A COMBINED X-RAY DIFFRACTION AND ABSORPTION STUDY OF Li$_2$Si$_2$O$_5$ DOPED WITH VANADIUM

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Lithium-based conducting glasses are promising candidates for electrolyte materials of thin-film batteries because they exhibit isotropic ionic conductivity. However, at room temperature most of such conducting glasses exhibit relatively low ionic conductivity values, in the range $10^{-7}$ to $10^{-8}$ S/m. In order to increase the conductivity, some specific additives have been used, one of them being vanadium. In a recent work on borate glasses, vanadium dopant at a level of several percent was used for this purpose [1-3]. It has been noticed that annealing of vanadium doped borate glass results in a change of physical properties [1]. This may suggest that vanadium ions occupy specific crystallographic sites.

In this work, a related material, vanadium-doped lithium silicate glass is studied. The glass was prepared by heating a mixture of quartz (SiO$_2$), lithium carbonate (Li$_2$CO$_3$) and vanadium pentoxide (V$_2$O$_5$) at a level of up to 5.5 weight percent at 1400°C for 3 h and then cooled. As prepared glass was annealed for 4 h at 550°C. The X-ray diffraction experiments were performed at a conventional diffractometer.

The described synthesis procedure gives a virtually pure Li$_2$Si$_2$O$_5$ phase of orthorhombic Ccc2 space group [4] with vanadium present in the lattice and with traces of impurity phases. We noticed that the observed crystallisation is faster than that reported in literature for phosphate glasses [5]. Rietveld refinements were performed using various models assuming a partial occupation at Li or Si sites. The results indicate that location of vanadium at Si sites is more likely. The lattice parameters are found to vary isotropically with increasing vanadium content.

The X-ray absorption experiment was conducted at the Cemo beamline (Hasylab, Hamburg). XANES spectra at the vanadium K edge were measured at room temperature using fluorescence and transmission detection mode. In all cases, a very pronounced pre-pik was observed. According to Ref. [6], this feature indicates that vanadium atoms are in the +5 ionic state.

References