Crystal and microstructure evolution of zirconolite-based glass-ceramic for minor actinides immobilization

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Durable matrices must be developed for immobilizing minor actinides (Np, Am, Cm) due to their long term radiotoxicity in high level radioactive waste even after hundreds of years. Glass-ceramic waste form is considered as a double-barrier containment for minor actinides, where specific crystals are grown to incorporate minor actinides and also encapsulated by residual glass. For example, zirconolite-based glass-ceramic has been proposed as a candidate for minor actinides immobilization. In this work, the crystal and microstructure evolutions in CaO-SiO_2-Al_2O_3-TiO_2-ZrO_2-Na_2O glass during thermal treatment were investigated. X-ray diffraction (XRD) results show that cubic-zirconia was firstly crystallized in the initial stage of all crystallization temperatures. Electron backscattered diffraction result indicates this cubic-zirconia crystal grew in one direction and produced a dendritic microstructure. Prolonging crystallization time induced phase transformation from cubic-zirconia to 2M-zirconolite. Results from transmission electron microscopy and selected area electron diffraction found heavy stacking faults in the 2M-zirconolite crystal, and this is different from the zirconolite crystals derived from the powder sintering process. Rietveld quantitative XRD analysis shows that the amount of zirconolite is around 19 wt.% in the system, regardless crystallization temperature and time. Moreover, prolonging crystallization time also led to the formations of other crystals (anorthite and wollastonite), fractures and voids in the final products. A two-stage crystallization method was also developed to obtain different microstructures of the zirconolite-based glass-ceramic. Results of this study will facilitate the design of a more durable zirconolite-based glass-ceramic for minor actinides immobilization.