Evidence of phase separation phenomena in {La_2O_3 - B_2O_3- SiO_2} system by high resolution NMR spectroscopy

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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 (La_2O_3-B_2O_3-SiO_2 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 La_2O_3/B_2O_3 molar ratio. Phase separation occurs when this ratio is lower than 1. According to ^{11}B NMR experiments, apparition of a secondary BO_3 species towards 13 ppm is observed when glasses are phase separated. At the same way, ^{29}Si NMR MAS spectra show a progressive polymerization of the network with appearance of a new Q^4 species.

For a complete structural description, based on homonuclear NMR correlation experiments INEDEQUATE ^{29}Si and ^{11}B, and on heteronuclear NMR correlation experiments HMQC probing $^{29}Si/^{11}B$ 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.