Synthesis of Gadolinium-Iron-Garnet Ceramic Waste Form for Actinide Immobilization

Jinyoung Lee, Jong-Il Yun*
Department of Nuclear and Quantum Engineering, KAIST, Korea
**Corresponding author: jiyun@kaist.ac.kr*

1. Introduction

Actinides are an important component of high-level radioactive waste (HLW). In particular, long-lived actinides such as ^{237}Np, ^{239,240}Pu, and ^{241,243}Am have high radiotoxicity [1] and should therefore be incorporated into durable matrices to prevent environmental leakage. These matrices are also referred to as waste forms and play an important role in the deep geological disposal system. Since the disposal system is expected to be at an elevated temperature due to the decay heat and the geothermal gradient, the waste form must have high thermal stability. Borosilicate glass is the most widely used and mature technology for immobilization of HLW, but it is prone to devitrify when exposed to higher temperatures [2]. As an alternative waste form, crystalline ceramic waste forms come into question, which are significantly more durable than borosilicate glass under repository conditions.

Garnet is one of the candidate ceramic matrices, which has an $A_3^{[VIII]}B_2^{[VI]}T_3^{[IV]}O_{12}$ structure. Natural garnet is usually found as a silicate mineral with low concentration of REE. However, ferrate garnet can incorporate large cations including actinides into the A-site [3]. In this study, we synthesized gadolinium-iron-garnet (GdIG) by cold pressing and sintering.

2. Experimental

2.1. Powder preparation

The precursor was prepared from Gd_2O_3 (99.9%, Sigma-Aldrich), Fe_2O_3 (96%, Sigma-Aldrich), and CeO_2 (99.9%, Sigma-Aldrich). Gd and Ce were added as neutron absorber and actinide surrogate, respectively. The stoichiometric amount of the target precursor compositions (Table I) was placed in a grinding bowl with high purity 2mm zirconia balls and ethanol used as the medium for the wet milling. And then the powder was mixed and milled with a high energy ball mill (Pulverisette 7, Fritsch) at 500 rpm for 3 hours. The final mixture was dried in an oven at 95℃ for 1 hour and ground again with an agate mortar. The powder was filtered through the 425μm sieve and stored in the desiccator before use.

2.2. Pellet fabrication and characterization

The pellets were made by the conventional sintering method. The mixed powder was pressed into a 10 mm stainless steel die using a uniaxial press under a load of 300 MPa. The green pellets were sintered under atmospheric conditions in a muffle furnace (S-1700 mini, Hantech) at different temperatures. The initial heating rate was 5℃/min before 300℃, holding at 300℃ for 30 minutes, and heated to the sintering temperature at a rate of 10℃/min. The pellets were sintered at the target temperature for 8 hours and then furnace cooled to room temperature. The sintered pellets were characterized with an X-ray diffractometer (XRD/SmartLab, Rigaku) and energy dispersive X-ray spectroscopy (EDS/Octane Elite, Metek). The morphology of the sample was analyzed by scanning electron microscopy (SEM/SU5000, Hitachi).

The process to prepare powder and fabricate the GdIG pellet is illustrated in Fig. 1.

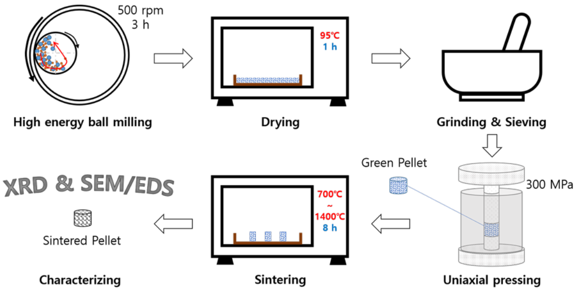

Fig. 1. Schematic diagram of synthesis process

Table I: Target elemental compositions

Sample name	*GdIG*	*Ce-GdIG*
Chemical formula	$Gd_3Fe_5O_{12}$	$Gd_{2.5}Ce_{0.5}Fe_5O_{12}$
Gd_2O_3 (wt%)	57.8	48.2
Fe_2O_3 (wt%)	42.2	42.5
CeO_2 (wt%)	-	9.2

3. Results and discussion

Fig. 2 shows the XRD patterns with the phase transformation trend as a function of the sintering temperature. Up to 700℃, there is almost no phase change compared to the precursor mixture. Between the 800℃ and 900℃, the phase was changed to the perovskite ($GdFeO_3$) structure. After 1000℃, the garnet structure was fully formed without changing the peak position up to 1400℃.

The surface images obtained by SEM (Fig. 3) show the process of densification. Densification was not complete until 1000℃, and neck growth was observed at 1200℃. At 1400℃, the apparent volume of the pellet had shrunk dramatically and the open pores disappeared.

The results of the EDS analysis confirmed that $Gd_3Fe_5O_{12}$ is the predominant phase of GdIG.

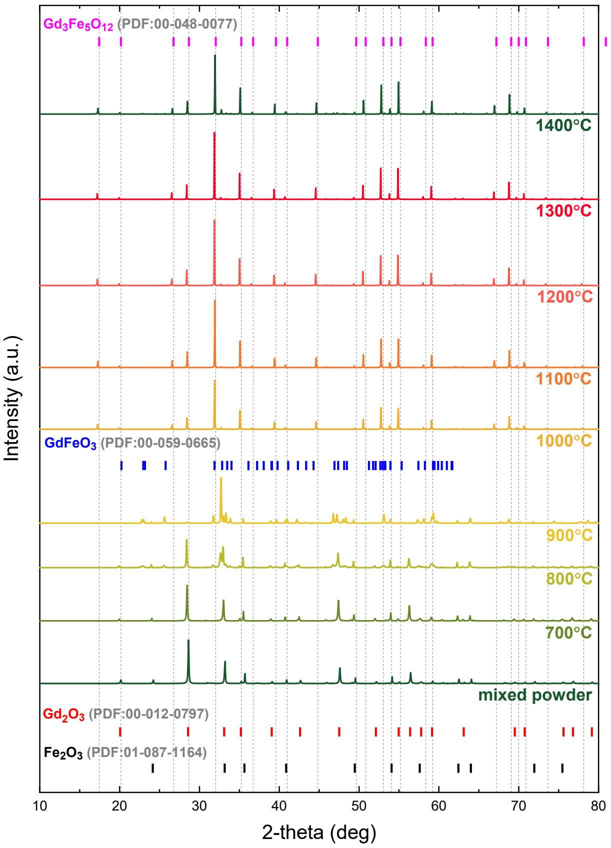

Fig. 2. XRD patterns of GdIG

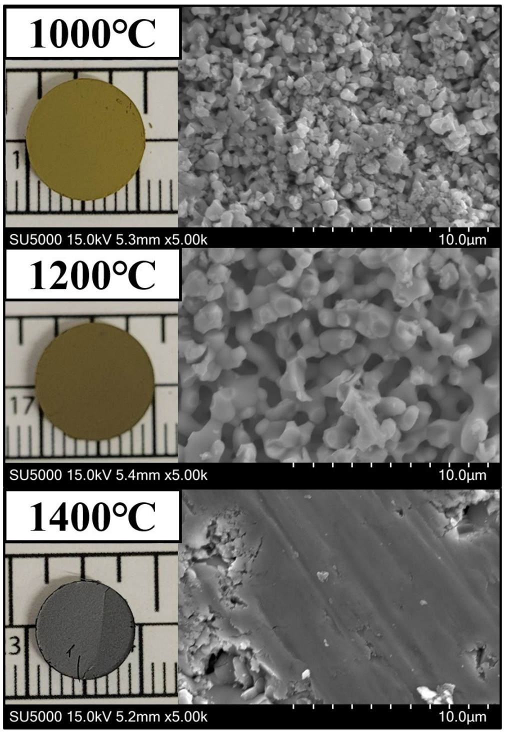

Fig. 3. Apparent and microstructure of GdIG (sample surface at 1400°C was polished)

The Ce-GdIG sample was synthesized at 1400°C. The XRD pattern of Ce-GdIG, as shown in Fig. 4, indicates the presence of secondary phases. The back-scattered electron image analysis (Fig. 5) shows three different phases that have formed on the sample surface. Based on the EDS analysis, the light gray color is identified as CeO_2, and the dark color as Fe_2O_3. The dominant phase shown in gray is the garnet structure, whose chemical formula is $Gd_{2.83}Ce_{0.40}Fe_{5.16}O_{12}$ from the quantitative EDS analysis (Fig. 6) normalized to 12 oxygen atoms.

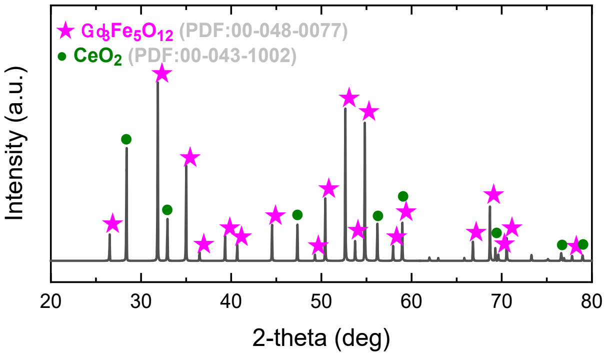

Fig. 4. XRD pattern of Ce-GdIG

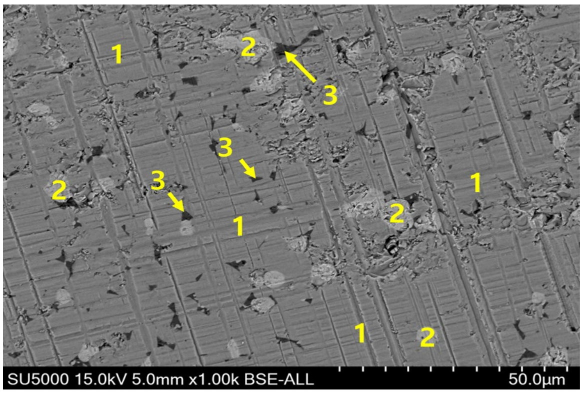

Fig. 5. Back-scattered electron image of Ce-GdIG (1) Garnet, (2) CeO_2, (3) Fe_2O_3

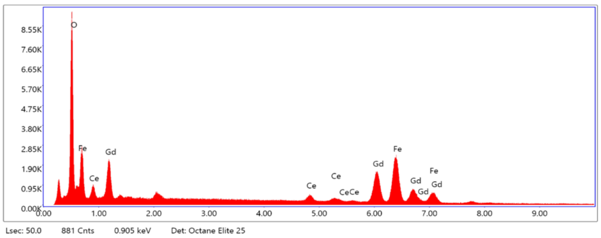

Fig. 6. EDS analysis result of garnet phase in Ce-GdIG

4. Conclusions

In this study, we demonstrated the possibility of immobilization of actinide in the gadolinium-iron-garnet structure. Cerium used as an actinide surrogate successfully replaced the Gd-site in the garnet lattice in the presence of minor secondary phases. Our garnet has five iron atoms in the structure, so it can be used for the treatment of iron-rich radioactive waste.

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