

Poster Presentation

MS48.P06

Structure investigations of nanocrystalline glass ceramics by ASAXS

A. Hoell¹, V. Raghuvanshi², C. Rüssel³

¹Helmholtz Zentrum Berlin, Microstructure and Stress Analysis, Berlin, Germany, ²Humboldt University, Institute of Chemistry, Berlin, Germany,

³Friedrich-Schiller-University Jena, Otto-Schott-Institut, Jena, Germany

Glass ceramics containing fluoride crystals such as BaF₂ or CaF₂ with crystallite sizes in the range from 5 to 100 nm are potential candidates for numerous photonic applications. Glass ceramics containing rare-earth-doped fluoride crystals are candidates for laser materials. The size distribution plays an important role and often a narrow size distribution is required for photonic applications. In the last years a hindered growth effect leading to a more narrow size distribution was observed during the crystallization of BaF₂ as well as CaF₂ nanocrystals in oxy-fluoride glasses. The aim of this study is a detailed quantitative structural and nano-chemical analysis of the formation of BaF₂ or CaF₂ in two glass ceramics by Anomalous Small-Angle X-ray Scattering (ASAXS) to reveal and understand the mechanism of hindered growth. Nanocrystals of BaF₂ precipitate during heat treatment of a silicate glass of composition 69.6SiO₂-7.52Al₂O₃-15.04K₂O-1.88Na₂O-4BaF₂-2BaO. X-ray diffraction measurement proved the formation of BaF₂ crystals in the glass matrix. High resolution TEM showed the formation of spherical particles of sizes in range from 10-40 nm surrounded by a layer enriched with SiO₂. SAXS reveal the growth of nanocrystals with increasing annealing time and temperatures. ASAXS experiments are done at four energies close to the Ba-L₃ X-ray absorption edge (5247eV). The ASAXS curves for the sample annealed at 540°C for 20h revealed a spherical core-shell model. It turned out that the layer surrounding the BaF₂ crystals is enriched with SiO₂. Sizes and compositions of these layers are analyzed quantitatively. Furthermore, the ASAXS analysis reveals the presence of very small nucleates of size of about 3 nm in the as melted glass sample already [1]. A precipitation of CaF₂ nanoparticles takes place during heat treatment of glasses of composition 7.65Na₂O-7.69K₂O-10.58CaO-12.5CaF₂-5.77Al₂O₃-55.8SiO₂ up to 40 hours. SAXS experiments and especially ASAXS near the Ca-K edge proves the formation of CaF₂ nanoparticle surrounded with SiO₂ enriched layers, quantitatively. The ASAXS effect is very pronounced at this untypical low energy for ASAXS studies at the Ca-K edge. The ASAXS result reveals crystal sizes between 10-20 nm surrounded by a shell of lower electron density. Additional very small heterogeneities are found after long annealing with diameters of about 1.6 nm [2].

[1] V.S. Raghuvanshi, A. Hoell, C. Bocker, C. Rüssel, *Cryst Eng Comm*, 2012, 14, 5215-5223, [2] A. Hoell, Z. Varga, V.S. Raghuvanshi, M. Krumrey, C. Bocker, R. Rüssel, *J Appl Cryst*, 2014, 47, 60-66

Keywords: ASAXS, glass ceramics, hindered growth process