	Experiment title: Structure of thin-film glassy electrolytes	**Experiment number**:
Beamline: ID01	**Date of experiment**: from: 31/1-2007 to: 5/2-2007	**Date of report**: 1/3-2007
Shifts: 15	**Local contact(s)**: Oier Bikonda	*Received at ESRF:*

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Report:

Ion conducting glasses are materials of high interest both from a fundamental point of view, e.g. for studies of charge transport in disordered media, and from an applied point of view as electrolytes in various electrochemical devices. Of particular interest is the possibility to prepare ion conducting glasses in thin-films configuration both for the potential application in micro-batteries but also since the sputtering process opens up the possibility to prepare materials outside the bulk glass-forming compositional region. Furthermore, the conductivity has been shown to depend on the sputtering conditions, e.g. it can be increased by incorporating nitrogen into the standard argon discharge gas.

In the glass structure the ion migration takes place by jumps between favourable sites in the structure that form interconnected pathways. Thus, both the short range order (1-5Å) and the intermediate range order (5-20) is of importance for the conduction process. The aim of the present experiment was to investigate the structure of thin film glassy electrolytes using wide-angle x-ray diffraction at the ID01 beam line in the $(Li_2SO_4)x$-$(Li_2O$-$B_2O_3)1$-x family (x=0-0.8). The goal was to determine how the glass structure changes both on the short and the intermediate length scale , due to the very high quenching rate in the preparation process and to investigate the influence of nitrogen in the structure.

In the initial set-up we used a grazing incidence geometry with an incidence angle of 0.5 deg. Even though this gave good signal from the films at low angles it turned out that we had a considerable contribution at higher angles from the substrate. This contribution was comparable to the signal from the film. As the substrate was single crystalline silicon wafer there should not be any contribution why the observed effect must come from surface imperfections of the substrate.

In order to overcome this problem we finally found the solution in going to very low incidence angles (<0.05 deg), below the critical angle of silicon. This procedure required very careful alignment of each sample in order to obtain conditions so that we have no or minimal contribution from the substrate. With this configuration we had only time to obtain good data on two systems: Li_2O-B_2O_3 thin films under Ar and N_2 and bulk and Li_2O-$2B_2O_3$ thin film under Ar and bulk. These systems was chosen as the salt doped samples (x>0) are slightly sensitive to ambient conditions and sample mounting in inert atmosphere would be preferred but was not available at the time. A new sample holder should be developed that could e mounted in inert atmosphere so that exposure to air could be avoided throughout the experiment.

An example of the data is shown in figure 1 where the uncorrected diffracted intensity is displayed as function of momentum transfer for the Li_2O-B_2O_3 samples. The rapid decay of the intensity at higher momentum transfers is mainly due to the form factor and geometrical effects that need to be accounted for in the data treatment. However, directly in the raw data we can observe a shift in the position of the first diffraction peak, around 1.5 $Å^{-1}$, between the bulk and the thin films. This indicates that there is a change in the intermediate range order, which can be related to the high quenching rate of the preparation method. One can also note that sputtering in N_2 does not have a significant influence on the intermediate range order, but that one can observe differences at higher Q related more to the short range order.

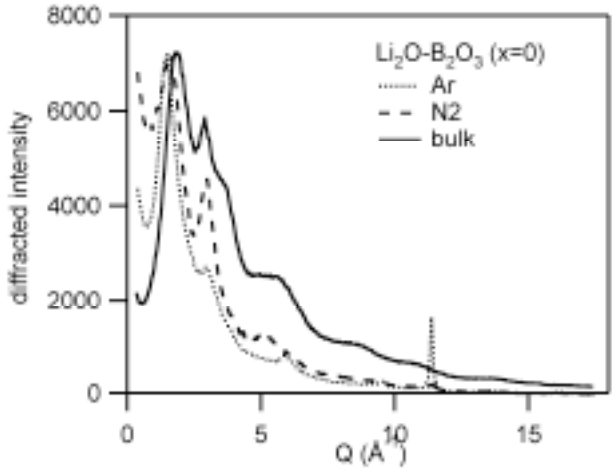

Figure 1. Diffracted intenstiy as a function of momentum transfer, Q, for the Li_2O-B_2O_3 thin film and bulk samples. The sharp feature in the Ar-sputtered thin film is a substrate contribution that could not fully be eliminated.