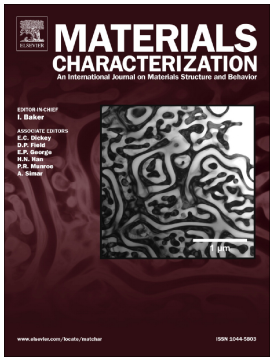

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TEM studies on thermally nanocrystallized vanadium-containing glassy analogs of $LiFePO_4$ olivine

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Abstract

Three series of glasses of the Li_2O-FeO-V_2O_5-P_2O_5 system were thermally nanocrystallized. and their microstructure was studied, at a nanometer resolution by transmission electron microscopy (TEM). Those observations were complemented by DTA and XRD studies on the same materials. It was shown that appropriate heating of the as-received glasses leads to formation of crystalline nanosize grains embedded in the glassy matrix. Average size of those grains reached even a few nm, was much smaller than that reported for $LiFePO_4$-based nanostructured materials obtained by other methods. The crystal structure of most nanograins was identified as that of the $LiFePO_4$ olivine, but some grains of the Nasicon-like $Li_3V_2(PO_4)_3$ phase were also present. The presence of both phases was confirmed independently by XRD patterns. Due to small size of crystalline grains (down to ca 5 nm) the interfacial regions around them occupy an important fraction of the total volume of the material and their properties can strongly influence the effective properties of the whole material. We have postulated that the defective nature of interfacial regions leads to an increased concentration of Fe^{2+}/Fe^{3+}, V^{4+}/V^{5+} or V^{3+}/V^{4+} aliovalent pairs, crucial for a small polaron hopping mechanism of the electronic transport, and to an enhanced electrical conductivity. The presence of highly conducting interfacial regions in the system where either the glass matrix and both crystalline phases ($LiFePO_4$ and $Li_3V_2(PO_4)_3$ are very poor conductors is the main

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