

Accommodation of Uranium into the Garnet Structure

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ABSTRACT

One promising host for actinide wastes is garnet-type phases of general formula $A^{\text{VIII}}_3B^{\text{VI}}_2[\text{XO}_4]_3$. To determine the isomorphic capacity of garnet for uranium, the $\text{CaO} - \text{Fe}_2\text{O}_3 - \text{Al}_2\text{O}_3 - \text{SiO}_2 - \text{ZrO}_2 - \text{Gd}_2\text{O}_3 - \text{UO}_2$ system was studied. Experiments were performed in air medium at 1400 – 1500 °C and 1 atm. The garnets have high capacity for Gd and Zr, while incorporation of U was found to be greatly dependent on the phase composition. Uranium content decreased from 18 wt.% in Ca-Zr-Fe garnet to 0.6 wt.% in Si-doped phases. Heavy ion irradiation (1.0 MeV Kr^{++}) experiments were carried out for a garnet with maximal U content, $(\text{Ca}_{2.7}\text{U}_{0.3})^{\text{VIII}}(\text{Zr}_{1.7}\text{Fe}_{0.3})^{\text{VI}}(\text{Al}_{1.1}\text{Fe}_{1.9})^{\text{IV}}\text{O}_{12}$. Amorphization dose of the phase was equal to 1.63×10^{14} ions/cm² that is close to the other actinide hosts, such as pyrochlore $\text{Gd}_2\text{Ti}_2\text{O}_7$.

APPROACH

A huge amount of actinide radioactive waste has accumulated throughout the world. The materials should be converted into a durable form before final underground disposal. B-Si and Al-P glasses currently employed for immobilization of liquid reprocessing HLW have limited loading for Pu and low chemical durability as well. Durable crystalline phases are possible alternative forms for wastes rich in actinides, such as the Zr-An-REE fraction after separation from HLW. One promising host for such waste is a garnet-type compound [1-3]. The structure of garnet ($A^{\text{VIII}}_3B^{\text{VI}}_2[\text{XO}_4]_3$, space group $Ia\bar{3}d$, $Z = 8$) consists of alternating XO_4 tetrahedral and BO_6 octahedral polyhedrons, joined by shared corners into three-dimensional framework [4]. Atoms of oxygen in this framework compose triangular dodecahedral cavities (the $[\text{A}]^{\text{VIII}}$ sites) occupied by large eight-coordinated cations. Both tetrahedron and octahedron have shared edges with the dodecahedron, which determines the dimensions of cations occupied at all three different structural positions of garnet-type compounds.

Synthetic garnet varieties with high content of REEs, Zr, and Th were obtained [1-7]. Taking into account a great degree of similarity between trivalent actinides and rare earth elements, the garnet structure is appropriate for accommodation of Am^{3+} and Cm^{3+} . At the same time, it was found that incorporation of tetravalent ions (Ce^{4+} and U^{4+}) into the rare earth – aluminum – gallium garnets was restricted to low values (4-6 wt.%) for each element [1]. Recently the same content has been obtained for solubility of plutonium in the Gd-Ce-Al-Ga composed garnet [2]. Silicate garnets close to the natural mineral andradite can include up to 10 wt.% ZrO_2 and $\Sigma\text{REE}_2\text{O}_3$ [3], but their ability to incorporate actinides has not been researched.

Table 1. Stoichiometry of the precursors, runs parameters, and final product compositions.

| NN | Bulk precursor composition | Parameters | Phases observed | Melting |
|------|---|-------------|-------------------------------------|---------|
| 2-U | $(\text{Ca}_{1.5}\text{GdU}_{0.5})(\text{FeZr})(\text{Al}_{2.5}\text{Fe}_{0.5})\text{O}_{12}$ | 1400 °C, 2h | Gar > Hib > Ox | No |
| 3-U | $(\text{Ca}_{1.5}\text{GdU}_{0.5})(\text{FeZr})\text{Fe}_3\text{O}_{12}$ | 1400 °C, 2h | Gar > Ox > Hib | Yes |
| 4-U | $(\text{Ca}_{2.5}\text{U}_{0.5})\text{Zr}_2\text{Fe}_3\text{O}_{12}$ | 1400 °C, 2h | Ox > Gar > Hib | Yes |
| 5-U | $(\text{CaGdU})\text{Fe}_2\text{Fe}_3\text{O}_{12}$ | 1400 °C, 1h | Ox > Gar > Hem | Yes |
| 6-U | $(\text{Ca}_2\text{Gd})(\text{UZr})\text{Fe}_3\text{O}_{12}$ | 1400 °C, 2h | Gar > Ur > Hem | No |
| 10-U | $(\text{Ca}_2\text{Gd})(\text{U}_{0.5}\text{Fe}_{1.5})(\text{Fe}_{1.5}\text{Si}_{1.5})\text{O}_{12}$ | 1400 °C, 2h | Gar > Hib > Ox | Yes |
| 11-U | $(\text{Ca}_2\text{Gd})(\text{U}_{0.25}\text{Zr}_{0.25}\text{Fe}_{1.5})(\text{Fe}_{1.5}\text{Si}_{1.5})\text{O}_{12}$ | 1400 °C, 2h | Gar > Ox | Yes |
| 12-U | $(\text{CaGd}_2)(\text{U}_{0.5}\text{Fe}_{1.5})(\text{Fe}_{2.5}\text{Si}_{0.5})\text{O}_{12}$ | 1500 °C, 1h | Gar > Ox > Mt | Yes |
| 13-U | $(\text{CaGd}_2)(\text{Zr}_{0.25}\text{U}_{0.25}\text{Fe}_{1.5})(\text{Fe}_{2.5}\text{Si}_{0.5})\text{O}_{12}$ | 1500 °C, 1h | Gar > Ox | Yes |

Gar – garnet, Ox – oxide, $(\text{U,Zr,Gd})\text{O}_{2-x}$; Hib – hibonite, $\text{Ca}(\text{Fe,Al})_{12}\text{O}_{19}$; Hem – hematite, Fe_2O_3 ; Ur – uranate, CaUO_4 ; Mt – magnetite, Fe_3O_4 .

Crystal-chemical analysis of the garnet structure peculiarities led us to conclude that tetravalent actinides (Th^{4+} , U^{4+} , Np^{4+} , Pu^{4+}) will be readily inserted into the $[\text{A}]^{\text{VIII}}$ -sites of the garnet structure if the $[\text{X}]^{\text{IV}}$ and $[\text{B}]^{\text{VI}}$ sites are occupied by low-charged large cations. Among the group of cations, Al^{3+} , Ga^{3+} , and Fe^{3+} , which can occupy both IV- and VI-coordinated sites of the structure, Fe^{3+} ($r_{\text{IV}} = 0.049$ nm, $r_{\text{VI}} = 0.065$ nm) has the largest dimension. To check the isomorphic capacity of the iron-based garnets to incorporate uranium, experimental research has been carried out.

EXPERIMENTAL

Initial oxide mixtures were fabricated from CaO , Fe_2O_3 , Al_2O_3 , SiO_2 , ZrO_2 , Gd_2O_3 , UO_3 or UO_2 considering an ideal garnet stoichiometry $\text{A}_3\text{B}_2[\text{XO}_4]_3$ (Table 1). These precursors were cold pressed and sintered in air at 1400–1500 °C for 1-2 hours in alumina crucibles. Melting was observed in some runs. It results in contamination of Al_2O_3 due to dissolution of the crucible in the melt. The samples were studied using SEM/EDS, TEM and XRD methods. One sample with maximal U content (# 4-U) was irradiated by 1.0 MeV Kr^{++} from ambient conditions to 1100 K using the IVEM – Tandem Facility at the Argonne National Laboratory. The amorphization process was studied using selected area electron diffraction and high-resolution electron microscopy at the University of Michigan.

RESULTS

Garnet content in the samples varied from 20 to 90 vol.%. Along with garnet, other phases are present as shown in Figure 1. Features of the melted and sintered samples are similar. The main difference is higher dimension (20-200 μm vs. 10-50 μm) and regular shape of

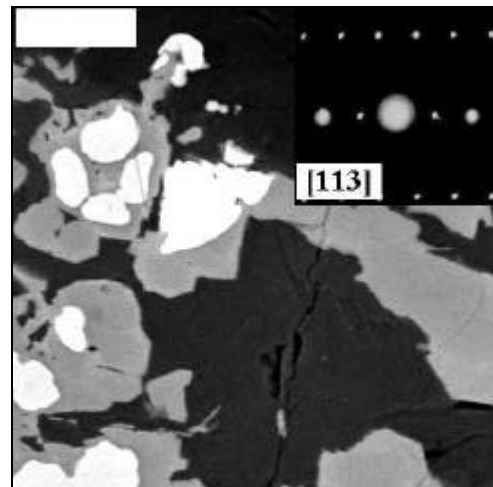


Figure 1. SEM/bse image of ceramic # 4-U. White – $(\text{Zr,U,Ca})\text{O}_{2-x}$, light-gray - garnet, dark - hibonite. Scale bar is 20 μm . TEM pattern for garnet is shown as insert.

grains in melted ceramics. Non-melted samples contain up to 10 vol.% of initial oxides. Analytical data (Table 1) show that ferrite garnets can incorporate large amounts Gd and Zr. Maximal U content reached 16-18 wt.% UO_2 in the Ca-Zr-Fe-Al-composed garnet (# 4-U). The lowest U content (0.6-0.8 wt.%) was observed in Si-doped garnets (## 10-U – 13-U).

Isomorphous Substitutions Influenced Compositions of Garnet

Garnet compositions can be described using five end members: $\text{Gd}_3\text{Fe}_2(\text{Fe},\text{Al})_3\text{O}_{12}$ – $\text{Ca}_3(\text{Zr},\text{U})_2\text{Fe}_3\text{O}_{12}$ – $\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$ – $(\text{Ca}_{2,5}\text{U}_{0,5})\text{Zr}_2\text{Fe}_3\text{O}_{12}$ – $(\text{CaGd}_2)(\text{FeU})\text{Fe}_3\text{O}_{12}$. The substitutions most important for U incorporation are: $^{\text{VIII}}[\text{Gd}^{3+}] + ^{\text{VI}}[\text{Fe}^{3+}] = ^{\text{VIII}}[\text{Ca}^{2+}] + ^{\text{VI}}[\text{U}^{4+}]$, $^{\text{VIII}}[2\text{Gd}^{3+}] = ^{\text{VIII}}[\text{Ca}^{2+}] + ^{\text{VIII}}[\text{U}^{4+}]$, and $^{\text{VI}}[\text{Zr}^{4+}] = ^{\text{VI}}[\text{U}^{4+}]$. Formulae of the garnets were calculated from SEM/EDS data based on ideal stoichiometry (Table 2). An assumption was made that cations fill different sites of the structure in accordance with their radius [8].

Table 2. Chemical compositions and hypothetical formulae of garnets.

| SAMPLE | CaO | Al ₂ O ₃ | SiO ₂ | SFe ₂ O ₃ | ZrO ₂ | Gd ₂ O ₃ | UO ₂ |
|--------|---|--------------------------------|------------------|---------------------------------|------------------|--------------------------------|-----------------|
| 2-U | 10.6 | 10.3 | - | 20.4 | 21.2 | 34.8 | 2.7 |
| | $(\text{Ca}_{1,5}\text{Gd}_{1,5})^{\text{VIII}}(\text{U}_{0,1}\text{Zr}_{1,4}\text{Fe}_{0,5})^{\text{VI}}(\text{Al}_{1,6}\text{Fe}_{1,4})^{\text{IV}}\text{O}_{12}$ | | | | | | |
| 3-U | 10.5 | 7.3 | - | 24.2 | 22.8 | 32.6 | 2.6 |
| | $(\text{Ca}_{1,5}\text{Gd}_{1,5})^{\text{VIII}}(\text{U}_{0,1}\text{Zr}_{1,5}\text{Fe}_{0,4})^{\text{VI}}(\text{Al}_{1,1}\text{Fe}_{1,9})^{\text{IV}}\text{O}_{12}$ | | | | | | |
| 4-U | 21.4 | 8.5 | - | 24.8 | 29.5 | - | 15.8 |
| | $(\text{Ca}_{2,7}\text{U}_{0,3})^{\text{VIII}}(\text{Zr}_{1,7}\text{Fe}_{0,3})^{\text{VI}}(\text{Al}_{1,1}\text{Fe}_{1,9})^{\text{IV}}\text{O}_{12}$ | | | | | | |
| 5-U | 3.3 | 5.5* | - | 38.2 | - | 47.3 | 5.7 |
| | $(\text{Ca}_{0,5}\text{Gd}_{2,5})^{\text{VIII}}(\text{Gd}_{0,3}\text{U}_{0,2}\text{Fe}_{1,5})^{\text{VI}}(\text{Al}_{1,0}\text{Fe}_{2,0})^{\text{IV}}\text{O}_{12}$ | | | | | | |
| 6-U | 10.8 | - | - | 32.7 | 22.9 | 28.9 | 4.7 |
| | $(\text{Ca}_{1,6}\text{Gd}_{1,4})^{\text{VIII}}(\text{U}_{0,1}\text{Zr}_{1,5}\text{Fe}_{0,4})^{\text{VI}}(\text{Fe}_{3,0})^{\text{IV}}\text{O}_{12}$ | | | | | | |
| 10-U | 8.3 | 3.1* | 8.6 | 35.9 | - | 43.4 | 0.7 |
| | $(\text{Ca}_{1,1}\text{Gd}_{1,9})^{\text{VIII}}(\text{U}_{0,01}\text{Al}_{0,5}\text{Fe}_{1,5})^{\text{VI}}(\text{Si}_{1,1}\text{Fe}_{1,9})^{\text{IV}}\text{O}_{12}$ | | | | | | |
| 11-U | 12.1 | - | 8.5 | 36.6 | 8.4 | 33.8 | 0.6 |
| | $(\text{Ca}_{1,6}\text{Gd}_{1,4})^{\text{VIII}}(\text{U}_{0,02}\text{Zr}_{0,48}\text{Fe}_{1,5})^{\text{VI}}(\text{Si}_{1,1}\text{Fe}_{1,9})^{\text{IV}}\text{O}_{12}$ | | | | | | |
| 12-U | 3.2 | 3.3* | 3.4 | 36.8 | - | 52.5 | 0.8 |
| | $(\text{Ca}_{0,5}\text{Gd}_{2,5})^{\text{VIII}}(\text{U}_{0,03}\text{Fe}_{1,97})^{\text{VI}}(\text{Si}_{0,5}\text{Al}_{0,5}\text{Fe}_{2,0})^{\text{IV}}\text{O}_{12}$ | | | | | | |
| 13-U | 5.4 | - | 2.9 | 38.7 | 5.9 | 46.5 | 0.6 |
| | $(\text{Ca}_{0,8}\text{Gd}_{2,2})^{\text{VIII}}(\text{U}_{0,02}\text{Zr}_{0,4}\text{Fe}_{1,58})^{\text{VI}}(\text{Si}_{0,4}\text{Fe}_{2,6})^{\text{IV}}\text{O}_{12}$ | | | | | | |

* - contamination due to dissolution of the crucible. $\text{SFe}_2\text{O}_3 = \text{Fe}_2\text{O}_3 + \text{FeO}$.

Irradiation Testing

A study of susceptibility of garnets to radiation-induced amorphization was completed by ion bombardment of sample # 4-U with 1.0 MeV Kr^{++} . The formula of garnet calculated from SEM/EDS is $(\text{Ca}_{2,7}\text{U}_{0,3})^{\text{VIII}}(\text{Zr}_{1,7}\text{Fe}_{0,3})^{\text{VI}}(\text{Al}_{1,1}\text{Fe}_{1,9})^{\text{IV}}\text{O}_{12}$. The critical amorphization dose at room

temperature was 1.63×10^{14} ions/cm² that is close to Gd-Ti pyrochlore [9]. The critical amorphization temperature is 870 K (for details see paper of S.Utsunomiya et al. in this book).

Natural silicate garnets have very low contents of REEs and do not contain actinides such as Th and U [10]. Thus, we cannot evaluate radiation stability of the structure under α -decay events by studying metamict minerals. The only relevant example is alteration of andradite that has experienced radiation damage from uraninite (UO₂) grains [11]. Evidently, the irradiation facilitates the alteration of the garnet to secondary chlorite. Width of the chlorite zone surrounding the uraninite is 10-15 μ m, approximately equal to range of an α -particle.

CONCLUSION

Uranium content reaches the highest value of 6-18 wt.% in the Ca-Zr-Fe-based garnets. Recalculation of the garnet compositions onto crystal chemical formulae shows that Gd and Zr are inserted into the [A]- and [B]-sites of the structure while U probably fills both the [A]^{VIII} and [B]^{VI} positions. Uranium content is lowest (0.6-0.8 wt.%) in Si-containing garnets. This is explained by small size of Si⁴⁺ ($r_{IV} = 0.026$ nm). Incorporation of Si⁴⁺ leads to contraction of the structural polyhedron preventing accommodation of large U⁴⁺ cation ($r_{VIII} = 0.10$ nm, $r_{VI} = 0.089$ nm) in the phase lattice.

Fe-based garnets may be used for immobilization of actinide wastes enriched with corrosion products (Fe, Al) and processing contaminants (Si). One of the advantages of these ceramics is low melting temperature that facilitates their fabrication.

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