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Novel nanocrystalline mixed conductors based on $LiFeBO_3$ glass

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ABSTRACT

Novel nanocrystalline mixed conductors were obtained by thermal nanocrystallisation of lithium–iron–borate glasses (nominally $LiFeBO_3$) prepared via melt-quenching method. After heat treatment, a glass–ceramics consisting of $FeBO_3$ and $LiFeBO_3$ phases was obtained. Grain sizes, estimated using Scherrer formula, were 45–50 nm and 70–80 nm, respectively. Value of electrical conductivity of the initial glass was estimated as $5.8{\cdot}10^{-12}$ S cm^{-1}. After annealing at 475 °C, a growth by a factor $2.4{\cdot}10^{6}$ was observed, leading to final conductivity value $1.4{\cdot}10^{-5}$S cm^{-1} at room temperature. The activation energy of electronic conductivity was lowered from 0.81 eV for glass to 0.18 eV for thermally treated material.

1. Introduction

Due to their high gravimetric energy and power, lithium ion (Li-ion) batteries are preferred energy sources for mobile devices and electric cars. Cathode performance and its production costs are the biggest bottlenecks in Li-ion technology development. Therefore, there is a high need for novel and inexpensive cathode materials. Lithium iron borate ($LiFeBO_3$) is one of the potential candidates. Due to low molar mass of the borate group, its gravimetric capacity reaches 220 mAhg^{-1} with one lithium ion exchanged. Also, thanks to high abundance of the substrate elements in Earth's crust, the material can be produced at low cost; it is also environmentally benign. On the other hand, $LiFeBO_3$ exhibits low electronic conductivity – when prepared in polycrystalline form, the value is $3.9 \cdot 10^{-7}$ S cm^{-1} [1], which is too low to obtain high current rates in Li-ion battery. It is also known that electrochemical performance of $LiFeBO_3$ is strongly reduced for grain sizes bigger than 100 nm [1].

Here, we would like to propose a novel method of materials' preparation, based on thermal nanocrystallisation of initially amorphous precursors. This method allows to obtain materials with highly enhanced conductivity and nanometric-sized grains. Recently, we have successfully applied this approach in case of cathode-like V_2O_5–P_2O_5 [2], LiF–V_2O_3–P_2O_5 [3] and Li_2O–FeO–V_2O_5–P_2O_5 [4] systems. In the latter case, the material with final conductivity value of 10^{-3} S cm^{-1} and microstructure consisting of 3–5 nm grains of $LiFePO_4$ olivine was obtained.

Inspired by previous results, we are determined to study other glass systems. A proposed borate system seems to be an ideal candidate for investigations because of a few reasons. First of all, boron (III) oxide is a good glass-former 5]. Also, boron-related materials are good Li^+ conductors, which allows their use as electrolytes (e.g. LIBOB salt [6]), glassy coatings on cathode materials providing better electrochemical efficiency [7] or as glassy cathodes exhibiting high performance itself [8].

2. Experimental

Glasses of nominal composition $0.25Li_2O \cdot 0.5FeO \cdot 0.25\ B_2O_3$ ($LiFeBO_3$) were prepared. Starting reagents: Li_2CO_3 (Aldrich, 99.9%), $FeC_2O_4 \cdot 2H_2O$ (Aldrich, 99.9%) and H_3BO_3 (Aldrich, 99.5%) were mixed and homogenised in Retsch planetary mill (400 rpm, 20 min). The obtained batches were melted for 10 min in furnace preheated to temperatures in 1000–1250 °C range. Double crucible method [9] was used to prevent iron oxidation. The melted batches were rapidly poured on a metal plate and quickly pressed with another metal plate (melt-quenching method.

X-ray diffractometry (Phillips X'Pert Pro with Bragg–Brentano configuration, using Cu$K\alpha$ line with $\lambda = 1.5406$ Å) was used to verify the amorphousness of obtained samples and for temperature-dependent investigations. In the latter case, Anton Paar HTK-1200 oven was used and the measurements were conducted in nitrogen flow. The temperature was stabilised for 40 min before each measurement.

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Temperatures of glass transition and crystallisation were obtained using differential thermal analysis method. TA Instruments SDT Q600 instrument was used. Measurements were performed with 1C min^{-1} and 10C min^{-1} heating rates, in argon flow.

Electrical properties were studied *in situ* during temperature ramps, using Solartron 1260 Gain Phase/Impedance Analyzer integrated with a furnace and a temperature programming module (Eurotherm 2404). Before each measurement, the temperature was stabilised for 40 min. Maximum temperatures were chosen in 400–500 °C range. Impedance spectra were collected in the 10 mHz–10 MHz frequency range for each temperature in the ramp. The applied voltage amplitude was equal to 0.1 V.

3. Results and discussion

3.1. XRD of as-prepared samples

For all melting temperatures in the investigated range, the materials obtained after quenching were amorphous with small traces of non-stoichiometric Fe_3O_4 phase (Fig. 1). The best match was obtained for $Fe_{2.897}O_4$ phase (PDF-2 reference code: 01-086-1337, later referred as Fe_3O_4). The amount of this phase decreased with increasing melting temperature. This was the reason why the material obtained by melting at the highest temperature (1250 °C) was chosen for further studies. The existence of non-stoichiometric Fe_3O_4 phase is also an indication of presence of Fe^{2+} and Fe^{3+} ions in glass, which are relevant for electronic hopping conductivity.

3.2. DTA of as-prepared samples

DTA curves obtained for 1 °C min^{-1} (blue) and 10 °C min^{-1} (red) are typical for glassy materials (Fig. 2) and consist of glass transition step which is interpreted as a change of heat capacity during devitrification, followed by a few exothermic peaks which may be attributed to crystallisation of different phases. The characteristic temperatures were collected in Table 1.

For lower rates, the transitions were less pronounced and the temperatures could be only estimated. This fact can be explained by the nature of DTA experiment, where the heat difference between analyzed and reference sample is measured. This difference can be written as follows:

$$\frac{dQ}{dt} = \frac{dQ}{dT}\frac{dT}{dt} = c_p\frac{dT}{dt}$$

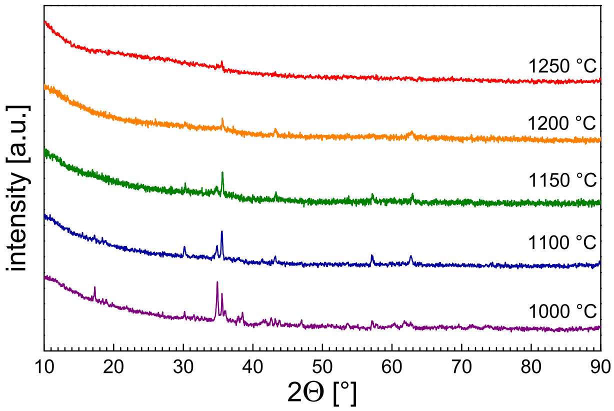

Fig. 1. X-ray diffractograms of glasses prepared with different temperatures of melting (shown on the right).

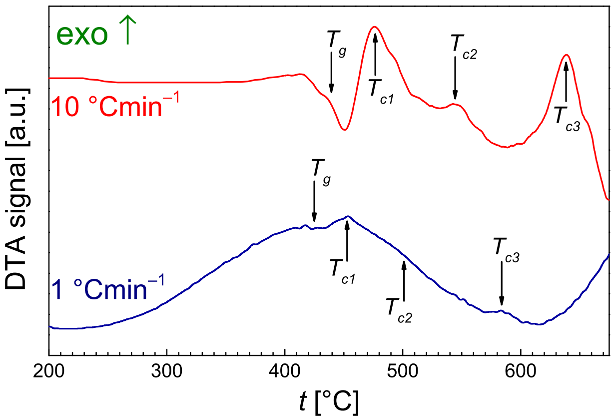

Fig. 2. DTA curves collected with heating rates 10 °C min^{-1} (red) and 1 °C min^{-1} (blue). Characteristic thermal events are marked by arrows. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

where c_p is the heat capacity of the material. Assuming c_p constant in current temperature, one can see that the heat difference dQ/dt is proportional to heating rate dT/dt.

3.3. Temperature XRD investigations

The results of XRD temperature-dependent measurements are presented in Fig. 3. Due to existence of small Fe_3O_4 inclusions in initial glass, this phase is the first to crystallise at temperatures in the 425–450 °C range. These are in proximity of glass transition and first crystallisation peak temperatures for low heating rate. As soon as the glass devitrifies (T_g), atoms movement is facilitated and they may form crystal structure based on initially present iron oxide units. The other phases – delithiated, hexagonal iron borate phase and monoclinic lithium iron borate phase – crystallise at ca. 525–550 °C. This temperature may be ascribed to second crystallisation peak (T_{c_2}), while the third one could be correlated with recrystallisation of lithium boron oxide ($Li_2B_4O_7$, reference code: 00-011-0408). The peak matched by this pattern firstly occurs at 525 °C at $2\theta \approx 22°$. Up to 600 °C, its intensity increases and then, for higher temperatures, decreases, to almost vanish at 650 °C.

Drawing conclusions based on DTA data collected for 1 °C min^{-1} is reasonable, because similar heating rate occurred during stabilisation of temperature in XRD measurements. The $FeBO_3/LiFeBO_3$ patterns were obtained from Crystallography Open Database [10] (COD IDs 1511131 and 1511129, respectively).

After cooling down the sample to room temperature, the grain sizes were estimated using Scherrer formula, taking into calculations the most intense peaks of $FeBO_3$ (the peaks of lithiated phase were hardly visible). The obtained result is 20–45 nm.

The intensities of peaks of $FeBO_3/LiFeBO_3$ phases in XRD data acquired during temperature-dependent measurements were relatively low, indicating slight content of these phases in obtained glass-ceramics. Therefore, in the next step, the as-prepared glass was isothermally annealed at 550 °C for 12 h (purple line in Fig. 4). The temperature was chosen as the one, at which $FeBO_3/LiFeBO_3$ peaks firstly occurred. During temperature-dependent measurements (green line), the sample was kept in one temperature for ca.

Table 1
Temperatures of characteristic thermal events.

Heating rate	T_g [°C]	T_{c_1} [°C]	T_{c_2} [°C]	T_{c_3} [°C]
1 °C min^{-1}	421	454	502	588
10 °C min^{-1}	435	476	546	639

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