

Behavior of natural and synthesized irradiated powellite by Raman and luminescent spectroscopies

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The fission products produced during the fission reactions in nuclear plants are vitrified as final waste. Crystalline phases could form spontaneously in the nuclear glass and have to be considered in the long term behaviour of glass ceramic in nuclear waste storage conditions. For low waste loading nuclear glass (R7T7), powellite, CaMoO_4 , is the main crystalline phase. It has a $I4_1/a$ space-group symmetry and C_{4h} point-group symmetry. During its crystallization process, actinides and lanthanides derived from fission reaction are preferentially incorporated into the CaMoO_4 crystalline and substitute the Ca sites. Due to the preferential incorporation of radioactive actinides, the structure of powellite could be modified after a certain dose of self-irradiation.

Besides, natural powellite formed in U-Mo rich deposits in South Kazakhstan (Bota-Burum) under exogenic conditions during the transformation of molybdenite. They incorporated great amount of rare-earth elements and overcame long term self-irradiation (7000 ppm U). Therefore these rare samples are interesting surrogates of nuclear matrixes.

Therefore, it is important and interesting to study the behaviours (swelling, structural damage, sites modification, etc.) of powellite under irradiations for both natural and synthesized samples. Eu and Nd were incorporated as dopants into powellite to imitate the FP surrogates. External Ar-ion beam bombardment was used to simulate the internal self-irradiation. Different damage levels, in unit of displacement per atom (DPA) were selected in order to follow the evolution of structural behaviour. Natural powellite was used for comparison.

Micro-Raman spectroscopy was conducted to investigate the medium range order modification of tetrahedral powellite structure after irradiation, while photoluminescence of rare-earth elements was used as probe of the local environment distortions. According to the Group theory, all the vibration modes can be divided into 26 of species $3A_g + 5A_u + 5B_g + 3B_u + 5E_g + 5E_u$. The internal symmetric stretching $\nu_1(A_g)$ (at 878 cm^{-1}) of $[\text{MoO}_4]$ tetrahedra which is Raman active, is isolated and selected to follow the evolution of line width in function of DPA.

The broadening of the Raman vibration mode is associated with the decrease of the medium-range order induced by the accumulation of defects during the Ar irradiation. Due to the physical anisotropy of powellite, the evolutions of the line width broadening of $\nu_1(A_g)$ in two directions (*a*- and *c*-axis) are notably different. The broadening in *a*-direction becomes saturated after 1.1 DPA while that in *c*-direction continues to increase.

Since 5D_0 as well as 7F_0 of Eu^{3+} are not split by the crystal field ($J = 0$), the number of luminescent lines appearing in the emission spectrum of ${}^5D_0 \rightarrow {}^7F_0$ transition corresponds to the number of Eu^{3+} sites in the structure. Modification of sites of the powellite structure was observed by means of micro-luminescence spectrum of Eu^{3+} , which represents the local properties of rare earth elements in the crystal field. The irradiation merged the difference among the local environments and reduced the number of Eu^{3+} sites, which can be inferred from the change in ratio of lines in the ${}^5D_0 \rightarrow {}^7F_0$ transition.