Oxygen environment in lithium borates and silicates: an X-ray Raman Spectroscopic study

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In crystalline and vitreous alkaline borates and silicates, both bridging (BO) and non-bridging (NBO) oxygen atoms are usually present, depending on their connectivity to the network. NBOs are defined as oxygen atoms bound to only one network forming cation (Si, B, P, ...) and bearing a negative charge. They are used as an indicator of the polymerization degree that impacts the physical and chemical properties of the compound. Detecting NBO in crystalline or amorphous system is especially relevant in materials science and Earth sciences. Recently, a specific signature of NBOs at the O *K*-edge spectrum in lithium borates has been evidenced by X-ray Raman Spectroscopy (XRS) measurements and validated by first-principles calculations. As silicates and borates present a similar structure for high amount of alkali, it is expected to find the NBO signature during XRS measurements on lithium silicates.

We present oxygen XRS *K*-edge spectra in alkaline borates and silicates recorded on dedicated Synchrotron beamlines. The experimental data are compared with calculated spectra thanks to the recent implementation of XRS in the module XSpectra of Quantum Espresso. The calculations, based on density functional theory, are performed on supercells in the presence of an absorbing atom obtained by removing one 1*s* core electron from its electronic configuration.

Calculations help unravelling the spectral signatures of oxygen atoms in inequivalent crystallographic sites such as BOs and NBOs. By comparison with experimental spectra, calculations allow the identification of a NBO specific peak in lithium silicates, shifted to lower energy on the oxygen *K*-edge XRS spectra. This study validates XRS as a technique that can be used to study the local structure around light-element environment in both crystalline and vitreous compounds.

The improvements of both the experimental instruments and the theoretical modelling of XRS make possible to see fine structure in the oxygen *K*-edge in alkaline borates and silicates. These spectral signatures that can be followed by *in situ* measurements, give information on the local structure and its changes under extreme conditions, as XRS is a powerful technique to carry out investigations on light element environment under extreme conditions.