Synthesis of Waste Form in the Gd-Fe-Al-Ni-Mn-Cr-O System

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ABSTRACT

Polyphase waste form which was the mixture of $Gd_3Fe_2Al_3O_{12}$ and $(Ni_xMn_{1-x})(Fe_yCr_{1-y})_2O_4$ was synthesized. Also, we are intended to examine phase relation and physicochemical properties of coexisted phases in the compositions and to confirm accommodation relation of elements and phases. Two types of phase series were observed: Garnet-perovskite-spinel and Garnet-spinel. The compositions of garnets and spinels were nonstoichiometric, and especially, this polyphase ceramics may be in a good waste form. The excessive Gd in garnets indicated the immobilization of higher content of actinides. The nonstoichiometric compositions of garnet and spinel were attributed to the formation of perovskite in that perovskite contained Gd, Fe and Al from garnet and Cr from spinel.

INTRODUCTION

Major sources of high level nuclear waste were (i) spent nuclear fuel from commercial and research nuclear reactor; (ii) liquid waste produced in the 1960s during the reprocessing of commercial spent nuclear fuel, and (iii) waste generated by the nuclear weapons and naval propulsion programs [1]. Various kinds of radio-nuclides and elements were contained in these wastes. Accordingly, many researchers have studied to develop the waste forms capable of immobilizing them.

Glass has been studied for a long time as a waste form for the radioactive waste. However, it 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.

Ringwood et al. (1988) suggested "SYNROC" as an alternative matrix of glass to minimize these disadvantages [2]. SYNROC is a polyphase ceramic using the concept of solid solution in mineralogy and their suggestion based on the fact that some natural minerals containing radioactive elements have retained their structure stable for millions years. SYNROC includes zirconolite (U, Zr, Np and Pu), hollandite (Cs, R b, Ba and fission product), perovskite (Sr and ultrauranic Np and Pu) and titanates that can accommodate important radionuclides selectively. Tailored ceramics, as another kind of polyphase waste form, was developed mainly at the Rockwell International Science Center [1, 3]. It was applied to immobilize the defense waste and contained magnetoplumbite, spinel, nepheline, uraninite and corundum. Until now, the synthesis and characterization study on various kinds of waste forms have been carried out [2, 4-14].

By the US Defense program the high-level actinide-containing wastes with large amounts of process contaminants (Fe, Al, Mn, Ni, Si, and Na) were stored in tanks at the Savannah River Plant in Aiken, South Carolina. SYNROC-D, a special polyphase waste form of the SYNROC family ceramics was developed to immobilize these wastes. The waste form was designed with a special phase assemblage comprising zirconolite (~16 wt.%), perovskite (~11 wt.%), spinel (~55 wt.%), and nepheline (~18 wt.%) with the processing contaminants being largely converted to the two latter phases [15]. In addition, it was known that garnet is a host phase for accommodation of fission products (rare earth elements), actinides and some corrosion products (Fe, Al), and that spinel can be incorporated various corrosion products and processing contaminants (Fe, Ni, Mn, Cr).

In this study, we selected the polyphase ceramic ($Gd_3Fe_2Al_3O_{12}$+(Ni_xMn_{1-x})(Fe_yCr_{y-1})$_2O_4$: x=0.1-0.9 and y=0.1-0.9) that contained garnet considered as a promising waste form and spinel composition, examined phase relation and physicochemical properties of coexisted phases in the compositions and confirmed accommodation relation of elements and phases.

EXPERIMENTAL

The synthesis of polyphase ceramic was performed by the Cold Press and Sintering (CPS) method. Gd_2O_3 (Cerac Co., 3N), Fe_2O_3 (Rare Metallic Co., 3N), Al_2O_3 (Rare Metallic Co., 3N), Cr_2O_3 (Rare Metallic Co., 3N), MnO (Rare Metallic Co., 3N) and NiO (High Purity Chemicals, 3N) were used as starting materials. These powders were mixed in the appropriate ratios, $Gd_3Fe_2Al_3O_{12}+(Ni_xMn_{1-x})(Fe_yCr_{1-y})_2O_4$ (x and y=0.1-0.9) with alcohol, using an alumina mortar and pestle. The mixed powders were pressed into pellets (10-mm diameter x 2-mm height) at a pressure of 400 kg/cm^2. The pellets were sintered at 1400-1600°C for 20 hr. Phase identification was determined by X-ray diffraction (reflection mode, CuKa radiation) using a Phillips X'pert MPD X-ray diffractometer attached with a graphite monochromer. The compositions of synthetic phases were analyzed with a SEM/EDS analyzer.
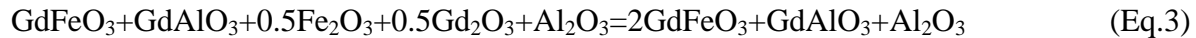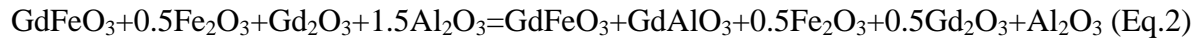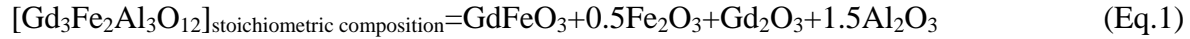
RESULTS

The Synthesis of Garnet

Gd_2O_3, Al_2O_3, and perovskite-I (d=2.7A) were observed at 1000°C (Table I). Perovskite-II (d=2.6A) first was formed, and perovskite-I showed the strongest intensity at 1100°C. Garnet was first formed along with the disappearance of Gd_2O_3 at 1200°C. Perovskite-I, Al_2O_3 and perovskite-II disappeared at 1300°C, 1400°C and 1500°C, respectively. Single phase of garnet was synthesized at 1500°C (Table I) and the XRD pattern of specimen did not change even at 1600°C. Accordingly, 1500°C seems to be the optimal synthetic temperature of garnet was 1500°C. Considering d values of the strongest peaks of perovskite-I and perovskite-II, they were turned out to be $GdFeO_3$ and $GdAlO_3$, respectively.

Table I.   Relative Intensities of Phases synthesized in the Composition of $Gd_3Fe_2Al_3O_{12}$.

No.	Conditions			Gd_2O_3	Al_2O_3	P-I [a]	P-II [b]	G [c]
	Temp.	Hours	At					
$Gd_3Fe_2Al_3O_{12}$								
GFG-63	1000	20	O_2	100	18	53	-	-
GFG-65	1100	20	O_2	51	17	100	39	-
GFG-57	1200	20	O_2	-	14	100	24	58
GFG-59	1300	20	O_2	-	4	28	-	100
GFG-61	1400	20	O_2	-	-	5	-	100
GFG-67	1500	20	O_2	-	-	-	-	100
GFG-69	1600	20	O_2	-	-	-	-	100

[a] perovskite, d=2.7A, [b] perovskite, d=2.6A, [c] Garnet

In the results of SEM/EDS analysis, garnet observed in matrix, coexisted with minor perovskite and Al_2O_3, an abrasive material in the holes. The composition of garnet was $Gd_{3.5-3.6}Fe_{2.4-2.5}Al_{1.9-2.0}O_{12}$ which the content of Gd and Fe were excessive, whereas that of Al was depleted. It suggested that such nonstoichiometric compositions of garnets were due to the formation of perovskite. Based on XRD data, the reaction equation in the chemical composition can be inferred as the following equations:

$$[Gd_3Fe_2Al_3O_{12}]_{stoichiometric\ composition}=GdFeO_3+0.5Fe_2O_3+Gd_2O_3+1.5Al_2O_3 \qquad (Eq.1)$$

$$GdFeO_3+0.5Fe_2O_3+Gd_2O_3+1.5Al_2O_3=GdFeO_3+GdAlO_3+0.5Fe_2O_3+0.5Gd_2O_3+Al_2O_3 \ (Eq.2)$$

$$GdFeO_3+GdAlO_3+0.5Fe_2O_3+0.5Gd_2O_3+Al_2O_3=2GdFeO_3+GdAlO_3+Al_2O_3 \qquad (Eq.3)$$

$$2GdFeO_3+GdAlO_3+Al_2O_3=Gd_3Fe_2Al_3O_{12} \qquad (Eq.4)$$

The peak of Fe_2O_3 in Eq. 1 was not observed clearly in the XRD pattern, but the peaks of Fe_2O_3 were observed faintly. It would be attributed to the small content of Fe_2O_3 at 1000^oC. With the increase of temperature, perovskite-II was formed (Eq. 2) and the intensity of perovskite-I increased (Eq. 3). The reaction of Gd_2O_3-Fe_2O_3, and Gd_2O_3-Al_2O_3 were followed by the increase of intensity of perovskite-I and the formation of perovskite-II, respectively. Finally, garnet was formed by Eq. 4. Of course, these equations do not distinctly show all reactions which can be occurred in this composition, but they indicate systematically the process of the formation of garnet.

The Synthesis of Spinel

We selected $(Ni_xMn_{1-x})(Fe_yCr_{1-y})_2O_4$ as the composition of spinel considering the composition of liquid HLW from reprocessing, and carried out the synthetic experiment of spinel (Table II). In the results of XRD analysis, single phases of spinels were observed in the temperature range of 1100 and 1300^oC except the composition of x=0.1 and y=0.9. In low temperatures, coexisted phases were closely related to the stoichiometric compositions, especially the mixed oxides of Cr_2O_3 and Fe_2O_3 were always observed at y=0.5.

The compositions of spinels were similar to the stoichiometric compositions as follows: $(Ni_{0.0-0.1}Mn_{0.9-1.0})(Fe_{0.1-0.1}Cr_{0.9-1.0})_2O_4$ (x=0.1 and y=0.1), $(Ni_{0.6}Mn_{0.5})(Fe_{0.1}Cr_{0.9})_2O_4$ (x=0.5 and y=0.1), $(Ni_{0.7-0.9}Mn_{0.2-0.3})(Fe_{0.1}Cr_{0.9})_2O_4$ (x=0.9 and y=0.1), $(Ni_{0.1}Mn_{0.9-1.0})(Fe_{0.5}Cr_{0.5})_2O_4$ (x=0.1 and y=0.5), $(Ni_{0.5-0.6}Mn_{0.5})(Fe_{0.5-0.6}Cr_{0.4-0.5})_2O_4$ (x=0.5 and y=0.5), $(Ni_{0.9-1.0}Mn_{0.1-0.2})(Fe_{0.4-0.5}Cr_{0.5})_2O_4$ (x=0.9 and y=0.5), $(Ni_{0.1}Mn_{1.0})(Fe_{0.8}Cr_{0.1})_2O_4$ (x=0.1 and y=0.9), $(Ni_{0.5}Mn_{0.5})(Fe_{0.9}Cr_{0.1})_2O_4$ (x=0.5 and y=0.9), $(Ni_{0.8-0.9}Mn_{0.1})(Fe_{0.9}Cr_{0.1-0.2})_2O_4$ (x=0.9 and y=0.9).

The Synthesis of Polyphase Ceramics

As described above, single phases of garnet and spinel were formed at 1500°C and 1200-1300°C, respectively. From these results, we performed the synthetic experiment of polyphase ceramic in the temperature range of 1400-1600°C. Two types of phase assemblages observed: garnet-perovskite-spinel and garnet-spinel (Table III).

In the cases of the lowest content of Fe (y=0.1), the diffraction intensities of garnets were reversely proportional to temperature, but garnet showed the strongest intensity except these compositions (x=0.1-0.9 and y=0.1). The intensities of perovskites increased with temperature but they decreased with the content of Fe. Especially, perovskite did not observe in the highest content of Fe (Table III and Fig. 1). Although garnet and perovskite showed the change of intensity with temperature or the content of Fe, the intensities of spinels were relatively regular (Table III).

Table II.   Relative Intensities of Phases synthesized in the Composition of $(Ni_xMn_{1-x})(Fe_yCr_{1-y})_2O_4$.

No.	Temp.	hours	At	Fe2O3	Cr2O3	Mn2O3	Fe-Cr oxide	Sp
(Ni0.1Mn0.9)(Fe0.1Cr0.9)2O4								
SP-33	1000	20	O2	-	4	-	-	100
SP-21	1100	20	O2	-	2	-	-	100
SP-25	1200	20	O2	-	-	-	-	100
SP-29	1300	20	O2	-	-	-	-	100
(Ni0.5Mn0.5)(Fe0.1Cr0.9)2O4								
SP-3	1000	20	O2	-	14	-	-	100
SP-8	1100	20	O2	-	7	-	-	100
SP-13	1200	20	O2	-	2	-	-	100
SP-18	1300	20	O2	-	-	-	-	100
(Ni0.9Mn0.1)(Fe0.1Cr0.9)2O4								
SP-35	1000	20	O2	-	14	-	-	100
SP-23	1100	20	O2	-	6	-	-	100
SP-27	1200	20	O2	-	-	-	-	100
SP-31	1300	20	O2	-	-	-	-	100
(Ni0.1Mn0.9)(Fe0.5Cr0.5)2O4								
SP-5	1000	20	O2	-	-	-	24	100
SP-10	1100	20	O2	-	-	-	26	100
SP-15	1200	20	O2	-	-	-	-	100
SP-20	1300	20	O2	-	-	-	-	100
(Ni0.5Mn0.5)(Fe0.5Cr0.5)2O4								
SP-2	1000	20	O2	-	-	-	24	100
SP-7	1100	20	O2	-	-	-	5	100
SP-12	1200	20	O2	-	-	-	-	100
SP-17	1300	20	O2	-	-	-	-	100
(Ni0.9Mn0.1)(Fe0.5Cr0.5)2O4								
SP-4	1000	20	O2	-	-	-	19	100
SP-9	1100	20	O2	-	-	-	8	100
SP-14	1200	20	O2	-	-	-	1	100
SP-19	1300	20	O2	-	-	-	-	100
(Ni0.1Mn0.9)(Fe0.9Cr0.1)2O4								
SP-34	1000	20	O2	52	-	100	-	32
SP-22	1100	20	O2	98	-	-	-	100
SP-26	1200	20	O2	78	-	-	-	100
SP-30	1300	20	O2	61	-	-	-	100
(Ni0.5Mn0.5)(Fe0.9Cr0.1)2O4								
SP-1	1000	20	O2	28	-	-	-	100
SP-6	1100	20	O2	8	-	-	-	100
SP-11	1200	20	O2	-	-	-	-	100
SP-16	1300	20	O2	-	-	-	-	100
(Ni0.9Mn0.1)(Fe0.9Cr0.1)2O4								
SP-36	1000	20	O2	15	-	-	-	100
SP-24	1100	20	O2	-	-	-	-	100
SP-28	1200	20	O2	-	-	-	-	100
SP-32	1300	20	O2	-	-	-	-	100

Table III.   Relative Intensities of Phases synthesized with the Batch Composition, $Gd_3Fe_2Al_3O_{12} +(Ni_xMn_{1-x})(Fe_yCr_{1-y})_2O_4$.

	T.	Hr	At	Pe	Sp	Gat
	$Gd_3Fe_2Al_3O_{12}+(Ni_{0.1}Mn_{0.9})(Fe_{0.1}Cr_{0.9})_2O_4$					
GFA-26	1400	20	Air	59	54	100
GFA-30	1500	20	Air	100	57	73
GFA-34	1600	20	Air	100	36	17
	$Gd3Fe2Al3O12+(Ni0.5Mn0.5)(Fe0.1Cr0.9)_2O_4$					
GFA-3	1400	20	Air	72	34	100
GFA-8	1500	20	Air	100	42	30
GFA-13	1600	20	Air	100	36	20
	$Gd3Fe2Al3O12+(Ni0.9Mn0.1)(Fe0.1Cr0.9)_2O_4$					
GFA-28	1400	20	Air	100	42	63
GFA-32	1500	20	Air	100	37	24
GFA-36	1600	20	Air	100	38	15
	$Gd3Fe2Al3O12+(Ni0.1Mn0.9)(Fe0.5Cr0.5)_2O_4$					
GFA-5	1400	20	Air	5	39	100
GFA-10	1500	20	Air	22	46	100
GFA-15	1600	20	Air	91	48	100
	$Gd3Fe2Al3O12+(Ni0.5Mn0.5)(Fe0.5Cr0.5)_2O_4$					
GFA-2	1400	20	Air	9	27	100
GFA-7	1500	20	Air	34	24	100
GFA-12	1600	20	Air	98	87	100
	$Gd3Fe2Al3O12+(Ni0.9Mn0.1)(Fe0.5Cr0.5)_2O_4$					
GFA-4	1400	20	Air	21	33	100
GFA-9	1500	20	Air	46	29	100
GFA-14	1600	20	Air	84	44	100
	$Gd3Fe2Al3O12+(Ni0.1Mn0.9)(Fe0.9Cr0.1)_2O_4$					
GFA-27	1400	20	Air	-	40	100
GFA-31	1500	20	Air	-	13	100
GFA-35	1600	20	Air	Melt		
	$Gd3Fe2Al3O12+(Ni0.5Mn0.5)(Fe0.9Cr0.1)_2O_4$					
GFA-1	1400	20	Air	-	16	100
GFA-6	1500	20	Air	-	19	100
GFA-11	1600	20	Air	Melt		
	$Gd3Fe2Al3O12+(Ni0.9Mn0.1)(Fe0.9Cr0.1)_2O_4$					
GFA-29	1400	20	Air	14	22	100
GFA-33	1500	20	Air	16	20	100
GFA-37	1600	20	Air	21	27	100

Figure 2 shows the back scattered electron (BSE) images of specimens sintered in the temperature range of 1400 and 1600°C. In all specimens, garnet, perovskite or spinel was observed as an aggregate form except some cases. The compositions of garnets were $Gd_{3.3-3.7}Fe_{2.1-3.6}Al_{0.8-1.9}O_{12}$ (included Cr: 0.2-0.6 and Ni: 0-0.1 in atomic number) which were

nonstoichiometric (Table IV). Their compositions were varied with the batch composition but had in common with each other in that Gd and Fe were excessive, Al was depleted, and Cr and Ni were contained. The excess of Gd indicated that this polyphase ceramics were good waste forms to immobilize more content of actinide. The compositions of spinels were very irregular at small content of Fe ($y=0.1$) and the contents of Fe were excessive. Also, 0.2-0.5 mole Al was contained in all compositions. The compositions of perovskites were $Gd_{1.0-1.1}Fe_{0.2-0.6}Al_{0.2-0.4}Cr_{0.1-0.5}O_3$ with deviations of composition.
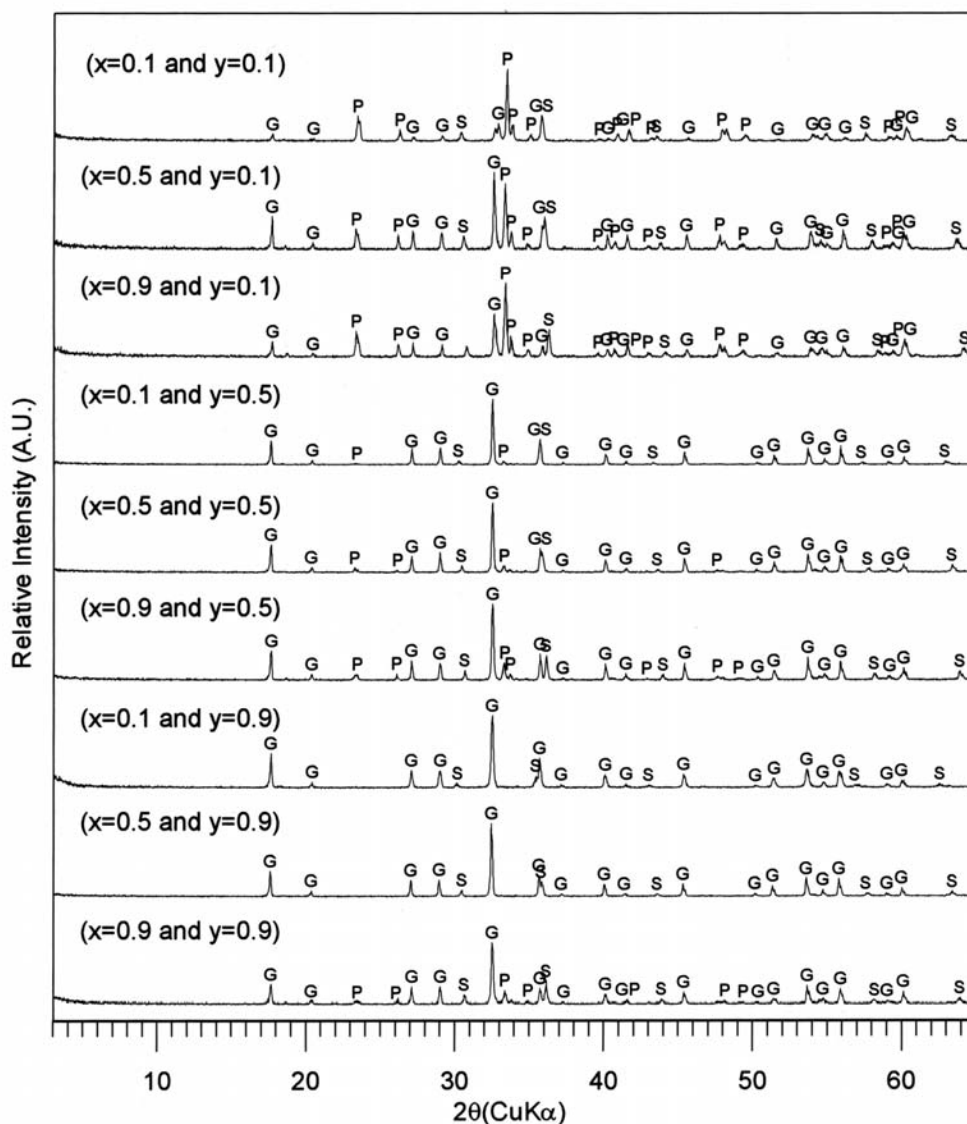

Fig. 1.　XRD patterns of $Gd_3Fe_2Al_3O_{12}+(Ni_xMn_{1-x})(Fe_yCr_{1-y})_2O_4$. G: garnet, P: perovskite and S: spinel.
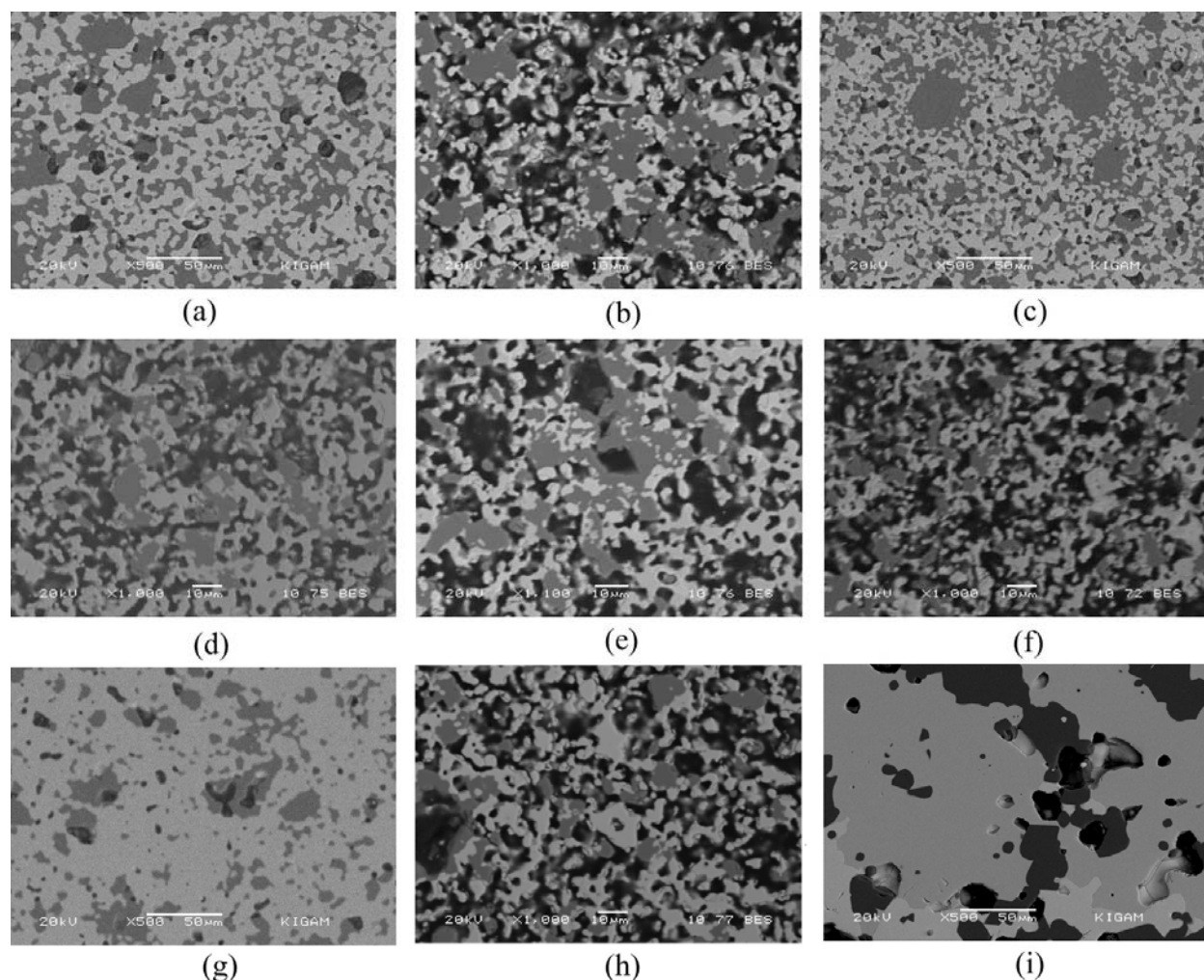
Fig. 2.   BSE (Back Scattered Electron) images of samples synthesized with $Gd_3Fe_2Al_3O_{12}+(Ni_xMn_{1-x})(Fe_yCr_{1-y})_2O_4$ in O_2. (a) GFA-34 (x=0.1, y=0.1; 1600℃/20hrs), (b) GFA-3 (x=0.5, y=0.1; 1400℃/20hrs), (c) GFA-36 (x=0.9, y=0.1; 1600℃/20hrs), (d) GFA-5 (x=0.1, y=0.5; 1400℃/20hrs), (e) GFA-2 (x=0.5, y=0.5; 1400℃/20hrs), (f) GFA-4 (x=0.9, y=0.5; 1400℃/20hrs), (g) GFA-31 (x=0.1, y=0.9; 1500℃/20hrs), (h) GFA-1 (x=0.5, y=0.9; 1400℃/20hrs), (i) GFA-37 (x=0.9, y=0.9; 1600℃/20hrs). White (Perovskite); Gray (Garnet); Dark gray (Spinel or Fe_2O_3); Black (Holes)

In results, the compositions of garnet and spinel show nonstoichiometric properties. Garnet contained the excess of Gd and Fe along with Cr from spinel composition in all compositions. In the case that perovskite had the strongest diffraction intensity (x=0.1, x= 0.9 and y=0.9), the nonstoichiometric character was more intensive than in the case that garnet had the strongest intensities. But perovskite had relative regular composition. Accordingly, the nonstoichiometric compositions of garnet and spinel were attributed to the formation of perovskite in that perovskite contained both elements of Gd, Fe and Al from garnet, and Cr from spinel.

Table IV. Chemical Formula of Phases which were contained Matrices synthesized with the Precursor Composition of $Gd_3Fe_2Al_3O_{12}+(Ni_xMn_{1-x})(Fe_yCr_{1-y})_2O_4$.

x	y	Garnet	Spinel	Perovskite
0.1	0.1	-	$(Ni_{0.1}Mn_{0.6})(Fe_{0.5-0.6}Cr_{0.3})_2O_4$ (Al: 0.4)	$Gd_{1.1}(Fe_{0.2-0.3}Al_{0.2}Cr_{0.5})O_3$
0.5	0.1	-	$(Ni_{0.3}Mn_{0.4-0.5})(Fe_{0.4}Cr_{0.3})_2O_4$ (Al: 0.6)	$Gd_{1.1}(Fe_{0.2-0.3}Al_{0.2-0.3}Cr_{0.3-0.4})O_3$
0.9	0.1	-	$(Ni_{0.6}Mn_{0.1})(Fe_{0.6}Cr_{0.3})_2O_4$ (Al: 0.5)	$Gd_{1.0-1.1}(Fe_{0.3}Al_{0.2}Cr_{0.5})O_3$
0.1	0.5	$Gd_{3.4-3.5}Fe_{2.2-2.3}Al_{1.7-1.8}O_{12}$ (Cr: 0.5-0.6, Ni: 0-0.1)	$(Ni_{0.1}Mn_{0.8-0.9})(Fe_{0.6}Cr_{0.2})_2O_4$ (Al: 0.4)	-
0.5	0.5	$Gd_{3.5-3.7}Fe_{2.2-2.4}Al_{1.4-1.7}O_{12}$ (Cr: 0.5-0.7)	$(Ni_{0.4-0.5}Mn_{0.5})(Fe_{0.6}Cr_{0.2})_2O_4$ (Al: 0.5)	-
0.9	0.5	$Gd_{3.5}Fe_{2.1}Al_{1.8-1.9}O_{12}$ (Cr: 0.6)	$(Ni_{0.8-0.9}Mn_{0.1})(Fe_{0.5-0.6}Cr_{0.2})_2O_4$ (Al: 0.6)	$Gd_{1.0-1.1}(Fe_{0.4}Al_{0.2-0.4}Cr_{0.2-0.3})O_3$
0.1	0.9	$Gd_{3.3-3.4}Fe_{3.5-3.6}Al_{0.8-0.9}O_{12}$ (Cr: 0.2)	$(Ni_{0.1}Mn_{0.9})(Fe_{0.8}Cr_{0.1})_2O_4$ (Al: 0.2-0.3)	-
0.5	0.9	$Gd_{3.4}Fe_{2.8-2.9}Al_{1.5-1.6}O_{12}$ (Cr: 0.2)	$(Ni_{0.5}Mn_{0.5})(Fe_{0.7}Cr_{0.05})_2O_4$ (Al: 0.5)	-
0.9	0.9	$Gd_{3.4}Fe_{3.3}Al_{1.1}O_{12}$ (Cr: 0.2)	$(Ni_{0.8}Mn_{0.1})(Fe_{0.8}Cr_{0.05})_2O_4$ (Al: 0.4)	$Gd_{1.1}(Fe_{0.6}Al_{0.2}Cr_{0.1})O_3$

CONCLUSIONS

In this study, polyphase waste form in the system of Gd-Fe-Al-Ni-Mn-Cr-O was synthesized using Gd as an imitator of Pu, phase relation and physicochemical properties of coexisted phases was examined in the system, and it was confirmed the accommodation relation of elements and phases. Two types of phase series, namely garnet-perovskite-spinel and garnet-spinel were observed in the synthetic experiment of polyphase ceramic in the temperature range of 1400-1600°C.

The compositions of garnets were nonstoichiometric: Gd and Fe were excessive, Al was depleted and Cr and Ni were contained. The excess of Gd indicated that this polyphase ceramic was in a good waste forms to immobilize more actinide content.

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The compositions of spinels also revealed nonstoichiometric: the excess of Fe and the addition of 0.2-0.5 mole Al. Those of perovskites were $Gd_{1.0-1.1}Fe_{0.2-0.6}Al_{0.2-0.4}Cr_{0.1-0.5}O_3$ with deviations of composition.

Accordingly, the nonstoichiometirc compositions of garnet and spinel were attributed to the formation of perovskite in that perovskite contained both elements of Gd, Fe and Al from garnet, and Cr from spinel.

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