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ABSTRACT:

Transport of Protons in the Energy Landscape of Glasses and Crystals

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The electric field assisted ion exchange (EFAIE) is an experimental technique which allows to manipulate the physical properties of solid electrolytes, in particular near the sample surface [1]. Native alkali cations such as Na⁺ are exchanged by foreign cations introduced with e.g. sputtered/molten electrodes [1, 2]. The ion exchange can e.g. lead to strengthening of the glass surface, but also alter biophysical and optical properties [2].

The alkali proton substitution (APS) is a special form of the EFAIE, where H⁺ ions are formed at a sputtered platinum electrode and replace the native (and mobile) alkali ions [3] in electric field driven transport towards a backside electrode.

In this work, we present results of APS experiments on alkali aluminum germanium phosphate glasses (MAGP) with the general composition $M_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$ (M = Li, Na, K). ToF-SIMS concentration depth profiles recorded subsequent to the APS reveal that each glass exhibits a specific characteristic for the ion migration evolving during the APS experiment. The concentration depth profiles of the APS treated MAGP glasses have been simulated by means of the Nernst-Planck-Poisson (NPP) theory [4]. The theoretical analysis shows a pronounced concentration dependent diffusion coefficient for the alkali ions. The concentration dependence of the diffusion coefficients directly reflects the site energy distribution (SED) operative in these glasses. The important result is, that the width of the populated part of the SED varies little in going from the LAGP over NAGP to KAGP. Thus, the SED is dominated by the network former in this glass. This sets the stage for going to mixed alkali AGPs, where we probe the relevant energy landscapes of two different native alkali ions by external protons. The results are compared to a previous H₂-plasma-CAIT experiment on LAGP [5].

Finally an experiment is presented, where protons are introduced into mono-crystalline strontium titanate (STO). At the temperatures considered, STO is discussed as an oxygen vacancy conductor [6]. Here, we demonstrate that the DC conductivity of STO increases pronouncedly with increasing exposure to protons.

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