

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 polycrystalline samples it allows the determination of coordination symmetry classes as well as hydration states of the incorporated 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% was investigated by site-selective TRLFS. As a fluorescent probe each sample contained also 50ppm Eu³⁺. The obtained results clearly show that a homogeneous solid solution series is present, exhibiting only one genuine Eu³⁺/Gd³⁺ species throughout the series. An unambiguous determination of the species' symmetry is, however, not possible.

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 C_{2v} 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.

High precision and high resolution SIMS – Having the cake and eating it too?

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Secondary Ionization Mass Spectrometry (SIMS) approaches levels of precision for isotopic and elemental analysis that in some instances are en par with the best available bulk techniques, while at the same time offering the advantage of spatially selective analysis (typically at μm to several 10s of μm lateral resolution). Concurrently, SIMS analysis has revealed complexities in natural or synthetic materials that are frequently at the resolution limit of commonly applied spot analysis. Recent examples for demonstrating unexpected spatial heterogeneity by SIMS (through depth profiling or spot analysis) include Uranium-series dating of growth layers in individual zircon that crystallized over >100,000 a, or irregular Pb-loss related to complex fracture patterns in Hadean zircon. The new frontiers of signal-limited SIMS analysis are manifold: enabling detection of Uranium series intermediate daughter isotopes in low-U materials, geochronology of very small or very young crystals or crystal domains, or precise stable isotopic or trace element mapping at sub-μm resolution. However, the fundamental conundrum in further enhancing spatial resolution is the diminishing number of detectable atoms in smaller and smaller sample volumes.

Approaches to overcome these limitations include primary beams yielding higher spatial resolution and/or sputter rates, in combination with secondary ions that are favorable in terms of ionization and transmission efficiency. The UCLA ims 1270 uniquely features a high-brightness liquid metal Ga⁺ source capable of sputtering at ~500 nm spatial resolution. The disadvantage of non-reactive Ga⁺ is partially offset by using Cs⁺ and Ga⁺ beams in tandem, whereby the sample is impregnated with Cs prior to Ga⁺ analysis. High sensitivity can be maintained by analyzing molecular ions, such as ²⁰⁸PbP⁺ and ²³²ThP⁺ in monazite (requiring m/Δm ~5000). Another example are doubly-charged secondary ions that can be analyzed at relatively high transmission (e.g. in the practically interference-free mass/charge region at ~20 amu for Ca-K dating). K⁺⁺ species are thereby suppressed by ~10³ relative to K⁺, leaving ⁴⁰Ca⁺⁺ free from any significant interferences. Lastly, there are potential advantages in new instrumental designs such as the UCLA MegaSIMS.