XRD total scattering and pair distribution function (PDF) measurements on $LiNi_{0.5}Mn_{1.5}O_4$ spinel

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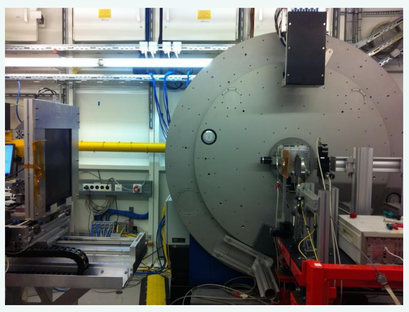
Introduction

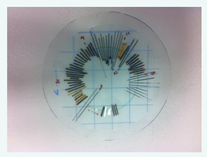
The knowledge about the local arrangement of the atoms in Li-ion battery materials is of central importance since it is correlated to parameters like capacity, rate capability, reversibility and life time. For this purpose the Pair Distribution Function (PDF)/Total scattering method is used to obtain information about the structural arrangement and about the disorder or local ordering that occurs due to (de)intercalation of lithium, which is correlated to degradation and fatigue in Li-ion battery materials. The PDF analysis/Total scattering technique, gives information about the local atomic arrangement in materials as well as the long range (average) structure. It mainly gives the probability of finding any two atoms at given distance "r" and it can be considered as a bond length distribution

The spinel $LiNi_{0.5}Mn_{1.5}O_4$ cathode shows impressive electrochemical performance like large reversible capacity at high operating voltage around 4.7 V which makes it a promising and suitable cathode material for high energy battery applications [1]. In this material all the Mn is expected to be in Mn^{4+} form, not Mn^{3+}, which is well-known as Jahn-Teller ion causing structural instability. But usually small amounts of Mn^{3+} remains as a result of oxygen deficiency after the high temperature synthesis process [2]. In this study the $LiNi_{0.5}Mn_{1.5}O_4$ samples were synthesized by a citric acid-assisted sol-gel method using metal acetates as precursors at different re-annealing temperatures. The effect of temperature on the structure of the material has been studied with pair distribution function (PDF) analysis.

Experimental Details



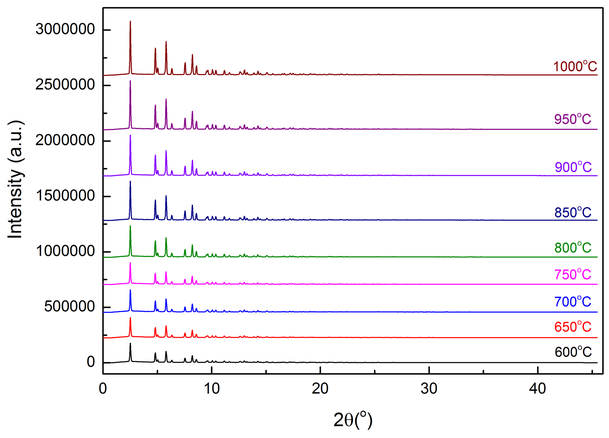
Experimental Setup at Petra III (P02.1)



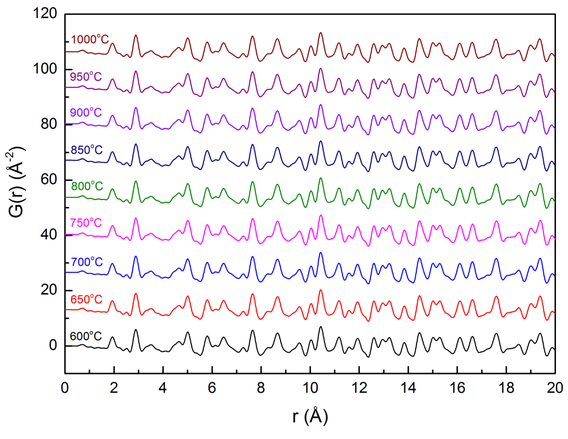
Capillary holder

X-ray diffraction experiments were carried out at the High Resolution Powder Diffraction beamline (P02.1) at PETRA-III, DESY, using X-rays with an energy of 60 keV (λ=0.20726 Å). The 2D diffraction patterns of $LiNi_{0.5}Mn_{1.5}O_4$ samples in kapton capillary (0.0403") are recorded on the flat panel detector (Perkin Elmer) in 2 min. and the sample-detector distance was approximately 400mm. The max. Q-value was about 24 $Å^{-1}$.

Results

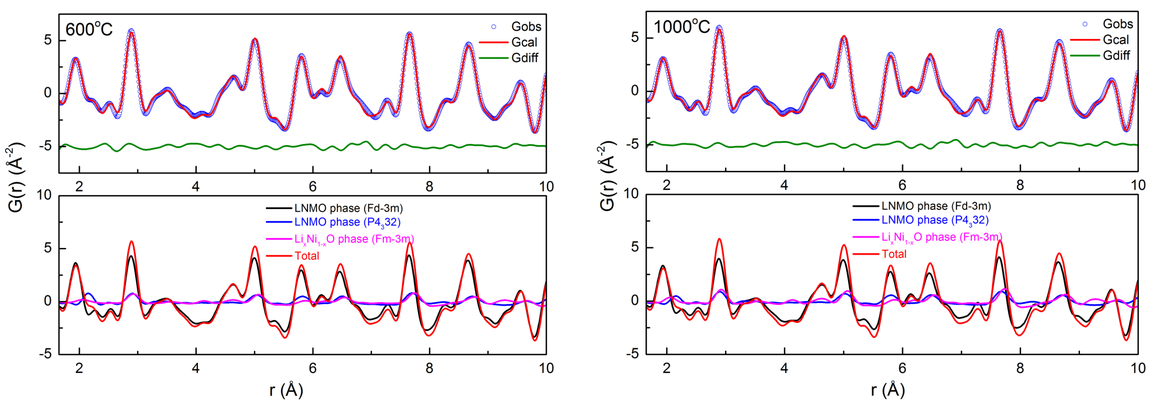


The X-ray diffraction patterns of $LiNi_{0.5}Mn_{1.5}O_4$ at different reannealing temperatures



Experimental PDFs of $LiNi_{0.5}Mn_{1.5}O_4$ samples at different reannealing temperatures.

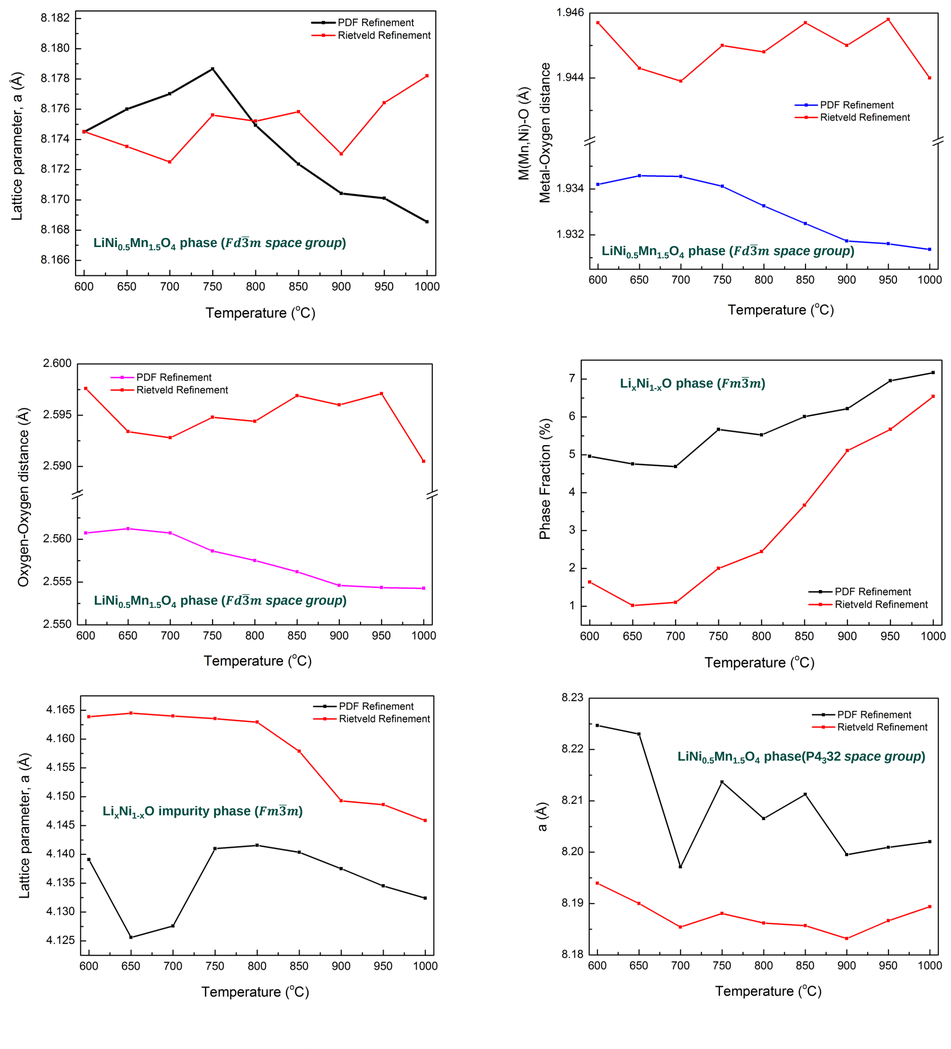
- The program Fit2D was used to convert 2-D images to 1-D diffraction patterns using cake integration. The sample-detector distance, beam center position and tilt angles of the detector were calibrated using LaB_6.
- Using the PDFgetX2 program, standard data corrections were implemented including subtraction of background scattering, sample absorption, multiple scattering, X-ray polarization, unwanted Compton intensity and then the PDFs were obtained. The obtained experimental pair distribution functions G(r) were refined and modeled in real space using PDFGui software. During the PDF refinement, instrumental parameter values (Q_{damp} and Q_{broad}) were used that were determined from the refinement of the standard material LaB_6 in PDFGui software.



PDF refinements and PDFs of individual phases of $LiNi_{0.5}Mn_{1.5}O_4$ samples at 600°C and 1000°C reannealing temperatures.

Temperature (°C)	600	650	700	750	800	850	900	950	1000
Particle size (Å)	583	567	592	650	830	2598	2220	2118	3374

Particle size of $LiNi_{0.5}Mn_{1.5}O_4$ samples at different reannealing temperatures from Rietveld refinement.



PDF refinement results of $LiNi_{0.5}Mn_{1.5}O_4$ samples

Conclusion

The $LiNi_{0.5}Mn_{1.5}O_4$ samples show three phases, $\boldsymbol{Fd\bar{3}m}$ (spinel ordered phase), $\boldsymbol{P4_332}$ (spinel disordered phase) and $\boldsymbol{Fm\bar{3}m}$ ($Li_xNi_{1-x}O$ impurity phase). The samples are reannelead at different temperatures for 12h to achieve high crystallinity and capacity. According to PDF refinement results, increasing the temperature up to 750°C, the cell parameter of the main phase ($\boldsymbol{Fd\bar{3}m}$) increases due to an increasing amount of Mn^{3+}, because the ionic radius of Mn^{3+} is larger (0.645 Å in the high spin state) than Mn^{4+} (0.53 Å) [3]. When the temperature is further increased, the amount of impurity phase ($Li_xNi_{1-x}O$ with a rocksalt structure) grows [1]. The appearance of this phase with Ni^{2+} reduces the amount of Mn^{3+} which results in a decreasing lattice parameter of the main phase.

Acknowledgement

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References

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