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Crystallization of a silicate apatitic phase in a glassy matrix, an in situ Raman study.

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The containment of long-lived separated radionuclides, minor actinides, would be profitably realized in a silicate apatite glass-ceramic obtained by controlled crystallization of parent glass. Indeed, the advantages of this waste form are numerous: glasses are easily handled and processed, both the glass and the silico apatite can be used to immobilize actinides and the chemical fluctuations of the waste are absorbed in the glassy matrix. Moreover apatite type compounds have shown their ability to incorporate minor actinide surrogates (lanthanides) in a large range of composition.

However, to be of real interest such an apatite glass-ceramic need to be internally stress less and to present a good partition coefficient of the actinides between crystals and residual glass. These two last criteria meet if the formed crystals are in the bulk, highly concentrated and small in size. Therefore the ability to control the crystal nucleation and growth from the parent glass is crucial.

In this work, trivalent minor actinides were simulated introducing Nd_2O_3 in the glass composition. Intense apatite crystallization was obtained in the bulk for two alumino borosilicate glasses containing up to 15 wt.% of Nd_2O_3. The nucleation and growth process was observed on quench samples at room temperature by Raman spectroscopy, electron microscopy and X-ray diffraction (XRD). Two different behaviors were found depending of the nature of the network modifier elements in the initial glass (Ca/Na or Na). Good agreement was found between the different techniques. Raman spectroscopy was especially noticeable in the first stage of growth, due to its sensibility to small amount of crystals. It allowed also following up the evolution of

the glassy matrix during the process.

Proved to be an efficient investigation, high temperature, in situ Raman spectroscopy measurements were realized. The crystallization process was followed at a 10 minutes interval from nucleation to completion. The crystallinity evolution of the silico apatite will be presented as well as the polymerization of the residual glass. And a global mechanism of nucleation and growth will be drawn out in terms of elements diffusion. Further this structural interpretation will be confronted to differential thermal analysis studies and viscous flow experiments.