KINETIC AND MAGNETIC STUDIES OF THE PHASE SEPARATION IN Li$_x$FePO$_4$ MIXED CRYSTALS

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In the last years, the development of novel materials for battery applications on lithium-basis has achieved great progress. Among them, LiFePO$_4$ is one of the most prominent and promising compounds[1]. The phase behaviour of the mixed system LiFePO$_4$ - FePO$_4$ is controversially discussed in the literature. There are different phase diagrams reported by Delacourt et al.[2] and Dodd et al.[3].

Time-resolved X-ray diffraction(F1 HASYLAB) was used to investigate the kinetics of phase separation in polycrystalline Li$_x$FePO$_4$ samples which were quenched from the homogeneous phase to lower temperatures. LiFePO$_4$ was synthesized via solid-state reactions according to Lee et al.[4]. For the preparation of mixed crystals with different concentrations of lithium we used the chemical delithiation route proposed by Dodd et al.[3]. On quenching from 380°C (homogeneous phase) to ageing temperatures around 100°C, we observed that the structural features of the formation of the two product phases LiFePO$_4$ and orthorhombic FePO$_4$, i.e. the splitting of selected Bragg reflections, appear on a time-scale of hours.

Figure 1 shows the time-evolution of the degree of decomposition in Li$_{0.5}$FePO$_4$ after quenching from 380°C to 150°C. Interestingly, there are some indications for a two-step demixing mechanism, which are similar to the findings in the silver-alkali halide systems [5].

![Figure 1. Time-evolution of the degree of decomposition in Li$_{0.5}$FePO$_4$ after quenching from 380°C to 150°C](image)

The kinetic behaviour seems to vary strongly with the ageing temperatures. In the case of quenching to temperatures lower than 50°C, no significant splitting of Bragg reflections is observed. Hence, the homogeneous phase may be stabilised by quenching to sufficiently low temperatures. A tentative TTT-Diagram of Bragg splitting is given in Fig. 2. The splitting of selected Bragg reflections appears on a time-scale of hours and depends strongly on the ageing temperatures.

We have tested the magnetic properties of our samples by SQUID-magnetometry. The mixture of pure compounds (LiFePO4 and FePO4) exhibits the known temperature dependence of the susceptibility with ordering temperatures of 122 K (FePO4) and 52 K (LiFePO4) as shown in Fig. 3. Also shown in the bottom part of this figure is the behaviour of a sample that was quenched from the homogeneous phase to
low temperatures. Obviously, the Curie temperature is shifted to about 90 K and no indication for another transition is observed.

Fig. 2: TTT-diagramm from Bragg splitting

Figure 3. Magnetic susceptibility of mixed crystals

References