Study of lithium silicates at ambient and high pressure using X-ray Raman Scattering spectroscopy

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Aim of the study

Non-bridging oxygen atoms (NBOs), which are defined as oxygen atoms bound to only one network forming cation (Si) and bearing a negative charge, ensure the neutrality of the system in crystalline and vitreous alkali silicates. Their detection is of particular interest for understanding the physical properties of melts or compressed materials, and requires an unequivocal spectral signature usable during in situ measurements, which is especially relevant to study Earth Sciences materials.

X-ray Raman Scattering (XRS) spectroscopy has already proven its efficiency to study K edges of light elements in alkali oxides and can be coupled with first-principle calculations to validate spectral signatures. This spectral signature can thus be used to follow structural changes under high-pressure measurements carried out in situ in diamond-anvil cells (DAC).

X-ray Raman Scattering (XRS)

What is XRS ?

A photon-in photon-out spectroscopy, also called Non-Resonant Inelastic X-ray Scattering (NRIXS)

A substitute for soft X-ray XAS (Z<10) under dipole approximation conditions (low value of the momentum transfer q)

NBOs spectral signature

Network depolymerisation

Structural changes in amorphous SiO2 due to the network modifier K2O

NBOs that are created during network depolymerisation processes show a different environment than BOs and can be distinguished by chemically sensitive spectroscopy.

O K edge XRS spectra at ambient pressure

An additional feature grows at 534 eV in crystalline lithium silicates, this peak is related to the appearance of NBO during the depolymerisation process. First-principle calculations were used to separate NBO and BO contributions in the crystalline compounds, showing that NBOs contributions appear below the O K edge of SiO2, which can then be used as a reference to evidence NBOs in amorphous compounds.

Behavior of v-Li2SiO3 under pressure

Si L2,3 edge and O K edge XRS spectra

Amorphous Li2SiO3 undergoes structural changes under pressure: the polymerization of the Si-O network increases due to recombination of NBOs with SiO4 units and formation of PO as shown at the O K edge. The polymerization of the network changes the silicon environment and the Si-O bond length, which explains the intensity variation of the first two peaks at the Si L2,3 edge.

The Si L2,3 and O K edges shift to higher energy under pressure as it has been previously shown for amorphous SiO2.

Influence of the network modifier

Vitreous SiO2 shows two different behaviours between 0 and 40GPa. Up to 20GPa both the Si L2,3 edge and the O K edge shift slowly to higher energies with the decrease of Si-O bond length. After 20GPa, v-SiO2 undergoes structural changes with formation of SiO2 and SiO2 units.

Vitreous Li2SiO3 follows a similar behaviour than v-SiO2 before 20GPa. Another behaviour starting around 25GPa indicates that new densification processes are then taking place.

Conclusion

X-ray Raman Scattering spectroscopy is a powerful technique to study light elements such as oxygen. Calculated spectra can help to interpret experimental data in terms of structural information about the compounds. Specific spectral signatures related to structural information can thus be used to follow structural changes during in situ measurements.

Lithium silicates are more depolymerized compounds than vitreous SiO2 but they present similar behaviour under low pressure with densification processes based on topological reorganisation of the Si-O network.

References :

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