Synthesis and phase relations in the system with garnet-type composition: \([\text{Ca}_{1.5}\text{GdCe}_{0.5}]^{\text{VIII}}[\text{ZrFe}]^{\text{VI}}[\text{Fe}_2\text{Al}_{3-x}]^{\text{IV}}\text{O}_{12}\]


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This study was aimed at the synthesis, study of phase relations and characterization of the garnet ([Ca\(_{1.5}\)GdCe\(_{0.5}\)]\(^{\text{VIII}}\)[ZrFe]\(^{\text{VI}}\)[Fe\(_2\)Al\(_{3-x}\)]\(^{\text{IV}}\)O\(_{12}\), \(x = 0–2\)) intended as promising matrix for actinides (Pu) immobilization. The optimum temperatures of the fabrication of the garnets ceramics are 1400 °C at \(x = 2\) and 1500 °C at \(x = 0–1\). The garnets lattice parameters and the content of Ce, as an imitator of Pu, increased with the content of iron. It was suggested that the ability of the garnet for incorporation of Pu was closely related to the ionic radii of the elements occupied the four- and six-coordinated sites of the structure.

Introduction

During decades the immobilization of fissioned Pu generated in the nuclear fuel cycle or recovered from dismantled nuclear weapons has become an active issue for the safety and health of mankind. Current strategies generally recognized around the world include the immobilization of the Pu (and the other long-lived minor actinides – Np, Am) into a stable host matrix followed either burning in a nuclear reactor or placing in a geologic repository for ultimate disposal.\(^1\) Vitrification has been studied for a long time as an immobilization method for radioactive waste. However, glass is thermodynamically unstable and subjected to devitrification. It can result in the decrease of its chemical durability and the escape of radionuclides into the environment.

To minimize these disadvantages, RINGWOOD et al.\(^2\) suggested titanate-based ceramics “Synroc” as an alternative matrix of glass. Their suggestion based on the fact that some natural minerals containing radioactive elements have retained their structure stable for millions years. Until now, the synthesis and characterization study on various kinds of matrices has been carried out.\(^3–7\) Important parameters for such immobilization matrices are chemical and radiation resistance, and technologichal effectiveness (efficiency of industrial-scale production).\(^5\) The cold pressing and sintering method used in this study is one of the common methods applied for matrix synthesis. It is an economic method that requires simple and cheaper equipment than other methods of crystalline matrix production such as hot pressing.\(^2–4\)

Among the various types of matrices, the garnet-structured materials with the general formulae of \(\text{VIII}A_3\text{VB}_2\text{IV}X_5\text{O}_{12}\cdot\), sp. group Ia\(3d\) are considered as promising actinide waste forms.\(^6,7\) On the basis of elements in the tetrahedral \([X]\) site, the garnet-type compounds can be divided into the following groups: aluminates, gallates, ferrates, silicates, germanates and vanadates (\(X = \text{Al}^{3+}, \text{Ga}^{3+}, \text{Fe}^{3+}, \text{Si}^{4+}, \text{Ge}^{4+}\) or \(\text{V}^{5+}\)). The ionic radius of iron is larger than that of other elements, and then it is expected that ferrate garnet should have the highest substitution ability for large actinide cations.\(^6\)

In order to confirm this hypothesis, we have carried out synthesis of garnet in the system with composition of \([\text{Ca}_{1.5}\text{GdCe}_{0.5}]^{\text{VIII}}[\text{ZrFe}]^{\text{VI}}[\text{Fe}_2\text{Al}_{3-x}]^{\text{IV}}\text{O}_{12}\) (\(x = 0–2\)). Here, Ce\(^{3+/4+}\) and Gd\(^{3+}\) were used as imitators for Pu\(^{3+/4+}\), one of major actinides and a neutron absorber, respectively. Studying phase relations in these compositions is very important in that new phases can be found as promising confinement matrices for actinides.

Experimental

\(\text{CaCO}_3\) (High Purity Chemicals, 4N), \(\text{Gd}_2\text{O}_3\) (Cerac Co., 3N), \(\text{ZrO}_2\) (Rare Metallic Co., Ltd., 3N) \(\text{Ce}_2\text{O}_3\) (Johnson Matthey, 3N), \(\text{Al}_2\text{O}_3\) (Rare Metallic Co., 3N) and \(\text{Fe}_2\text{O}_3\) (Rare Metallic Co., 98%) were used as starting materials. These powders were mixed in ratios, corresponding to the formula ([Ca\(_{1.5}\)GdCe\(_{0.5}\)]\(^{\text{VIII}}\)[ZrFe]\(^{\text{VI}}\)[Fe\(_2\)Al\(_{3-x}\)]\(^{\text{IV}}\)O\(_{12}\); \(x = 0–2\)), using an alumina mortar and pestle. The batches were pressed into pellets (10-mm diameter \(\times\) 2-mm height) at a pressure of 400 kg/cm\(^2\). The pellets were sintered at 1000–1500 °C for 20 hours in oxygen atmosphere to maintain Ce in the highest oxidation state (IV). Phase identification was made by X-ray diffraction (reflection mode, Cu K\(\alpha\) radiation) using a Phillips X’pert MPD X-ray diffractometer attached to a graphite monochromator. Compositions of the phases were analyzed with a SEM/EDS analyzer.
Results and discussion

Phase relations

\[ \text{[Ca}_{1.5}\text{GdCe}_{0.5}]^{VIII}[\text{ZrFe}]^{VI}[\text{Fe}_{x}\text{Al}_{3-x}]^{IV}\text{O}_{12}: x = 2 \]

(Fig. 1a and Fig. 2a): At 1000 °C, Gd\text{$_2$}O\text{$_3$} showed the strongest diffraction intensity at the XRD patterns, and two kinds of garnets (G1: \(d = 2.57\) Å and G2: \(d = 2.78\)Å) and perovskites (P1: \(d = 2.72\) Å and P2: \(d = 2.82\) Å; here, d-spacing corresponds to the peak with the strongest intensity of each phase) were observed along with Ca\(_{0.15}\)Zr\(_{0.85}\)O\(_{1.85}\) (CZO). Because of the similarity of the diffraction patterns of Gd\text{$_2$}O\text{$_3$} and CeO\text{$_2$}, we expressed them as “lanthanide oxides”. At 1100 °C the diffraction intensities of G1, G2 and P2 slightly increased with decrease of those of lanthanide oxides and P1 and the disappearance of CZO. Especially, it was distinctively visible that a new kind of garnet (\(d = 2.8\) Å: G3) with the strongest intensity was formed. With the increase of temperature G3 was observed continuously as a main phase, and minor P1 was also found in the range of 1200–1300 °C. G3 was observed as single phase at 1400 °C and its diffraction intensity was not changed until 1500 °C, the highest temperature in this experiment. Namely, G3 was observed as a final product in this composition. From these results, we confirmed that optimal temperature for synthesis of garnet was 1400 °C. The characteristics of this composition were the coexistence of a few kinds of garnet and perovskite in the range of 1000–1100 °C.

Fig. 1. XRD patterns of specimens with composition Ca\(_{1.5}\)GdCe\(_{0.5}\)ZrFe\(_x\)Al\(_{3-x}\)O\(_{12}\) sintered for 20 hours. (a) \(x = 2\), (b) \(x = 1\) and (c) \(x = 0\). Arrows indicate the main peaks of identified phases.