NANOCRYSTALLIZATION OF GLASSES IN LITHIUM-BORATE SYSTEM

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In the electrochemical energy storage field nanomaterials have established their position as a common solution to gravimetric capacity and cyclability of a cell related problems. There is a diversity of synthesis routes to produce nanostructured materials with desirable structure and properties. Most of them usually require sophisticated devices and preparation which cannot be easily scaled to industrial needs (e.g. MBE, MOCVD) or require many time-consuming steps of synthesis in various conditions (like sol-gel method).

Some time ago, interesting compounds with the composition $LiMBO_3$ (M = Fe, Mn) have emerged as potential cathode materials for Li-ion batteries [1]. The polycrystalline samples of those have exhibited low electronic and ionic conductivity which has led to insufficient gravimetric capacity and cyclability. Herein, we present our recent results of studies on selected physical properties of compounds obtained by thermal nanocrystallization of $LiMBO_3$ glasses. Previously, we have successfully applied this method e.g. in case of $LiFePO_4$-like system: Li_2O–FeO–V_2O_5–P_2O_5. The heat-treated materials exhibited an advantageous microstructure and significantly enhanced electric conductivity (up to 10 orders of magnitude!) [2].

In this work, $LiFe_xMn_{1x}BO_3$ (x = 0, 0.25, 0.5, 0.75, 1) glasses were successfully synthesized and subsequently nanocrystallized. Glasses were obtained using melt-quenching method and characterized with thermal (DTA), structural (XRD, SEM) and electrical (IS) methods. Also nuclear magnetic resonance (NMR) was used to study the local environment of lithium ions. Manganese-rich samples exhibited better glass-forming properties, but the increase of electric conductivity after nanocrystallization was modest and the final conductivity was quite low. Addition of iron led to better conductivity and higher increases after nanocrystallization, but caused worse glass-forming properties. The dependencies of log(conductivity) and the activation energy on composition were linear (Fig. 1). These interesting results may be explained on the basis of Mott's theory of electron hopping. Also, by NMR and SEM methods, the presence of two lithium environments were proposed.

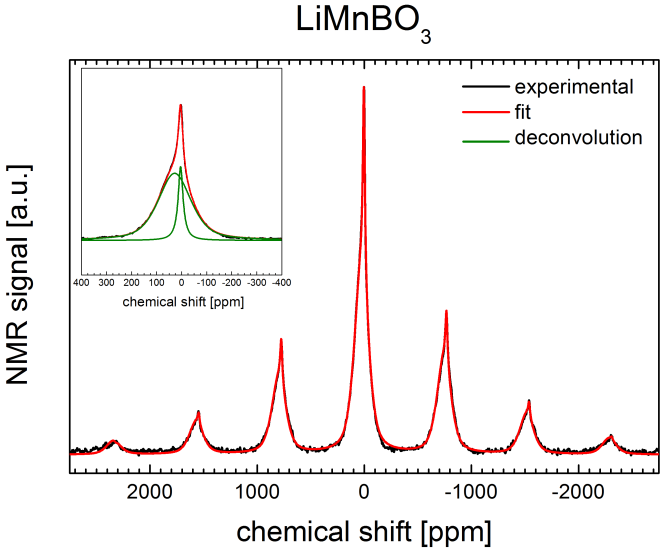

Fig. 1. Experimental (black line) and best-fit simulated (red line) 1D ^{7}Li MAS NMR spectrum of the initial glass (black line) at 1.9 T with a MAS frequency of 30 kHz. The inset shows an expansion of the central transition. The simulated ^{7}Li spectrum is the sum of two distinct lineshapes (displayed as olive lines in the inset).

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