

OH species on Crystal-Glass border in LAS Glass-Ceramics

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Li₂O-Al₂O₃-SiO₂ (LAS) ceramics is characterized by a specific two-stage ceramization process, which allows separation of the nucleation stage from that of crystal growth (e.g. Petzoldt and Pannhorst, 1991). Fujita e.a. (2003) found that IR spectra of the LAS - based glass in the region of the water-related band around 3500 cm⁻¹ changed during crystallization due to shift of the peak position towards lower wavenumber. We studied a nature of this phenomenon on glass ceramic materials produced from the same LAS parent glass under variable time-temperature conditions at the stage of crystal growth.

Parent glass which contains 55%SiO₂, 25%Al₂O₃, 6%Li₂O, 7%P₂O₅, 1,7%ZrO₂, 1,4%TiO₂, 1,4%ZnO, 1%MgO, admixtures of As, K and Na, were preheated during 15 min at nucleation temperature 760°C. From this material a series of 0,2 mm thick double-side polished platelets were prepared. One part of the platelets was heated during 30 min at different temperatures in interval 795-900°C, another part was heated at 815°C during different time (5-90 min). The materials obtained were investigated using IR transmission spectrometry, transmission electron microscopy (TEM), and X-ray diffraction methods.

TEM study confirmed development of LAS glass-ceramics with small (20-40 nm) inclusions of (Ti,Zr)O₂ phases, and variable number of larger crystals (70-500 nm). X-ray investigation allowed identifying the latter crystals as β-eucryptite LiAlSiO₄.

The IR absorption spectra were measured at room and LN temperature in the spectral range 7000-1000 cm⁻¹ by means of a Bruker FTIR spectrometer IFS 66. Spectra were scanned at a spectral resolution of 2 cm⁻¹, the signal was collected over 200 scans. Curve fitting of overlapping absorption bands was performed with the PeakFit4 program.

NIR spectra of all samples show presence of only weak band at 4500 cm⁻¹, assigned to SiOH vibration (e.g. Dawis and Tomozawa, 1996). Absence of H₂O band at 5200 cm⁻¹ prove that hydrogen is present in the form of OH groups in both unheated glass and glass ceramics formed at 800-900°C. Broad OH band near 3600 cm⁻¹ preserves its intensity, position and form during heating at 760°C, when TEM detects nucleation of Ti-Zr oxides' nanocrystals, and at further heating up to 800°C. Annealing between 800 and 830°C causes drastically shift of the OH band maximum to 3500 cm⁻¹ and changes configuration of the absorption envelope. TEM study detects growth of β-eucryptite crystals in this temperature interval. Deconvolution of the absorption envelope onto 5 components shows that its red shift in heated samples is caused by decrease of intensity of the component band at 3600 cm⁻¹ in combination with simultaneous increase of the band centred near 3500 cm⁻¹. No new bands were found in heated LAS ceramics. Correlation between intensity changes of bands at 3600/3500 cm⁻¹, and calculated total surface of eucryptite crystals in LAS ceramics leads to conclusion that observed spectral shift of OH band is caused by redistribution of the main LAS elements during eucryptite crystallization and repulsion of H from the "dry" crystals. This leads to concentration of hydrogen on the crystal-glass border, where it forms silanol groups.

References:

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