

A Fe-XANES STUDY OF AMORPHOUS ANALOGS OF PHOSPHO-OLIVINES Li_xFePO_4

M. Wasiucinek*, R. Bacewicz, J. Antonowicz, J.E. Garbarczyk, and P. Józwiak

Faculty of Physics, Warsaw University of Technology, Koszykowa 75, 00-662 Warsaw, Poland

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* e-mail: mwas@mech.pw.edu.pl

In recent years crystalline phospho-olivines LiFePO_4 have attracted much interest of many scientific and R&D groups worldwide as very promising cathode materials for Li-ion batteries [1]. Their performance in batteries is comparable to that of LiCoO_2 used in commercial cells, but they are safer, less toxic, more stable and much cheaper than the latter and therefore have a potential to replace them in the near future. The only major problem with olivines is their low electronic conductivity at room temperature. One of the possible solutions to this problem is nanocrystallization of the amorphous analogs of crystalline olivines [2].

A number of studies have shown that the electrical conduction phenomena in olivines depend much on their local structure and relative population of aliovalent Fe^{2+} and Fe^{3+} sites. XANES is an adequate tool to probe the local order around Fe ions and valence states of these ions. It is especially effective when used in conjunction with other methods.

A series of glassy analogs of phospho-olivines of the general formula Li_xFePO_4 , where $0 \leq x \leq 1$, were prepared by a standard melt-quenching method [2]. The samples were characterized using a number of techniques: impedance spectroscopy, differential thermal analysis DTA, chemical analyses by ICP. The ICP analyses showed a slight deviation of the actual chemical composition from the nominal one.

Several compositions, corresponding to $x = 0, 0.4, 0.8$ and 1 were studied by XAFS spectroscopy (at K-absorption edge of iron) at the A1 station in HASYLAB in Hamburg. Samples were characterized, not only in their "as-received" form, but also after heat treatment at temperatures 510–530°C. At these temperatures, determined by DTA, the nanocrystallization of the glassy samples took place. Our studies have shown that the annealing at such conditions leads to appearance of crystalline grains, not exceeding 100 nm in size, embedded in the glassy matrix.

A XANES part of X-ray absorption spectra for as-received samples Li_xFePO_4 with intermediate lithium contents ($x = 0.4$, Fig. 1a) consists of a pre-peak with a maximum at 7112.8 eV containing a shoulder at 7111 eV, and an absorption edge with the mid-point at ca 7119 eV. After the annealing, the height of the prepeak decreases and more clearly is visible its complex structure. The peak consists of two overlapping contributions from Fe^{2+} and Fe^{3+} central ions. The

absorption edge does not shift following the annealing (Fig. 1a).

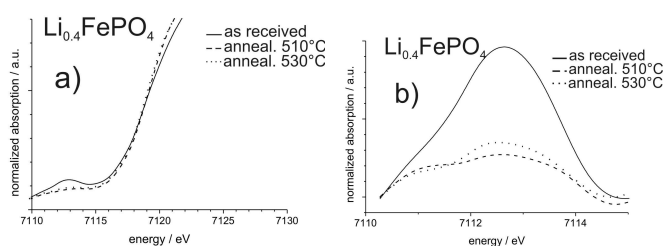


Figure 1. Fe K-edge X-ray absorption spectra of samples $\text{Li}_{0.4}\text{FePO}_4$: a) prepeak and absorption edge, b) close-up of the prepeak.

The observed change in the relative sizes of two components of the prepeak (*i.e.* centred at 7111 eV – Fe^{2+} , and at 7112.8 eV – Fe^{3+}) after the annealing, indicates that the relative populations of Fe^{2+} and Fe^{3+} sites become comparable to each other. Such a situation is advantageous for the electrical conduction via a small-polaron hopping mechanism. Since the subsequent hops of a small polaron occur between aliovalent $\text{Fe}^{2+}/\text{Fe}^{3+}$ sites, comparable concentrations of these sites should lead to higher values of the overall electrical conductivity. Our conductivity measurements have indeed shown that the annealing leads to an increase in electrical conductivity [2].

Summarizing, the XANES spectra have confirmed that the conductivity increase of the samples annealed at 510–530°C can be explained by a change of relative populations of $\text{Fe}^{2+}/\text{Fe}^{3+}$ sites.

Further studies on correlations between XANES spectra and results of other investigations of the amorphous analogs of olivines are in progress.

References

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