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Guest ion speciation in a homogeneous solid solution by polarisation-dependent TRLFS

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The formation of solid solutions with various host minerals has recently been recognized as an effective mechanism for the retention of radionuclides released from a nuclear waste repository. However, few solid solution systems have been characterized or understood in detail. Frequently, the solid solutions do not form over the complete range of composition or the radionuclide containing end members are even unknown. Here we present our recent results on the incorporation of Gd3+ into the secondary glass corrosion product powellite CaMoO4.

Site-selective TRLFS has proven a valuable tool for the speciation of actinides and their 4f-homologues, the lanthanides. Applied to polycristalline samples it allows the determination of coordination symmetry classes as well as hydration states of the incoporated ions. Thus often times allowing to characterize the chemical and structural environment of the guest ion. When applied in a polarisation dependent fashion to single crystal samples the obtainable information can be increased even farther and point group accuracy can be achieved.

In this study we characterize the solid solution Ca2(MoO4)2 - NaGd(MoO4)2. A series of powder samples with Gd3+ contents from 10 to 100

By polarisation dependent measurements on a single crystal of the Na, Gd end member of the series cut to the (100) surface this data could be refined. It could be determined that the cation point group changes from S4 for Ca2+ in powellite to C2v for Eu3+ in the solid solution. This transformation can be explained by minor shifts of the ligands resulting in a loss of the reflection-rotational symmetry.