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Garnet nuclear waste forms – Solubility at repository conditions

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HIGHLIGHTS

- Rare-earth elements are a significant waste stream produced by nuclear fuel cycles.
- Suitability of garnets as potential waste forms.
- Single-crystal X-ray structural refinements for grossular, LuAG and YAG.
- Garnets have low solubility, flexible crystal structure to take on large cations.
- Demonstrate garnets are potentially robust waste forms for radioactive REE.

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ABSTRACT

Radioactive rare-earth elements (REEs) constitute a significant waste stream produced from modified open and full nuclear fuel cycles. Immobilization of these REE radionuclides is thus important for sustainable nuclear energy growth. In this work, we investigated the suitability of garnets as potential waste forms for REEs by measuring their aqueous stability at repository conditions. Three garnet samples, including one natural grossular ($Ca_3Al_2Si_3O_{12}$) and two synthetic phases (LuAG – $Lu_3Al_5O_{12}$ and YAG – $Y_3Al_5O_{12}$), were studied. Single-crystal X-ray structural refinements show that the unit-cell volumes increase from 1657.19 Å^3 for grossular to 1679.8 Å^3 for LuAG and to 1721.7 Å^3 for YAG. This trend is due to increases in ionic radii in both the 8-coordinated X (from Ca to Lu to Y) and 4-coordinated Z (from Si to Al) cations. Hydrothermal experiments of the three samples were performed at 200 °C and 150 bar for 4 weeks using water and brine solutions to evaluate their solubility. The natural grossular sample exhibited Al leach rates ranging from 2.5×10^{-4} to 6.43×10^{-5} g/L·day and Ca leach rates from 1.39×10^{-3} to 4.57×10^{-3} g/L·day, indicating incongruent nature of the cation dissolution. The LuAG sample exhibited Lu leach rates of 3.73×10^{-4} to 2.19×10^{-4} g/L·day, and the YAG sample had Y leach rates of 1.29×10^{-4} to 5.64×10^{-5} g/L·day. Although these samples are generally more soluble in brine (which is more representative of repository conditions) than in water, as evidenced by both water chemistry and microstructural features, all the dissolution rates are relatively small. Thus, the high aqueous stability, together with the flexibility of the garnet structure to incorporate large cations, demonstrate that garnets are potentially robust waste forms for storing radioactive REEs.

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1. Introduction

Nuclear waste disposal is one of the most daunting challenges for sustainable nuclear energy growth. If the United States government chooses to pursue a modified open or full nuclear fuel cycle approach, one significant waste stream would contain the radioactive lanthanide or rare-earth elements (REE). Lanthanide fission products in calcined, reprocessed spent light-water reactor (LWR) nuclear fuel contains an average of 28 wt.% REE oxides (Ringwood, 1985), of which over half (15 wt.%) are comprised of Pr, Nd, and Pm. These radionuclides have half-lives ranging from 2.6 years (^{147}Pm) to 3.7×10^{10} years (^{176}Lu), and all of them are strong beta and gamma emitters. Furthermore, many other fission products are large radius cations such as Am, Np, and Cm. The ability to sequester these elements in a stable waste form would be paramount. The most obvious engineered waste forms should be derived from natural, stable minerals. In particular, garnets are robust silicate minerals, which can be stable over a large range of pressures and temperatures and over geological time scales.

Silicate garnets have an isometric structure with the general formula $X_3Y_2(ZO_4)_3$. The naturally occurring garnet group is composed of minerals where X = Mg, Fe^{2+}, or Ca; Y = Al, Cr, or Fe^{3+}; and

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Z = Si. The X-site is 8-coordinated, the Y-site is 6-coordinated (octahedral) and the Z-site is 4-coordinated (tetrahedral) (Smyth and Bish, 1988). Because of the flexibility of this structure, garnets have the ability to incorporate significant amounts of large radius REE cations replacing part of the major elements. This ability makes the garnet structure a potentially excellent candidate for sequestering a wide range of large radius fission products (Burakov et al., 1999). However, to evaluate the suitability of garnets as waste forms, it is essential to investigate their solubility behavior at aqueous repository conditions, which is the motivation of this study.

2. Previous work

It is well known that the major element chemistry of minerals can play a dominant role in REE substitutions and abundance in the structures (Oberti and Caporuscio, 1991). For example, varying the X cation in garnet can have a significant effect on its unit-cell volume. When Ca dominates in the X site, as in the natural calcic bearing garnet (grossular) Ca_3Al_2 $(SiO_4)_3$, the structure becomes expanded, giving more room for incorporating a variety of REEs. Mantle grossular garnets typically have a 50 ppm total of REEs (Caporuscio, 1988), while grossular garnets from other geologic domains may have up to 500 ppm REEs. Recent work on the grossular-pyrope solid solution (Oberti et al., 2006b) has brought further insights into the non-ideal nature of REE substitution into the X site of grossular garnet structure. Moreover, synthetically produced garnets, such as yttrium aluminum garnet (YAG), can be produced on an industrial scale.

Much work has been performed on garnet stability (Meagher, 1982) and chemistry (Oberti et al., 2006a,b); however, little has been done to show if garnets may be a suitable nuclear waste form for REEs and other cations with a large ionic radius. This is an extremely important study arena, since REEs could make up to 30 wt.% of reprocessed nuclear waste. Rak et al. (2011) performed first-principles calculation of $Ca_3(Ti\ Zr\ Hf\ Sn)_2Fe_2SiO_{12}$ garnet to determine structural incorporation of uranium into the phase. Laverov et al. (2010) measured high REE contents in synthetic garnets but did not systematically map out their crystal chemical systematics. Galuskina et al. (2010) described a uranian garnet (Elbrusite) from Russia with over 25 wt.% UO_3. Patel and co-workers have previously identified mechanisms of non-stoichiometry in YAGs (Patel et al., 2008) by comparing atomistic simulations of defect volume with experimentally measured lattice parameters. This study allowed for a simple identification of defect structures in YAGs and fundamentally altered 50 years of phase diagram determination that showed no indication of non-stoichiometry. The purpose of the current work is to explore the limits of stability of REE enriched garnets under aqueous conditions. The garnets used are a natural grossular sample (sample name Grs) from Lake Jaco, Mexico and two REE garnets (a lutetium aluminum garnet and an yttrium aluminum garnet, sample names LuAG and YAG, respectively) produced in the laboratory. Our research will investigate the dissolution mechanisms of REE-bearing garnets at elevated pressure (P), temperature (T) repository conditions.

3. Experimental techniques

3.1. Materials synthesis

LuAG and YAG single crystals were synthesized by the Czochralski method. The starting materials were lutetium oxide (Lu_2O_3) and yttrium oxide (Y_2O_3) from Advanced Materials Resources Inc., with a purity of 99.998%, and aluminum oxide (Al_2O_3) from Cerac Inc. (now a part of Materion Advanced Chemical Business Group) with a purity of 99.99%. The starting powders in stoichiometric ratios were roll blended for 24 h to ensure uniform mixing. The mixtures were then packed and sintered in an alumina crucible at 1600 °C for 12 h (for the YAG sample)) or 24 h (for the LuAG sample) to produce high-density pellets to charge the iridium crucible for the melt. The crystals were grown under an ultra-high purity argon atmosphere with an oxygen partial pressure of 2000 (LuAG) or 3000 (YAG) ppm. An iridium single crystal wire was used as a seed for the crystal growth. The resulting crystals were transparent and colorless with no evidence of scattering centers.

A K-Na-Ca-Cl-based salt solution was chosen to replicate a deep groundwater composition at Stripa nuclear repository underground research laboratory (URL) in Sweden (total dissolved solids (TDS) = ~1934 ppm; ~583 ppm K, ~167 ppm Na, ~89 ppm Ca, ~1045 ppm Cl). The salt solution was prepared using reagent grade chemicals dissolved in double deionised (DDI) water. KOH and HCl were added to adjust the initial solution pH to ~9. This solution was then filtered through a 0.45 μm filter. The salt solution was added at a 5:1 water:garnet ratio.

3.2. Structure and chemistry analysis

To obtain single crystal XRD analysis and structure refinements, the garnet crystals were mounted in a nylon cryoloop from Paratone-N oil. The data were collected on a Bruker D8 diffractometer, with APEX II charge-coupled-device (CCD) detector, and Cryo Industries of America Cryocool G2 low temperature device (120 K). The instrument was equipped with graphite monochromatized MoKα X-ray source (λ = 0.71073 Å), and a 0.5 mm monocapillary. A hemisphere of data was collected using ω scans, with 10-second frame exposures and 0.5° frame widths. Data collection and initial indexing and cell refinement were handled using APEX II[1] software. Frame integration, including Lorentz-polarization corrections, and final cell parameter calculations were carried out using SAINT+[2] software. The data were corrected for absorption using redundant reflections and the SADABS[3] program. Decay of reflection intensity was not observed as monitored via analysis of redundant frames. The structure was solved using Direct methods and difference Fourier techniques. The final refinement included anisotropic temperature factors on all atoms. For the grossular garnet an Fe impurity was refined on the Al site, with site-occupancy-factors tied to 1.0 and atomic coordinates and anisotropic displacement factors constrained to be equal for Fe and Al atoms. The final Fe occupancy was refined to 0.089(8). Structure solution, refinement, graphics, and creation of publication materials were performed using SHELXTL.[4]

Powder X-ray diffraction (XRD) was used to determine mineral phases. Each sample was ground with 20 wt.% corundum (Al_2O_3) for quantitative XRD analysis. XRD measurements were conducted with a Siemens D500 diffractometer using Cu-Kα radiation. Data were collected from 2–70° 2θ with a 0.02° step-size and count times of 8–12 s per step. Mineral identification and unit-cell parameters determination were performed using the Jade© 7.5 X-ray data evaluation program and ICDD PDF-4 database.

Electron microscopic analyses were performed using a FEI™ Inspect F scanning electron microscope (SEM). All samples were Au-coated prior to SEM analysis. Imaging with the SEM was performed using a 5.0 kV accelerating voltage and 1.5 μ spot size. Energy dispersive X-ray spectroscopy (EDX) was used to provide chemical data on the various phases. EDX analyses were performed with a 30 kV and a 3.0 μ spot size, with total counts no less than 10,000.

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[1] APEX II 1.08, 2004, Bruker AXS, Inc., Madison, Wisconsin 53719, USA.

[2] SAINT+ 7.06, 2003, Bruker AXS, Inc., Madison, Wisconsin 53719, USA.

[3] SADABS 2.03, 2001, George Sheldrick, University of Göttingen, Germany.

[4] SHELXTL 5.10, 1997, Bruker AXS, Inc., Madison, Wisconsin 53719, USA.