A.; Bottke, P.; Wilkening, M.; Heitjans, P.; Senyshyn, A.; Ehrenberg, H.; Lotnyk, A.; Duppel, V.; Janek, J. *J. Phys. Chem. Chem. Phys.* **2011**, *13*, 19378-19392.
- [4] Geiger, C.A.; Alekseev, E.; Lazic, B.; Fisch, M.; Armbruster, T.; Langner, R.; Fechtelkord, M.; Kim, N.; Pettke, T.; Weppner, W.; *Inorg. Chem.* **2011**, *50*, 1089-1097.

- [5] Rettenwander, D.; Geiger, C. A.; Amthauer, G; *Inorg. Chem.* **2013**, 52, 8005-8009.
- [6] Rettenwander, D.; Geiger, C. A.; Tribus, M.; Tropper, P.; Amthauer, G.; *Inorg. Chem.* **2014**, in press.
- [7] Cheng, L.; Park, J.S.; Hou, H.; Zorba, V.; Chen, G.; Richardson, T.; Cabana, J.; Russo, R.; Doeff, M.; *J. Mater. Chem. A* 2014, 2, 172.