

MS13-P1 “Li₇La₃Zr₂O₁₂” garnet doped with Fe: Crystal Chemistry and possible use as a cathode material in Li-oxide batteries. Georg Amthauer, University of Salzburg, Austria
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Recent research has shown that certain Li-oxide garnets with more than 3 Li atoms per formula unit, such as Li₇La₃Zr₂O₁₂, have high-ionic conductivities, as well as good chemical and physical properties for use in solid-state batteries (see reviews of Ramzy and Thangadurai, 2010 and Cussen, 2010).

“Garnet” is the common name for a large number of natural and synthetic metal-oxide phases. Conventional oxide garnets have the general formula A₃B₂C₃O₁₂ and crystallize in the cubic space group *Ia3d*. The O²⁻ ions, in the general crystallographic positions 96h, form an oxygen-atom framework with interstices occupied by the A cations, such as Ca²⁺, Fe²⁺, Y³⁺, La³⁺ in the 8-fold coordinated position 24c (point symmetry 222), the B cations, such as Al³⁺, Fe³⁺, Zr⁴⁺, Sn⁴⁺, Sb⁵⁺, etc. in the 6-fold coordinated position 16a (point symmetry -3), and the C cations, such as Li⁺, Al³⁺, Fe³⁺, Ga³⁺, Ti⁴⁺, Si⁴⁺, etc. in the 4-fold coordinated 24d position (point symmetry -4). In addition to these cation sites, there are other interstices within the oxygen framework, which are empty in the conventional garnet structure, e.g. (i) the 6-fold coordinated 16b positions with point symmetry 32, (ii) the 6-fold coordinated 48g positions with point symmetry 2, and (iii) an additional 4-fold coordinated 96h position with point symmetry 1. These interstices can be filled by “excess” cations such as Li⁺ or H⁺ and this enables good ionic conductivity.

Murugan et al. (2007) showed, that cubic garnet of nominal composition Li₇La₃Zr₂O₁₂ (LLZO) has some of the highest ion conductivities measured to date, comparable to or even greater than those measured on other well-known fast Li-ion conductors such as Li₃N, Li-β-Al₂O₃ or LIPON. Geiger et al. (2011) reported that pure Li₇La₃Zr₂O₁₂ is tetragonal at room temperature with space group I4₁/acd and that it undergoes a phase transition to the cubic phase between 100 and 150 °C and that small amounts of Al³⁺ in the garnet structure stabilize the cubic phase to low temperatures. In the cubic phase, La³⁺ ions occupy the positions 24c, Zr⁴⁺ ions the positions 16a, and Li⁺ ions 2 different sites: 24d with an occupancy of about 0.33 and 96h with an occupancy of 0.28.

In our study, Fe in both oxidation states was incorporated in Li₇La₃Zr₂O₁₂ in order to investigate its crystal chemistry and phase stability upon changes in Fe content. Samples were synthesized at controlled oxygen fugacity using sintering techniques and characterized by XRD and SEM. The oxidation state and site distribution of Fe is being studied with Mössbauer spectroscopy. A goal of this work is to develop LLZO garnets doped with Fe²⁺ and Fe³⁺ as cathode materials for batteries.

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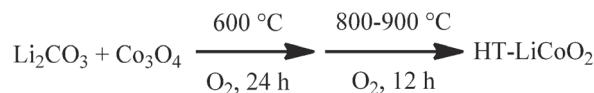
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MS13-P2 LiCoO₂: from the precursors to the oxide. Jean-Pierre Brog, Aurélien Crochet, Katharina M. Fromm. University of Fribourg, Chemistry Departement, Chemin du Musée 9, 1700 Fribourg, Switzerland.
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High-Temperature Lithium cobalt oxide is currently one of the most common compounds used for secondary lithium ion batteries. Its industrial synthesis requires long and high energy demanding heat treatments.[1]



In order to decrease the necessary time, the energy and by extension the manufacturing cost of this cathode material, a new way for the formation of lithium cobalt oxide has been investigated. This new way is based on the formation and the combustion of pre-organized complexes using O-donors ligands such as aryloxides and alkoxides.



Different precursors have been successfully synthesized.[2] The total time of preparation has been reduced to less than 12 h and the temperature required has been lowered to 450 °C. Finally, it has been found that the size of the particles could be tuned to nanoscopic scale, which improves the discharge capacity and the rate capability.[3]

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Keywords: bimetallic clusters; heavy metal oxides; lithium batteries.