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Disorder in $LiMn_2$-$xTixO_4$ determined from combined diffraction and XAS studies

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Spinel type lithium metal oxides are attractive cathode materials for rechargeable lithium ion batteries. In particular, LiMn2O4 was considered a promising cathode material as it is relatively cheaper, environmentally more friendly and safer to operate than the widely used LiCoO2. Doping of LiMn2O4 with tetravalent titanium was reported to increase the stability of the structure. The presence of Ti4+ is able to suppress the Jahn-Teller effect of Mn3+ resulting in a more stable spinel framework and therefore, the cycling ability is significantly improved. In addition, a recent study on nanophase LiMnTiO4 showed that capacities up to 290 mA h g-1 are achievable, rendering the material a very attractive electrode material indeed [1].

This presentation focuses on the structural investigation of LiMn2-xTixO4 as prepared through solid state syntheses employing different heating and cooling regimes [2]. The phase behaviour of quenched and slowly cooled LiMn2-xTixO4 was confirmed through variable temperature synchrotron X-ray and neutron powder diffraction measurements. The distribution of Li between tetrahedral and octahedral sites was determined from diffraction data. Due to their very similar X-ray scattering factors, however, analysis of the Mn/Ti distribution in addition required Mn and Ti K-edge X-ray absorption near edge structure spectra. These revealed, e.g. for the x = 1 member, the presence of Mn3+ in primarily octahedral and Ti4+ in octahedral and tetrahedral environments, with very slight variations depending on the synthesis conditions. Magnetic measurements indicated the dominance of antiferromagnetic interactions in both the slowly cooled and quenched samples below 4.5 K.

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