
Evidence of phase separation phenomena in {La₂O₃ - B₂O₃- SiO₂} system by high resolution NMR spectroscopy

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Abstract

Rare-earth borosilicate glasses are of great interest for applications in many fields, including optical fibers, amplifiers and laser waveguides. Borosilicate glasses are also used widely to immobilize highly radioactive nuclear waste, because they provide high incorporation rate and good thermal stability. For all technological applications quoted previously, preventing or favoring devitrification is an important factor to produce either glasses or glass-ceramics, depending on the material function. It is therefore important to study structural modifications induced by phase separation in borosilicate networks to be able to control these phenomena.

Structural and microstructural properties of both homogeneous and phase separated lanthanum borosilicate (La₂O₃-B₂O₃-SiO₂ system) glasses were investigated. SEM, TEM and XRD analyses have been carried on to highlight the microstructure and the presence of crystalline phases for each sample.

High resolution solid state NMR has been used to probe the structural modifications induced by phase separation in borosilicate network. We observe dependence between phase separation and La₂O₃/B₂O₃ molar ratio. Phase separation occurs when this ratio is lower than 1. According to ¹¹B NMR experiments, apparition of a secondary BO₃ species towards 13 ppm is observed when glasses are phase separated. At the same way, ²⁹Si NMR MAS spectra show a progressive polymerization of the network with appearance of a new Q₄ species.

For a complete structural description, based on homonuclear NMR correlation experiments INEQUATE ²⁹Si and ¹¹B, and on heteronuclear NMR correlation experiments HMQC probing ²⁹Si/¹¹B vicinity (D-HMQC) or chemical bonding properties (J-HMQC), a description of the chemical environments modifications induced in this system in presence of phase separation will be proposed.

Keywords: Glass structure, phase separation, Solid state NMR

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