

Reactions of rare earth acetates with aluminum isopropoxide in ethylene glycol: Synthesis of the garnet and monoclinic phases of rare earth aluminates

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The reactions of mixtures of rare earth (RE) acetates and aluminum isopropoxide (Al/RE = 3/5) in ethylene glycol at 300 °C afforded amorphous products. The IR spectra of these products were essentially identical with each other and indicated the presence of an acetate group and ethylene glycol moiety. When the content of RE (La–Gd) acetate in the starting mixture was increased, a crystalline glycol complex of RE oxide acetate was also formed together with the amorphous phase, but the reactions of acetates of the smaller RE ions (Tb–Lu) yielded amorphous products with wider compositions (Al/RE = 5/3–1/6). Phase-pure RE₃Al₅O₁₂ (garnet) and RE₄Al₂O₉ (monoclinic) were obtained by calcination of the amorphous products with the corresponding stoichiometric compositions at low temperatures. © 1998 Kluwer Academic Publishers

1. Introduction

In the rare earth (RE) oxide–aluminum oxide pseudo-binary systems, there exist four phases, monoclinic RE₄Al₂O₉, REAlO₃ having the perovskite structure, RE₃Al₅O₁₂ having the garnet structure and RE₂O₃·11Al₂O₃ with a β -alumina-type structure [1–4]. The stabilities of these phases depend on the ionic size of the RE element. The garnet phases were reported to be thermodynamically stable for all the RE elements from Tb to Lu. Although a number of papers have reported the synthesis of Gd₃Al₅O₁₂ [5–9], this garnet has not appeared in the Gd₂O₃–Al₂O₃ stable phase diagram [10–13]. It is known that lattice strain of the perovskite phase increases with the decrease in the ionic size of the RE element, and YbAlO₃ was reported to be a metastable phase [14], although single-phase YbAlO₃ has been prepared [15, 16]. The monoclinic phases with the RE elements, Nd~Lu and Y, have been prepared, but Nd₄Al₂O₉ did not appear in the Nd₂O₃–Al₂O₃ stable phase diagram reported by Mizuno *et al.* [17]. The RE₂O₃·11Al₂O₃ phase is known for La~Nd [18]. However, the phase diagrams are still controversial because of complex solidification behavior of the melt [19–22].

Among these RE aluminum binary oxides, yttrium aluminum garnet (YAG, Y₃Al₅O₁₂) has been studied most extensively because it is now widely used in lasers [23, 24]. Because large single crystals are required for this use, most work has been directed toward flux growth, Verneuil-flame fusion, Czochralski-pulling from the melt or the floating zone method [25, 26]. The powder of YAG is used as phosphors [27], and polycrystalline YAG has a potential use as

an advanced ceramic material [28–31] and for lasers [32, 33]. However, synthesis of YAG by the reaction of mixed aluminum and yttrium oxide powders normally requires a temperature higher than 1600 °C with a prolonged heating period. If processing temperatures are too low, the product contains additional phases (e.g., YAlO₃ and Y₄Al₂O₉) [3, 34–36]. Thus, to lower the crystallization temperature of YAG by preparing the starting materials in which aluminum and yttrium atoms are homogeneously mixed, several methods have been developed: Thermal decomposition of a hydrated nitrate mixture [37], alkoxide processes [38–41], coprecipitation methods [36, 42, 43], carboxylate complex methods [44, 45] and a reverse strike precipitation method [46] have been reported. However, these processes still required calcination temperatures higher than 1000 °C to crystallize the YAG phase.

Hydrothermal synthesis of YAG was reported by several workers. In all cases, higher temperatures (350–600 °C) and pressures (70–175 MPa) [47–50] were required to form single-phase YAG. Moreover, with the increase in ionic size of the RE element, the hydrothermal synthesis of aluminum garnet needs more severe conditions, and the lower temperature limit for the hydrothermal synthesis of Tb₃Al₅O₁₂ was reported to be 420–450 °C [47].

Besides the garnet phase, the monoclinic phase also gathers interest as a new ceramic material because it shows martensitic transformation at temperatures higher than zirconia [51, 52].

Only a few works have addressed the use of organic media in place of water for the hydrothermal method. Thus, Bibby and Dale synthesized

silica–sodalite, a novel compound that cannot be prepared from the aqueous system [53]. Fanelli and Burlew reported the synthesis of fineparticle-size transition alumina by the treatment of aluminum *sec*-butoxide in *sec*-butanol [54]. Figlarz *et al.* reported the synthesis of metal powders of nickel, cobalt and platinum group metals by the treatment of metal hydroxide in glycol [55].

The present authors have explored the synthesis of inorganic materials in organic media at elevated temperatures (200–300 °C) under autogenous pressure of the organics [56–60] and found that single-phase yttrium aluminum garnet ($Y_3Al_5O_{12}$) was directly formed by the reaction of the stoichiometric mixture of aluminum isopropoxide (AIP) and yttrium acetate in 1,4-butanediol (1,4-BG) at 300 °C [59, 60]. This reaction procedure was termed “glycothermal” because of the use of glycol in place of water for hydrothermal reaction. Neither $YAlO_3$ nor $Y_4Al_2O_9$ was formed, and YAG was the only binary oxide detected in the products from the starting composition of the Y/Al ratio of 0.05–2 [60]. Preferential formation of garnet is rather surprising, because nucleation of the garnet phase from the melt was reported to be a difficult process, which was attributed to the complex crystal structure of garnet, counting eight formula units of $RE_3Al_5O_{12}$ and a total of 160 atoms in each unit cell [11]. It was also found that the glycothermal method can be applied for the synthesis of other RE aluminum garnets and that samarium and europium aluminum garnets that have never been prepared by any other methods were also formed by this method [60].

The present authors also reported the formation of the other binary oxides such as $ZnAl_2O_4$ (spinel) [61], $LiNbO_3$ (ilmenite) [62] and $Gd_3Ga_5O_{12}$ (garnet) [63] by the glycothermal reactions of the mixtures of the two starting materials (alkoxide, acetylacetonate or acetate). An interesting point of this procedure is that crystalline products were directly formed by the reaction, whereas alkoxides subjected to hydrolysis usually afford amorphous products.

In this paper, we explored the reactions of the mixtures of aluminum isopropoxide and RE acetates in ethylene glycol (EG) to elucidate the mechanism for the formation of garnets under glycothermal conditions.

2. Experimental procedure

2.1. Materials

Aluminum isopropoxide (AIP; extra pure grade, Nacal Tesq) was used without further purification. Acetates of the RE elements and glycols were purchased from Wako Pure Chemical Industry.

2.2. Typical reaction procedure

Aluminum isopropoxide (4.26 g, 20.8 mmol) and yttrium acetate (4.24 g, 12.5 mmol) were suspended in 88 ml of EG in a test tube serving as an autoclave liner, and the mixture was placed in a 200-ml autoclave. An additional 18 ml of EG were placed in the gap between the autoclave wall and the test tube. The autoclave was

completely purged with nitrogen, heated to the desired temperature (usually 300 °C) at a rate of 2.3 °C/min, and kept at that temperature for 2 h. The resulting products were gelatinous and were not sedimented by centrifuging. Concentrated ammonium hydroxide solution was added dropwise to the mixture until the upper part of the mixture became clear and particles began to settle. The mixture was then centrifuged, and the product was repeatedly washed with methanol by vigorous mixing and centrifuging.

2.3. Analyses

X-ray powder diffraction (XRD) was determined on a Shimadzu XDD1 diffractometer using $CuK\alpha$ radiation and a carbon monochromator. Infrared (IR) spectra were recorded on a Shimadzu IR-430 spectrometer using the usual KBr technique or on a Jeol JIR-6500 Fourier transformation infrared (FTIR) spectrometer using the diffuse reflectance method. Thermal analyses were performed on a Shimadzu TG-50 thermal analyzer at a heating rate of 10 °C/min in a 40 ml/min flow of dried air.

3. Results and discussion

3.1. Reactions of aluminum isopropoxide and RE acetates with the garnet composition in EG

The reactions of mixtures of AIP and RE acetates (Al/RE = 5/3, stoichiometric composition for garnet) in EG at 300 °C afforded amorphous products, except for lanthanum acetate where a small amount of a crystalline phase was formed together with the amorphous phase (see below). As reported previously [59, 60], the use of 1,4-BG in place of EG of the present procedure gave microcrystalline aluminum garnets for the reaction of Sm~Lu. Therefore, the present result shows a clear contrast against the results reported previously and confirms the argument that 1,4-BG is specific for the formation of crystalline binary oxides in the glycothermal reactions [60].

The glycothermal reaction of AIP alone affords the glycol derivative of boehmite [56, 64, 65], the crystallite size of which varied with carbon number of glycol and increased in the following order: $2 < 3 < 6 \ll 4$ (carbon number of glycol) [65]. This result was interpreted in terms of heterolytic cleavage of the C–O bond of $HO(CH_2)_n-O-Al<$ formed by the alkoxyl exchange reaction; when 1,4-BG ($n = 4$) was used, the cleavage of the C–O bond in $HO(CH_2)_4-O-Al<$ proceeds most easily because of intramolecular participation of the hydroxyl group [66]. Similarly, the formation of the amorphous product in the present reaction can be interpreted by the difficulty in the cleavage of the C–O bond of the intermediate glycoxide formed by the reaction of AIP with ethylene glycol, whereas the ease in the cleavage of the C–O bond seems to be the prime factor for the formation of crystalline garnets by the reaction in 1,4-BG.

The glycothermal reactions of RE acetates alone in EG yielded two novel crystalline products depending

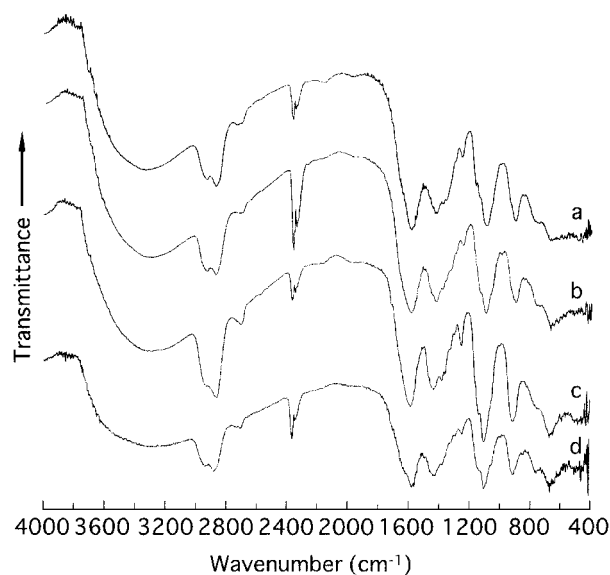


Figure 1 FTIR spectra of the products obtained by the reaction of (a) cerium acetate; (b) europium acetate; (c) holmium acetate; and (d) ytterbium acetate; with aluminum isopropoxide (Al/RE = 5/3) in ethylene glycol at 300 °C for 2 h.

on ionic size of the RE element [67]. One, designated as Phase A, was formed from the acetates of La~Gd and the other, designated as Phase B, from the acetates of Tb~Lu and Y. These phases were glycol complexes of RE acetate (hydroxide) oxide, and empirical formulas were tentatively assigned as $\text{RE}_2\text{O}(\text{OCH}_2\text{CH}_2\text{O})(\text{OCOCH}_3)_2$ (Phase A) and $\text{RE}_2\text{O}(\text{OCH}_2\text{CH}_2\text{OH})_2(\text{OCOCH}_3)(\text{OH})$ (Phase B) [67]. Because the reactions of the mixtures of AIP and RE acetates gave amorphous products, the presence of AIP in the reactions of RE acetate somehow prevented the development of the crystalline structures of these glycol complexes.

Some representative IR spectra of the products obtained by the reactions of AIP and RE acetates are shown in Fig. 1. All the products exhibited essentially the same IR spectra. Absorption bands due to the acetate group were observed at 1425 and 1580 cm^{-1} . The spectra at this region resembled, to some extent, those of the Phase B products, but Phase B showed characteristic bands due to the structural OH group [67], whereas these bands were not observed in the present products. The strong absorption bands at approximately 1095 and 900 cm^{-1} are attributed to the EG moiety. With the decrease in ionic size of the RE element, slight but significant shifts of both of these two bands toward higher frequency were observed, which suggests the presence of some interaction between the EG moiety and RE elements.

When the amorphous products were calcined at 1100 °C for 30 min, aluminum garnets were crystallized for the RE elements of Tb~Lu. Because gadolinium aluminum garnet is a metastable phase, all the thermodynamically stable garnets can be prepared by calcination of the present products at relatively low temperatures. For the products obtained from the acetates of La~Gd, except Ce, the perovskite phase was crystallized. The product obtained by the reaction of the mixture of cerium acetate and AIP showed rather

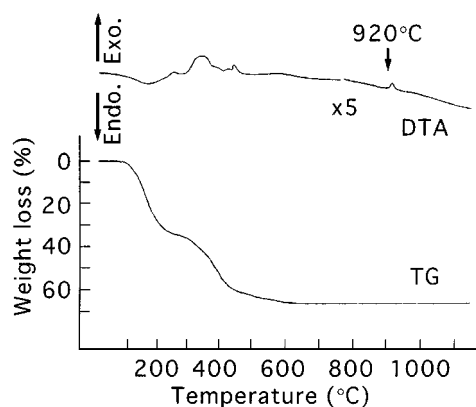


Figure 2 Thermal analyses of the product obtained by the reaction of yttrium acetate with aluminum isopropoxide (Al/Y = 5/3) in ethylene glycol at 300 °C for 2 h.

unexpected behavior: In the XRD pattern of the calcined product, only CeO_2 was detected and aluminum phases were not detected. Calcination of the product obtained from Pr acetate also gave Pr_4O_{13} together with the perovskite phase.

The results of simultaneous thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of the product obtained from yttrium acetate and AIP are shown in Fig. 2 as representative data. The TGA trace showed gradual weight decrease from room temperature to ~200 °C with an endothermic response in DTA. This weight decrease is attributed to desorption of water and/or EG molecules adsorbed or occluded in the product. The second weight decrease was observed at the temperature range of 300~400 °C with a highly exothermic response in DTA. This weight decrease is explained by the oxidative degradation of organic moieties present in the product. At 920 °C, an exothermic peak was observed, which was not associated with the weight change.

Crystallization behavior of YAG was examined by calcination of the product at the desired temperatures for 30 min. As shown in Fig. 3, the crystalline YAG phase was already observed in the sample calcined at 800 °C. Because of the difference in the heating profile, the final exothermic peak detected in DTA is attributed to the crystallization of the garnet phase. The crystallization was completed at 1000 °C, and at these temperatures a small amount of YAIO_3 (hexagonal) was also detected. Yamaguchi *et al.* also reported the formation of the hexagonal phase from the gel derived by the hydrolysis of an aluminum–yttrium double alkoxide [39, 40].

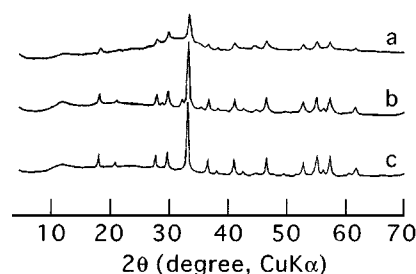


Figure 3 XRD patterns of the sample obtained by calcination of the glycolthermal product described in the caption of Fig. 2.

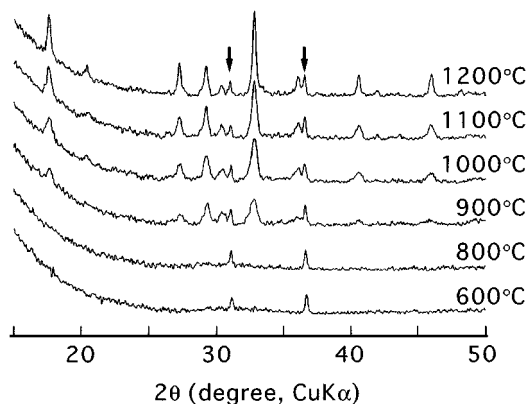


Figure 4 High-temperature XRD patterns of the product obtained by the reaction of erbium acetate with aluminum isopropoxide in ethylene glycol at 300 °C for 2 h. The peaks indicated by arrows are due to the sample holder (α -alumina).

Other products showed essentially the same thermal decomposition behavior. The exothermic peak due to the crystallization of the garnet phase was observed at around 930 °C, but crystallization of terbium aluminum garnet required a slightly higher temperature (956 °C). Because this garnet is the thermodynamically stable one with the largest RE ion, its crystallization seems to require additional thermal energy. A similar increase in crystallization temperature in the hydrothermal synthesis of aluminum garnets was reported [47]. The products of Sm and Gd also exhibited the exothermic peak due to the crystallization of the perovskite phase at 934 °C and 899 °C, respectively, but the other products obtained from La–Eu did not show the exothermic peak due to the crystallization of the perovskite phase.

High-temperature XRD patterns were also taken to examine the crystallization behavior of the products. Fig. 4 shows the crystallization of the garnet phase from the Er sample as a representative datum. The garnet phase crystallized at 900 °C, and no other phases were formed on further heating at higher temperatures.

3.2. Reactions of aluminum isopropoxide and RE acetates with various compositions in EG

Effects of the charged ratios of AIP to RE acetate on the reaction were examined for La, Gd, Tb and Y. Selection of Gd and Tb is based on the fact that the reaction of the acetate salts of these two neighboring elements in EG yielded different products: Phase A from Gd acetate and Phase B from Tb acetate [67]. As shown in Fig. 5, the product obtained by the reaction of AIP with lanthanum acetate with the charged ratio of Al/La = 5/3 was essentially amorphous, but a small amount of Phase A was detected in the product. With the increase in the La content in the starting mixture, intensities of the XRD peaks due to Phase A increased and unidentified phase was detected at $2\theta = 10.22, 10.75$ and 19.94° for the sample with Al/La = 2/3–1/3. For gadolinium acetate, the products from the mixtures of Al/Gd = 5/3–1/2 were amorphous (see Table I). Further increase in the gadolinium charged ratio (Al/Gd = 1/3–1/6) resulted in formation of Phase A in the product,

TABLE I Phases obtained by the glycothermal reaction of aluminum isopropoxide and RE acetate with various starting composition

Al/RE	Rare earth element			
	La	Gd	Tb	Y
5/3	Amr, PA	Amr	Amr	Amr
4/3	Amr, PA	Amr	Amr	Amr
1	Amr, PA	Amr	Amr	Amr
2/3	PA, UI	Amr	Amr	Amr
1/2	PA, UI	Amr	Amr	Amr
1/3	PA, UI	Amr, PA	Amr	Amr
1/6	PA	PA, Amr	Amr, PB	Amr, PB
0	PA	PA	PB	PB

Amr, Amorphous; PA, Phase A; UI, Unidentified; PB, Phase B

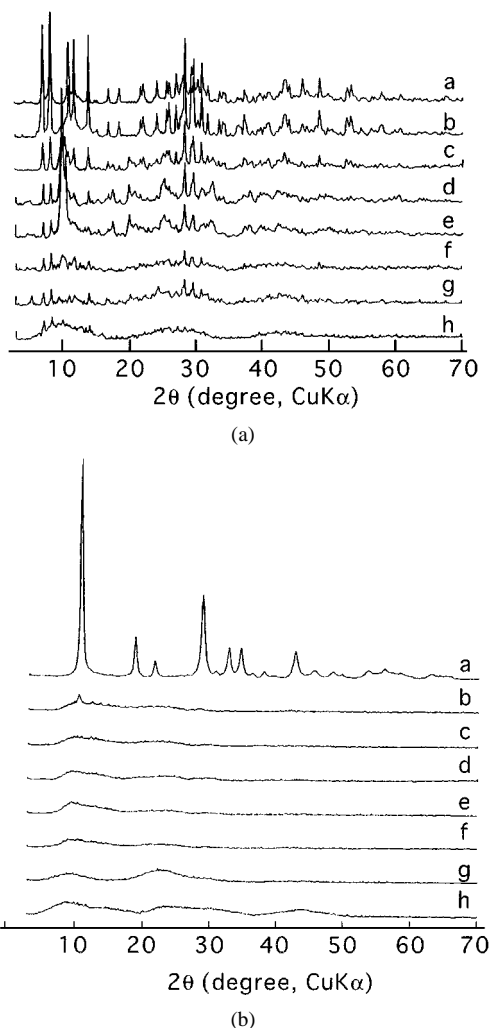


Figure 5 XRD patterns of the products obtained by the reactions of (A) lanthanum acetate and (B) yttrium acetate, with aluminum isopropoxide with the ratio of Al/RE = (a) 5/3; (b) 4/3; (c) 1; (d) 1/2; (e) 1/3; (f) 1/6; (g) 0 (that is, the reaction of rare earth alone); each in ethylene glycol at 300 °C for 2 h.

and intensities of the Phase A peaks increased with the increase in the Gd content in the starting mixture, suggesting that these products are mixtures of Phase A and the amorphous phase. The difference between the behavior of these two RE elements can be explained either by the decrease in the interaction between RE species and aluminum species or by the ease in the crystallization of Phase A with the increase in ionic size of the RE element.

TABLE II Phases crystallized from the products obtained by the glycothermal reaction of aluminum isopropoxide and RE acetate with various starting composition

Al/RE	Rare earth element			
	La	Gd	Tb	Y
5/3	P	P	G	G
4/3	P, (O)	P, (M, O)	P, G	G, P
1	P, O	P, (M, O)	P, M, G	G, P, M
2/3	O, P	P, M, (O)	P, M	P, M
1/2	O, P	M, (O)	M	M
1/3	O, P	M, O	M, (O)	M, O
1/6	O, (P)	O, M	O, M	O, M

G, garnet; P, perovskite; M, monoclinic phase; O, rare earth oxide

The phases detected in the samples obtained by the calcination of these products at 1200 °C for 30 min are summarized in Table II. On calcination of the products of Al/Gd = 4/3–2/3, perovskite was crystallized but small amounts of Gd oxide and the monoclinic phase were also detected. Calcination of the product of Al/Gd = 1/2 gave the monoclinic phase, but again a small amount of the oxide phase was detected. With further increase in the Gd content, the yield of the monoclinic phase decreased and the yield of Gd₂O₃ increased.

Calcination of the products obtained by the glycothermal reactions of La(OCOCH₃)₃ and AIP gave similar results. However, because the monoclinic phase is not thermodynamically stable in the La₂O₃–Al₂O₃ system [68–70], only perovskite and lanthanum oxide were detected. The yield of the perovskite increased with the increase in AIP content in the reaction mixture, and XRD patterns of the products from Al/La = 5/3 and 4/3 were due to the essentially pure perovskite phase. This does not mean, however, that aluminum species were not precipitated by the glycothermal reaction, but aluminum oxide was not detected by XRD because of its low crystallinity. It is known that the presence of lanthanum species retards phase transformation from amorphous to γ - to δ - to θ - and finally to α -alumina [71, 72].

Because the reaction product was the mixture of the amorphous phase and Phase A, lanthanum oxide seems to be formed from Phase A, and the perovskite phase is likely to be formed from the amorphous phase present in the products. Similarly, formation of small amounts of Gd₂O₃ from the amorphous products with Al/Gd = 4/3–1/2 suggests that Phase A with a very small crystallite size is contaminated in the products.

On the other hand, for the RE acetates that gave the Phase B products in their own reactions, their reactions with AIP afforded amorphous products for a wider range of the starting compositions (Table I). Although the reaction in the presence of a small amount of AIP (charged ratio Al/Y(Tb) = 1/6) gave a product that showed low intensity diffraction peaks due to Phase B, the products from the charged ratio of Al/Y(Tb) = 1/3–5/3 were amorphous. These results indicate that the development of the crystalline structure of Phase B was prevented by the addition of a very small amount of AIP to the reaction of yttrium (or

terbium) acetate, which seems to be due to the interaction between aluminum and RE species. Apparently, crystallization of Phase B was more severely affected by the presence of AIP than that of Phase A, a fact that may be connected with the fact that the Phase B products have much smaller crystallite size than the Phase A products.

When the amorphous products obtained by the reaction of AIP and yttrium or terbium acetate were calcined at 1300 °C, the garnet, perovskite and/or monoclinic phases were crystallized depending on the starting composition. Results are also given in Table II. Although from the composition of Al/RE = 1, the theoretical composition for the perovskite phase, the monoclinic and garnet phases were also crystallized together with the perovskite phase, single-phase monoclinic RE₄Al₂O₉ was obtained from the starting composition of Al/RE = 1/2. Because Al ions can easily diffuse into the RE₂O₃ matrix, the monoclinic phase always appears first in the solid-state reaction between Al₂O₃ and RE₂O₃ [36, 73]. However, formation of pure monoclinic phase by the solid-state reaction requires much higher temperatures with a prolonged heating period. It must be noted that from the products with the compositions of Al/RE = 5/3–1/2, neither Al₂O₃ nor RE₂O₃ was crystallized. Because of the relatively low crystallization temperature of RE₂O₃ [74], it would be formed, if a RE-rich phase such as Phase B were present in the products. This was not the case, suggesting that the products obtained from the above compositions are truly amorphous.

Gowda [38] examined crystallization behavior of the gels obtained by the hydrolysis of aluminum alkoxide and yttrium acetate by using a technique originally developed by Yoldas [75]. He found that the garnet and monoclinic phases crystallized from the gels with the composition of Al/Y = 5/3 and 1/2 but that from the gel with the composition of Al/Y = 1, crystallization of the monoclinic and garnet phases took place at lower temperatures followed by crystallization of the perovskite phase [38]. Therefore, the crystallization behavior of the present products was essentially identical to those of the gel obtained by Gowda using a sol–gel process.

It must be noted that the alkoxide process requires stringent control of hydrolysis condition and prevention of the partial hydrolysis of alkoxide before use. It was reported that direct hydrolysis of yttrium and aluminum alkoxides with the garnet composition yielded a diphasic gel, from which the monoclinic phase crystallized first [41]. On the other hand, the present method appears to be more straightforward and requires fewer precautions or no special equipment but an autoclave. Actually, we did not re-distill AIP before use; nevertheless, we achieved sufficient reproducibility of the reaction. This is closely connected with the fact that the glycothermal reactions of both AIP and aluminum hydroxide give the same product, the glycol derivative of boehmite, with the identical morphology [56, 65], which suggests that the two reactions proceed via the same intermediate. This is further connected with the fact that alkoxide and water is in equilibrium with hydroxide and alcohol [76]. Glycol, having a highly

hygroscopic nature, acts as a dehydration agent for hydroxide to yield glycoxide at high temperatures. Therefore, partially hydrolyzed AIP can be used for the present method (glycothermal reaction).

4. Conclusions

In conclusion, the reactions of mixtures of RE acetates and AIP (Al/RE = 3/5) in EG at 300 °C afforded amorphous products, which contained acetate groups and ethylene glycol moieties. Because the individual reactions of AIP and RE acetates yielded an EG derivative of boehmite and crystalline glycol complexes of RE acetate oxide (Phase A and Phase B), formation of the amorphous products suggested that interaction between two starting materials took place in the reaction. When the content of acetate of large RE ions (La–Gd) was increased, a crystalline phase (Phase A) was also formed together with the amorphous phase. On the other hand, the reaction of acetates of the smaller RE ions (Tb–Lu) afforded amorphous products with wider compositions (Al/RE = 5/3–1/6). Thermal transformation sequence of these amorphous products was essentially identical to that of the gels obtained by the sol–gel processes with controlled hydrolysis procedure or from a double alkoxide, and the garnet and monoclinic phases were crystallized at low temperatures. In the present procedure, the starting materials were thermally decomposed instead of the hydrolysis for the sol–gel process and stringent control of the hydrolysis conditions required by the sol–gel process can be avoided.

Acknowledgement

This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas “New Development of Rare Earth Complexes” No. 07230251 and 08220240 from The Ministry of Education, Science, Sports and Culture, Japan.

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*Received 14 July 1997
and accepted 6 August 1998*