



Structure and thermodynamics of uranium-containing iron garnets

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Received 16 December 2015; accepted in revised form 30 May 2016; available online 14 June 2016

Abstract

Use of crystalline garnet as a waste form phase appears to be advantageous for accommodating actinides from nuclear waste. Previous studies show that large amounts of uranium (U) and its analogues such as cerium (Ce) and thorium (Th) can be incorporated into the garnet structure. In this study, we synthesized U loaded garnet phases, $\text{Ca}_3\text{U}_x\text{Zr}_{2-x}\text{Fe}_3\text{O}_{12}$ ($x = 0.5\text{--}0.7$), along with the endmember phase, $\text{Ca}_3(\text{Zr}_2)\text{SiFe}_2^+\text{O}_{12}$, for comparison. The oxidation states of U were determined by X-ray photoelectron and absorption spectroscopies, revealing the presence of mixed pentavalent and hexavalent uranium in the phases with $x = 0.6$ and 0.7 . The oxidation states and coordination environments of Fe were measured using transmission ^{57}Fe -Mössbauer spectroscopy, which shows that all iron is tetrahedrally coordinated Fe^{3+} . U substitution had a significant effect on local environments, the extent of U substitution within this range had a minimal effect on the structure, and unlike in the $x = 0$ sample, Fe exists in two different environments in the substituted garnets. The enthalpies of formation of garnet phases from constituent oxides and elements were first time determined by high temperature oxide melt solution calorimetry. The results indicate that these substituted garnets are thermodynamically stable under reducing conditions. Our structural and thermodynamic analysis further provides explanation for the formation of natural uranium garnet, elbrusite-(Zr), and supports the potential use of $\text{Ca}_3\text{U}_x\text{Zr}_{2-x}\text{Fe}_3\text{O}_{12}$ as viable waste form phases for U and other actinides. © 2016 Elsevier Ltd. All rights reserved.

Keywords: Uranium; Garnet; X-ray absorption spectroscopy; X-ray photoelectron spectroscopy; Calorimetry; Structure

1. INTRODUCTION

Safe disposal of highly radioactive waste from nuclear reactors or dismantled nuclear weapons is a daunting challenge due to potential deleterious environmental effects over

thousands or even millions of years. Currently in the United States, France, United Kingdom, Belgium, Germany, Japan, and Russia, vitrification processes using borosilicate or aluminophosphate glassy matrices (Ewing, 1999, 2006; Grambow, 2006; Laverov et al., 2008; Lutze and Ewing, 1988; Weber et al., 2009) have been industrialized for immobilization of commercial nuclear waste. However, it

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remains unclear whether such glass-based systems are sufficiently stable for permanent encapsulation of long lived nuclides, such as the higher actinides. Since the 1970s, there have been numerous investigations of alternative waste forms. Considerable efforts have been focused on crystalline ceramics (Sinclair and Ringwood, 1981; Ringwood, 1982; Kesson and Ringwood, 1983; Weber et al., 1997, 2009; Burakov et al., 1999; Yudinsev et al., 2002, 2007; Ewing et al., 2004; Rusakov et al., 2005; Urusov et al., 2005; Utsunomiya et al., 2005; Lumpkin, 2006; Omel'yanenko et al., 2007), which may serve as more durable and thus safer waste forms with high loadings of radionuclides. Various tailored ceramic forms containing mineral phases such as garnet, perovskite, monazite, pyrochlore, zircon, zirconolite, and defect fluorite, (Lumpkin, 2006; Yudinsev et al., 2007; Navrotsky et al., 2013) have been studied in terms of their chemical durability, waste loading, radiation tolerance and other related properties.

Garnet, a relatively new host for accommodation of actinides, was proposed in a number of recent studies (Burakov and Strykanova, 1998; Burakov et al., 2000; Zamoryanskaya and Burakov, 2000; Yudinsev et al., 2002, 2007; Utsunomiya et al., 2002a,b, 2005; Rusakov et al., 2005; Livshits, 2008; Galuskina et al., 2010; Laverov et al., 2003, 2010; Stefanovsky et al., 2010; Zhang et al., 2010; Rak et al., 2013b; Guo et al., 2015a) due to its large loading of actinides and good chemical flexibility. The garnet structure has been shown to incorporate actinides in various oxidation states (Burakov and Strykanova, 1998; Burakov et al., 2000; Zamoryanskaya and Burakov, 2000; Yudinsev et al., 2002; Rusakov et al., 2005; Galuskina et al., 2010; Laverov et al., 2010; Stefanovsky et al., 2010; Rak et al., 2013b; Guo et al., 2014a). Notably, significant amounts of U were found in natural uranium bearing garnets, kimzeite (Galuskina et al., 2008) (~22 wt.% U) and elbrusite-(Zr) (Galuskina et al., 2010) (~27 wt.% U), as well as in synthetic garnets (~30 wt.% U) (Burakov and Strykanova, 1998; Burakov et al., 1999; Zamoryanskaya and Burakov, 2000; Utsunomiya et al., 2002a; Yudinsev et al., 2002; Yudinseva, 2005; Laverov et al., 2010). The presence of U-containing natural garnets highlights their long-term stability as a mineral analogue for ceramic waste forms (Lumpkin, 2006; Livshits, 2008; Galuskina et al., 2010). Furthermore, the negligible influence of alpha decay damage on the leaching rate of garnets in aqueous solution (Livshits, 2008) suggests their robust chemical durability in nature; they can maintain their crystalline integrity when exposed to subsurface water. Garnet has been studied extensively for its response to alpha decay radiation damage (Utsunomiya et al., 2002a,b, 2005; Yudinsev et al., 2002; Laverov et al., 2003; Zhang et al., 2010). Radiation tolerance measurements show that the average amorphization dose for garnet is comparable to that for zircon (Utsunomiya et al., 2002a,b; Zhang et al., 2010), and the radiation response of garnet is topologically constrained, thus being less related to its actual chemical composition (Zhang et al., 2010). The implication is that garnets with different compositions may have similar high degrees of radiation tolerance. In addition, the chemical stability of

garnets is not compromised significantly by amorphization (Livshits, 2008; Laverov et al., 2010), where partially amorphized garnets remain more resistant to leaching than other ceramic waste forms (Lumpkin, 2006; Livshits, 2008).

However, so far only ferric garnets have been found to incorporate significant amounts of actinides, including U, Np, Pu, or Ce and Th as surrogates of higher actinides (Yudinsev et al., 2002; Urusov et al., 2004; Livshits, 2008; Laverov et al., 2010; Stefanovsky et al., 2010; Guo et al., 2015a). A garnet framework with large unit cell dimensions, forming from $[\text{FeO}_6]$ octahedra and $[\text{FeO}_4]$ tetrahedra, can accommodate large actinide ions. Particularly, Np- and Pu-containing garnet ceramics were previously reported in a ferric garnet system (Stefanovsky et al., 2010). A positive correlation exists between the capacity of garnet to accommodate actinides and Fe content (Burakov et al., 1999; Yudinsev et al., 2002; Yudinseva, 2005; Omel'yanenko et al., 2007; Laverov et al., 2010). Recent density functional theory (DFT) calculations on incorporation of actinides (U, Np, and Pu) in $\text{Ca}_3(\text{Ti,Zr,Hf,Sn})_2(\text{Fe}_2\text{Si})\text{O}_{12}$ confirmed the crucial role of Fe 3d states in stabilizing actinides within the ferric garnet structure. Crystal chemical and energetic insights about ferric garnets have also been obtained by studying the garnet phases with surrogates of higher actinides such as Ce and Th. Previous studies showed that $\text{Y}_3\text{Fe}_5\text{O}_{12}$ (YIG) can incorporate high concentrations of Ce in its structure, (Gramsch and Morss, 1994; Zamoryanskaya and Burakov, 2000; Kum et al., 2004; Laverov et al., 2010; Guo et al., 2014a, 2015a) and the substituted Ce may be in different oxidation states (Guo et al., 2014a). Ce at high concentrations tends to be tetravalent, coupled with reduction of tetrahedral Fe^{3+} to Fe^{2+} in YIG (Guo et al., 2014a). Calorimetric analysis of $\text{Ce}^{3+}\text{Fe}^{3+}\text{-Ce}^{4+}\text{Fe}^{2+}$ coupled substitution in Ce:YIG revealed that the energetically unfavorable Fe reduction causes strain energy attenuation favoring Ce incorporation (Guo et al., 2014a). Similar behavior was observed in Th substituted YIG (Guo et al., 2014c). Hence, the presence of Fe^{3+} in garnets can facilitate incorporation of actinides via reduction of Fe^{3+} to Fe^{2+} .

Despite the extensive studies described above, the mechanisms of U incorporation in Fe garnets remain largely unclear (Yudinsev et al., 2002; Utsunomiya et al., 2002b; Yudinsev, 2003; Rak et al., 2011). This is due to difficulties of determining the multiple oxidation states (tetravalent, pentavalent, and hexavalent) and associated coordinations and occupancies (dodecahedral and octahedral sites) of U in the garnet structure. Crystal chemical arguments dictate that U^{4+} only fits dodecahedral sites, while U^{6+} occupies octahedral sites. The presence of U^{5+} in octahedral sites was suggested to occur by transferring its extra electron to neighboring tetrahedral Fe^{3+} , based on first principles calculation (Rak et al., 2013a). Correspondingly, the octahedral site, even though smaller than the dodecahedral site, may be more flexible to incorporate U with higher oxidation states.

In this study, we synthesized several iron garnet phases incorporating octahedral U, as revealed by X-ray photoelectron spectroscopy (XPS) and X-ray absorption near edge structure (XANES) measurements. Three garnet

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