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Synthesis of Yttrium Aluminum Garnet Precursor Powders by Homogeneous Precipitation

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Abstract

A study was performed to characterize the homogeneous precipitation of yttrium aluminum garnet (YAG) precursor particles by the thermal decomposition of urea in aqueous solutions. Cation concentrations were varied from 0·005 M to 0·30 M. Observation of powder morphology together with chemical analysis suggests a sequential precipitation process with aluminum ions forming a solid phase first. Fine-grained, reactive powders were obtained that crystallized to single-phase YAG upon heating to 850°C. The precipitate was a hydrated basic carbonate.

Die homogene Ausscheidung von Yttrium–Aluminium-Granat (YAG) Vorläuferteilchen, deren Herstellung durch thermische Zersetzung von Urea in wässriger Lösung erfolgte, wurde untersucht. Die Kationenkonzentration wurde zwischen 0·005 M und 0·3 M variiert. Aus der Pulvermorphologie in Kombination mit der chemischen Analyse läßt sich schließen, daß ein sequenzieller Ausscheidungsprozeß stattfindet, beginnend mit den Aluminiumionen, die eine feste Phase bilden. Es konnten feinkörnige, reaktive Pulver hergestellt werden, die bei einer Erwärmung bis zu 850°C zu einem einphasigen YAG kristallisierten. Bei der Ausscheidung handelte es sich um ein hydratisertes, einfaches Karbonat.

L'objet de cette étude est de caractériser la précipitation homogène de particules de précurseur pour le grenat d'yttrium et d'aluminium (YAG) par décomposition thermique d'urée en solution aqueuse. La concentration en cations est comprise entre 0·005 M et 0·30 M. L'observation de la morphologie des poudres associée à l'analyse chimique suggère un mécanisme de précipitation par étape, les ions aluminium formant d'abord une phase solide. On a obtenu des poudres fines et réactives qui cristallisent en un composé monophase de YAG par chauffage à 850°C. Le précipité est un carbonate hydrate basique.

1 Introduction

Powder processing studies with the Y_2O_3-Al_2O_3 system have largely been directed at optical applications. The $Y_3Al_5O_{12}$ (YAG) phase is cubic and does not exhibit any birefringence effects at the grain boundaries. Gazza & Dutta reported translucent YAG with hot pressing.[1] More recently, DeWith[2] described the synthesis of transparent YAG using a conventional sintering technique. During the past few years, ceramic matrix composites have been actively investigated to exploit their high temperature capabilities. Single-crystal alumina fibers have been used extensively as a reinforcement phase with a variety of a host ceramic matrices. Yttrium aluminum garnet has a negligible solubility for alumina, and could potentially act as a suitable matrix for alumina fibers. The cubic structure of YAG is beneficial in providing isotropic thermal expansion. Furthermore, the

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thermal coefficient of expansion (CTE) of single-crystal alumina is $9{\cdot}0 \times 10^{-6}$/K in the *c* direction and is $7{\cdot}9 \times 10^{-6}$/K in the *a* direction.[3] The CTE of YAG is fortuitously between these two values, $8{\cdot}9 \times 10^{-6}$/K.[4] Therefore the YAG-Al_2O_3 system should form a structurally sound composite.

A variety of processing techniques have been investigated to form single-phase YAG powder. Attempts to form the desired phase by solid-state reactions typically require temperatures above 1700°C.[5] More sophisticated routes have employed precipitates from yttrium and aluminum salt solutions,[6] sol–gel procedures and alkoxide hydrolysis.[7] These and other similar approaches have been focused on synthesizing very fine-grained powders that will react at lower temperatures to form the desired YAG phase. Previous studies in the authors' laboratory have evaluated the precipitation of yttrium and rare earth cations from aqueous solutions by the thermal decomposition of urea (NH_2CONH_2).[8–10] Similarly, urea has been used to prepare basic aluminum sulfate particles.[11] Urea provides the advantage of slow, uniform production of anionic species, e.g. OH^- and CO_3^{2-}, through the hydrolysis of its thermal decomposition products. The goal of this current work was to study the precipitation of yttrium and aluminum cations from aqueous solutions by the decomposing urea and follow the conversion of the precipitate to yttrium aluminum garnet upon calcining.

2 Experimental Procedures

2.1 Materials

The yttrium source for this study was 99.99% Y_2O_3 prepared by the Materials Preparation Center of the Ames Laboratory. The aluminum source was hydrous aluminum nitrate from Fisher Scientific Co. Other reagents employed in the process, such as nitric acid and urea, were reagent grade from Fisher Scientific Co. and were used without further purification.

2.2 Precipitation

A yttrium stock solution was prepared by dissolving yttria in slightly excess nitric acid. The aluminum stock solution was made by dissolving the aluminum nitrate in distilled water. The molarities of Y^{3+} and Al^{3+} stock solutions were 0·40 and 0·32, respectively. The metal cation concentrations were measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES). After dissolution, the stock solutions were filtered through a 0·22 μm Teflon membrane.

Initially, precipitation experiments were performed using single cations in order to observe the characteristic powder morphologies of each system. The yttrium precipitate was obtained by adding 50 cm^3 of the 0·4 M stock solution with 13 g of urea to sufficient distilled water to make the total volume of clear solution 800 cm^3. The respective concentrations of Y^{3+} and urea in this batch were 0·025 M and 0·27 M. The solution was heated in a water bath held at 95°C. Aging was continued for 2 h after the first visible sign of precipitation, e.g. a bluish tint. The individual aluminum precipitation was performed using the same reagent concentrations and aging time described.

Table 1. Initial total cation and urea concentrations and resulting reagent ratios examined in this study

Batch number	$[Y^{3+}+Al^{3+}]_0$ *(M)*	$[urea]_0$ *(M)*	$[urea]_0{:}[Y^{3+}+Al^{3+}]_0$
1	0·005	0·27	54·0
2	0·025	0·27	10·8
3	0·075	0·27	3·6
4	0·005	0·054	10·8
5	0·025	0·27	10·8
6	0·075	0·81	10·8
7	0·10	1·08	10·8
8	0·30	3·24	10·8

Subsequently, the mixed, yttrium and aluminum precipitation experiments were carried out by changing the total cations and urea concentrations; however, a constant stoichiometric Y:Al ratio of 3:5 was maintained. The range of cation and urea concentrations studied are displayed together with the resulting urea-to-cation ratio in Table 1. Again the solutions were heated in a 95°C water bath and aged for 120 min after the first sign of turbidity in the clear solution. The pH of the solution was monitored during the experiments. After aging, the precipitate was separated from the supernatant by centrifugation. The powder was washed twice with water and acetone and then dried overnight in air at 80°C. Figure 1 illustrates the sequence of steps used in the precipitation experiments.

2.3 Characterization

Precipitate morphology was assessed from micrographs taken with a JEOL 840 scanning electron microscope. Analysis of the precipitate composition was performed by a combination of inductively coupled plasma-atomic emission spectroscopy (ARL 3410) for total yttrium and aluminum, combustion chromatography (Horiba EMIA 520) for total carbon and inert gas fusion (LECO TC-436) for total oxygen. DTA/TGA traces of the precipitate dried at 100°C were obtained with a Seiko Model 320 thermal analyzer by heating a 35–40 mg sample to 1200°C in air at a rate of 3°C/min. X-Ray diffraction patterns were

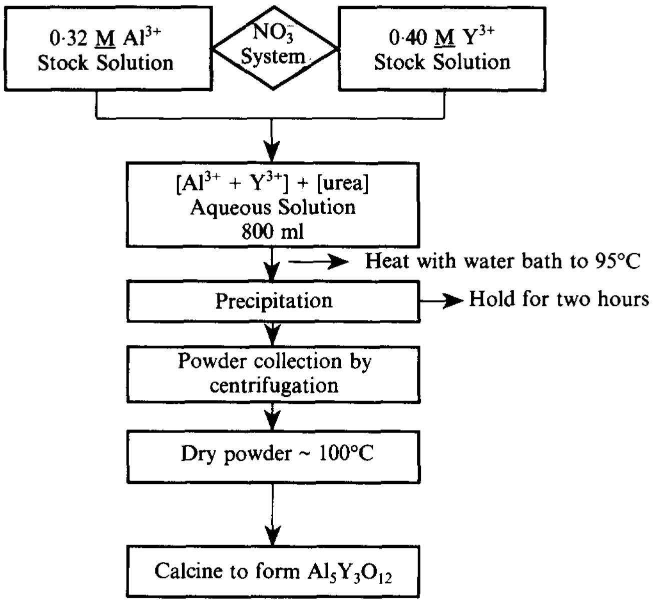

Fig. 1. Flow chart illustrating sequence used in precipitation experiments.

obtained from as-precipitated and heat-treated powders using a Scintag 2000 X-ray diffractometer with Ni-filtered CuK_α radiation.

3 Results and Discussion

3.1 Precipitation Characterizations

The concurrent temperature and pH rise of several precipitation experiments are shown in Fig. 2. The data are from conditions where sufficient urea was added to maintain a constant $[urea]_o$: $[Y^{3+} + Al^{3+}]_o$ of 10·8. Also, the starting pH of the solutions was adjusted slightly to bring all four solutions to a nominal initial pH value of 3.5. The X symbols on each pH curve indicate the first visible sign of precipitation. Despite the 20-fold difference in total cation concentration, the different solutions exhibited similar pH rises and precipitation characteristics. The pH rise is due to the decomposition of urea and subsequent hydrolysis of the products. This process has been discussed by numerous investigators and is now briefly explained. The homogeneous decomposition of urea can be represented by the following reactions

$$NH_2CONH_2 + 4\,H_2O \xrightarrow{T>83°C} 2NH_4OH + H_2CO_3 \tag{1}$$

$$NH_4OH \rightleftarrows NH_4^+ + OH^- \tag{2}$$

$$H_2CO_3 \rightleftarrows H^+ + HCO_3^- \tag{3}$$

$$HCO_3^- \rightleftarrows H^+ + CO_3^= \tag{4}$$

Equation (1) represents the decomposition of urea. Equations (2)–(4) represent the subsequent dissociation of the reaction products to yield OH^- and $CO_3^=$ ions. Basic carbonates may or may not form depending upon other supporting anions

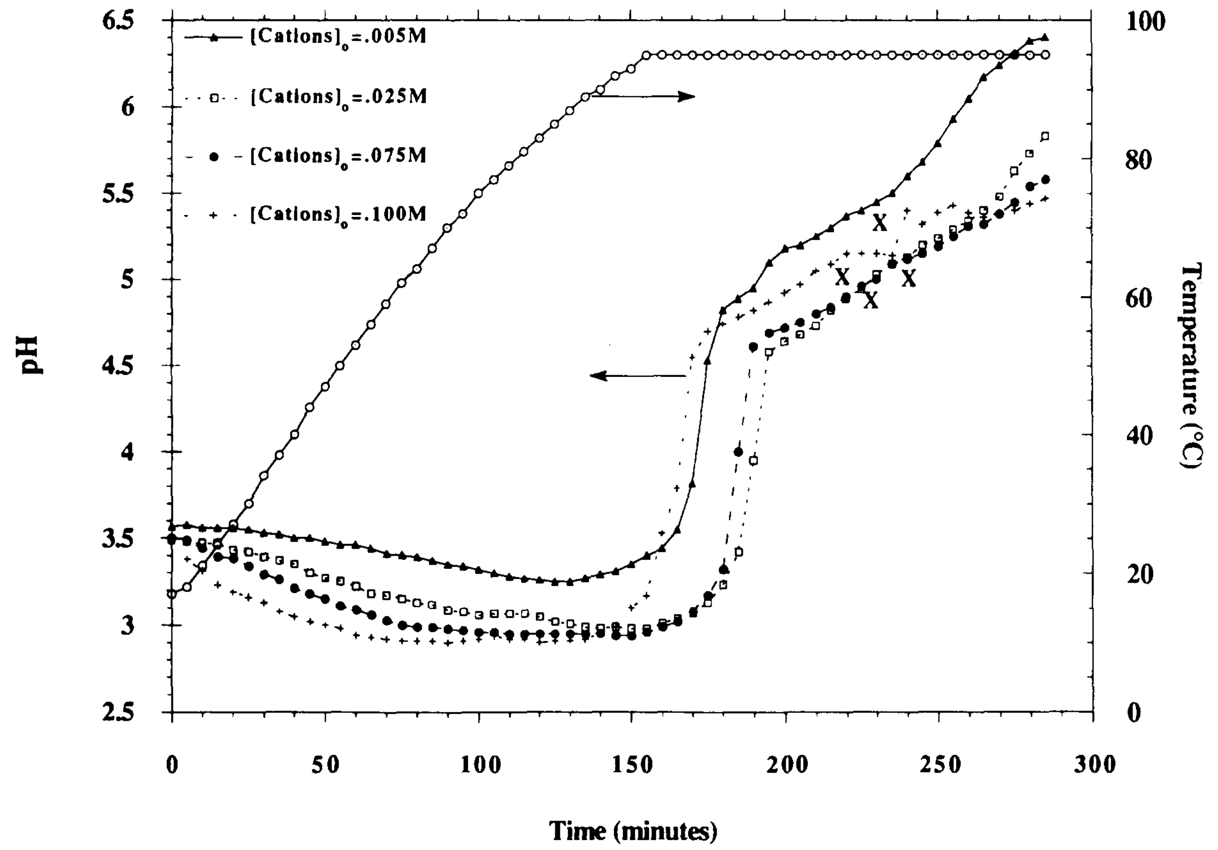

Fig. 2. Concurrent pH and temperature rises of several precipitation solutions as a function of time. Note X indicates the first visible sign of precipitation.

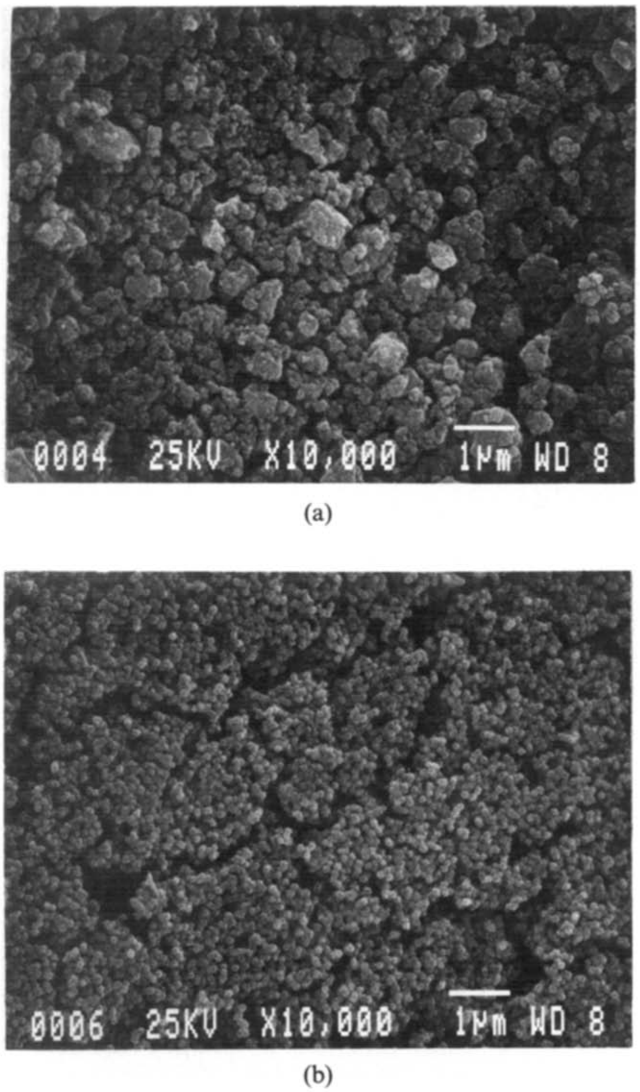

Fig. 3. SEM micrographs of precipitates obtained from individual cations, as follows: (a) aluminum, $[Al^{3+}]_o$ = 0·025 M and (b) yttrium, $[Y^{3+}]_o$ = 0·025 M.

present and solubilities of metal ions in solution. Basic sulfates of aluminum have been prepared using urea,[11] while basic carbonates of yttrium have been obtained by similar techniques.[8]

Referring back to Fig. 2, the pH of each solution remained constant until the temperature reached 95°C. At this time sufficient dissociation of ammonium and carbonic acid occurred to raise the pH to 5·0–5·5. Additional aging produced a visible solid phase. The last data points for each initial total cation concentration do not represent the time of complete precipitation. Rather, pH and temperature during precipitate formation was collected only for the duration shown. The actual conditions affecting complete precipitation are discussed in Section 3.4.

3.2 Precipitate morphology

The powders obtained from solutions with single cations are shown in Fig. 3. The morphology of the Al-based material, Fig. 3(a), is not necessarily representative of the primary precipitate particles.

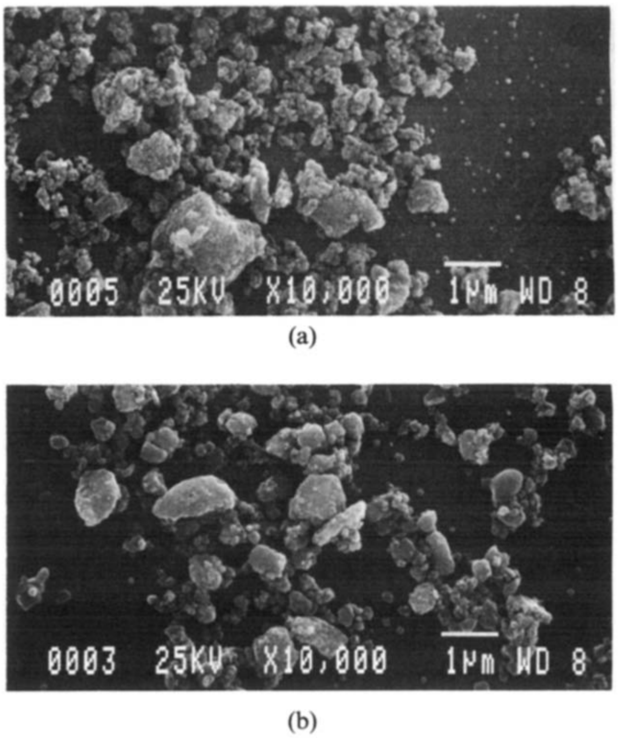

Fig. 4. SEM micrographs of precipitates obtained from mixed aluminum and yttrium cation solutions (a) after drying and (b) after calcining to 1000°C. $[Y^{3+} + Al^{3+}]_o$ = 0·025 M.

The solid phase formed during precipitation was gelatinous. This is not unusual in aluminum ion precipitation, which may be related to the various polynuclear species of aluminum complexes that can form in aqueous solutions.[12] Nevertheless, close examination of the powder did reveal the presence of very small particles within the larger aggregates seen in the micrograph. Prior to SEM examination, the powder displayed in Fig. 3(a) was dried at 80°C in air. This produced a hard mass, due to the aforementioned gel-like structure of the precipitate. Accordingly, the dried material was ground with a mortar and pestle and suspended in isopropanol before being deposited onto an SEM sample holder. The general morphology seen in Fig. 3(a) is most likely to be due to the grinding of the dried, hard material. The powders from yttrium-containing solutions are shown in Fig. 3(b). The monosized, spherical morphology has been reported previously.[8] The particles are approximately 0·2 μm in diameter and are monodispersed.

It is very interesting to compare the morphologies of the individual cation precipitates with the morphology of the precipitates obtained from the mixed Y^{3+} and Al^{3+} solutions. The powder formed from a total cation concentration $[Y^{3+} + Al^{3+}]$, of 0·025 M is shown in Fig. 4. The starting Y:Al was stoichiometrically 0·6 in this and all other mixed cation precipitation experiments. Note the very close similarity to the individual aluminum-based precipitate. The mixed cation precipitation yielded

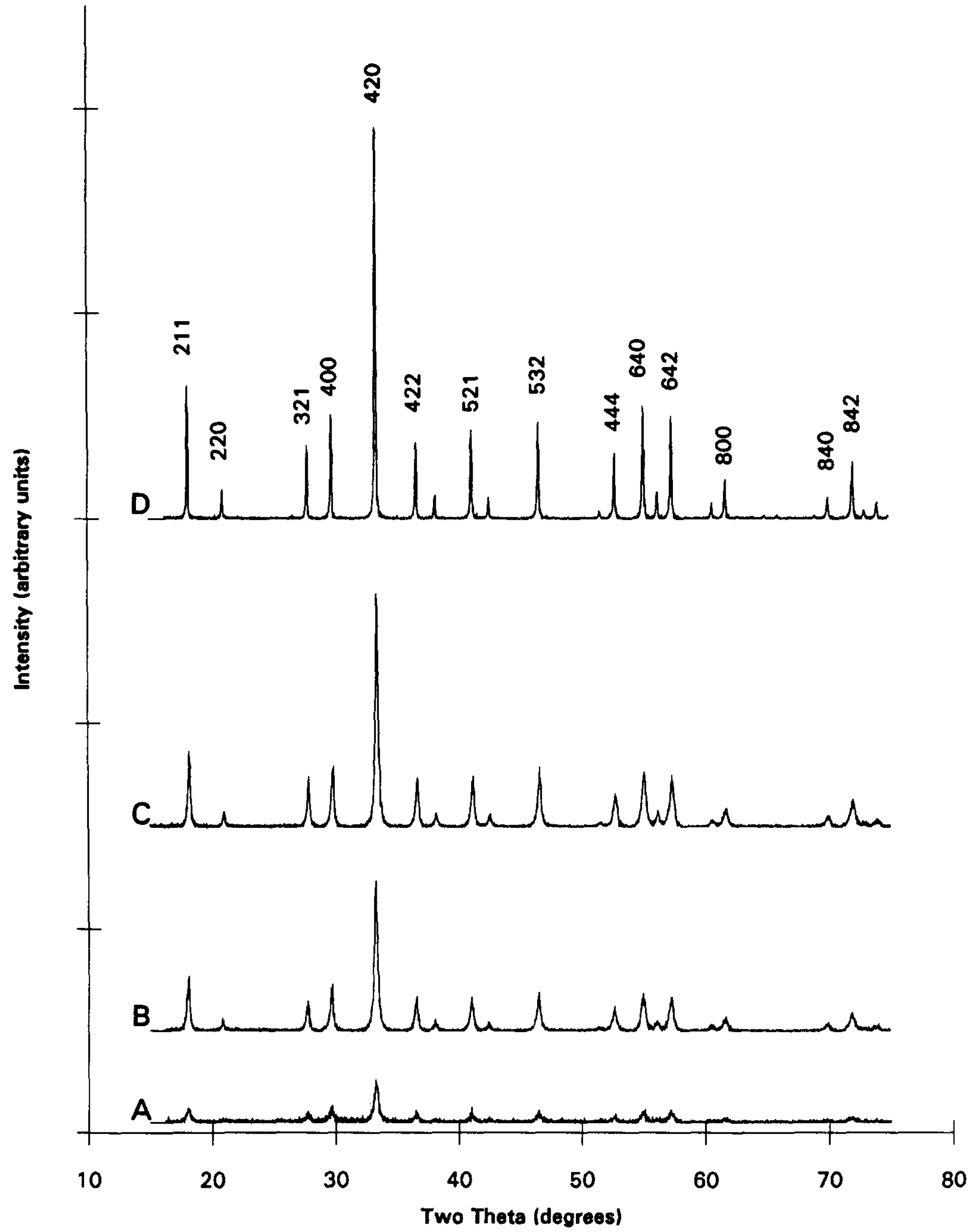

Fig. 5. X-Ray diffraction patterns from precipitates obtained from $[Y^{3+} + Al^{3+}]_0 = 0{\cdot}025$ M solutions after calcining to various temperatures for 6 h in air. A, 850°C; B, 900°C; C, 1000°C; D, 1400°C.

a gel-like solid phase which closely resembled the precipitate obtained from the aluminum nitrate system. The YAG precursor precipitate also formed a hard mass after drying to 80°C in air. The material shown in Fig. 4 is after grinding. The common particle structure between the individual aluminum-based precipitate and the YAG precursor precipitate is possibly an indication that the solid-phase formation is not occurring by a classic coprecipitation process. Rather, the precipitation appears to be sequential; aluminum ions precipitate initially, although perhaps not completely, followed by the yttrium ions. Chemical analysis of the precipitation solution further supports the concept of a sequential precipitation process, as will be discussed later. The morphology of the crushed powder in Fig. 4(a) is very representative of the other powders obtained from solutions with the total cation concentrations listed in Table 1. Similarly, these other concentrations also produced gel-like precipitates. Also note that no morphology change was seen after calcining to 1000°C, as shown in Fig. 4(b). However, the precipitate is converted to single-phase crystalline yttrium aluminum garnet, as discussed in the next section.

3.3 X-ray diffraction results

The as-precipitated powder was amorphous to X-ray diffraction. The crystallization of the precipitate with subsequent heat treatments is illustrated in Fig. 5. No peaks were seen in the XRD trace of

Table 2. Batch yield results obtained from several precipitation conditions

Batch number	*[urea]$_o$:[Y^{3+}+Al^{3+}]$_o$*	*Yield (%)*
3	3·6	75
5	10·8	95
6	10·8	96
7	10·8	96
8	10·8	98

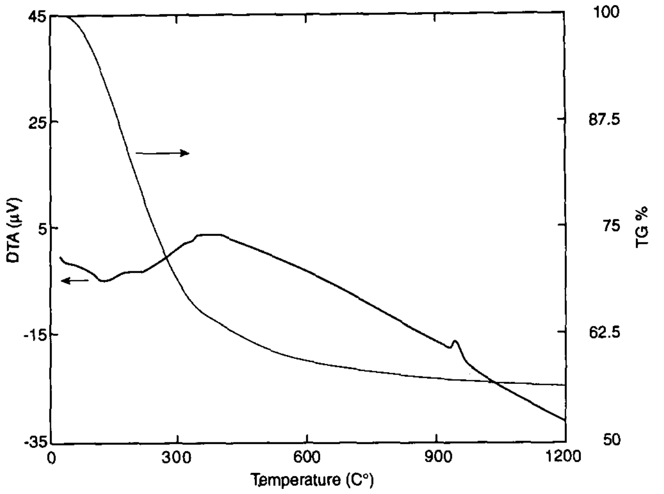

Fig. 6. TGA/DTA traces for precipitate obtained from solution with [Y^{3+} + Al^{3+}]$_o$ concentration of 0·075 M.

powder heated to 800°C, but peaks corresponding only to the yttrium aluminum garnet phase appeared after heating to 850°C and continued to grow in intensity upon further heating to 1400°C. Fine two-theta scans were performed to look for Al_2O_3, Y_2O_3 and yttrium aluminates, but no peaks were apparent. The relatively low temperature of crystallization and single-phase formation may be attributed to the extremely fine scale of primary particles and their intimate mixing during precipitation. The traces shown in Fig. 5 are from powders obtained from a 0·025 M total cation concentration solution. X-Ray diffraction patterns taken from powders prepared with other total cation concentrations were very similar to the 0·025 M case.

3.4 Batch yield

Precipitates were calcined to 1000°C for 6 h in air to form the YAG compound. Total recovered precipitates and total oxides formed after calcining to 1000°C for 6 h in air were weighed to calculate the powder yield during precipitation. The results of several experimental conditions are shown in Table 2. It appears that the critical factor in securing complete recovery is adequate urea content. At [urea]$_o$:[Y^{3+} + Al^{3+}]$_o$ $<$ 10·8, incomplete recovery was observed. The yield values from solutions with [urea]$_o$:[Y^{3+} + Al^{3+}]$_o$ $>$ 10·8 are all around 95% of theoretical. These values are likely to be somewhat lower than the theoretical yield due to incomplete collection of precipitated powder after centrifuging. Analysis for Y^{3+} and Al^{3+} by ICP-AES in Batch 5 after separating the precipitate from solution revealed less than 50 ppm of either cation.

3.5 Thermal analysis

Differential thermal analysis and thermal gravimetric (DTA/TGA) analysis were performed on powders prepared from solutions with total cation concentrations of 0·005 M, 0·025 M and 0·075 M. The results were very similar for the three different powders. The data collected with the powder obtained from the 0·075 M total cation concentration system are displayed in Fig. 6. As stated earlier, the precipitates were amorphous up to around 850°C. Accordingly, the TGA curve displayed a relatively continuous weight loss to near 900°C. The total weight losses were all around 37%; the small variations are likely due to differences in drying of the precipitate. Comparing the TGA and XRD results, it appears that the precipitates have completely decomposed to oxides at about the time when crystallization has begun. The DTA traces indicate a broad endothermic reaction centered around 150° that is likely to correspond to removal of physical and chemical water. Between approximately 900 and 920°C another small amount of heat is liberated. The slow but steady decrease in the DTA plot between 400 and 1200°C, is probably due to instrument drift. However, this second exothermic peak is not associated with a detectable weight loss. Presumably, this heat is related to crystallization of the YAG phase. These temperatures are somewhat higher than the conversion temperatures of 800–850°C seen from the XRD results, but the samples for XRD were held at their respective temperatures for 6 h while the DTA/TGA traces were taken at 3°C/min.

3.6 Chemical composition

Chemical analyses were coupled with the TGA data to determine an approximate chemical formula for the precipitate obtained from a solution with a total cation concentration of 0·025 M. Powders were put into solution and analyzed for total aluminum and yttrium by ICP-AES. The total carbon and oxygen values were measured by combustion chromatography and inert gas fusion respectively. Table 3 presents the results of the chemical analysis and total weight loss along with the calculated values based on the argument given as follows. Initially, an assumption was made that the precipitate was some form of a hydroxycarbonate, perhaps with some degree of hydration.

Table 3. Chemical analysis results of dried precipitate and calculated values based on $Al_5Y_3(OH)_{16}(CO_3)_4{\cdot}4H_2O$

Element	*Experimental (wt %)*	*Calculated (wt %)*
Y	27·4	27·1
Al	14·4	13·7
C	4·4	4·7
O	51·8	52·0
% LOI	38·6	39·8
Al:Y	0·53	0·51

This assumption was based on previous work with yttrium ions precipitated by urea that formed a hydroxycarbonate.[8] The general formula assumed is:

$$Al_5Y_3(OH)_{24-2x}(CO_3)_x \cdot yH_2O$$

The aluminum:yttrium ratio is fixed (by stoichiometry) and the x value will assure electrical neutrality. Both x and y were calculated using the total carbon results and the overall weight loss determined by TGA. Solving the simultaneous equations for x and y results in approximately a value of 4 for both x and y. Substituting these values into the general formula shown above yields the following formula:

$$Al_5Y_3(OH)_{16}(CO_3)_4 \cdot 4H_2O$$

This may be verified by calculating the theoretical weight fraction of individual metals and total oxygen and comparing to the experimental data. Table 3 shows fairly good agreement between the theoretical and analytical values. Differences are likely to be due to the variations in the weight loss values as a function of previous drying history. Also shown in Table 3 is the weight ratio of aluminum to yttrium. This is quite close to the theoretical value of 0·51, from stoichiometric YAG. It was expected that a stoichiometric ratio would be preserved, since the batch yield experiments showed that essentially all the metal cations were brought out of solution during precipitation.

3.7 Supernatant characterization

Comparison of the powder morphologies obtained from individual aluminum ion solutions, individual yttrium solutions and mixtures of both aluminum and yttrium solutions indicated that the aluminum ions began to precipitate before the yttrium ions. To further test this observation, samples of the 0·025 M mixed cation precipitating solution were removed from the 800 cm^3 batch at several time intervals after the first visible sign of precipitation. The samples, which were no longer clear due to the solid phase formation, were centrifuged to collect the precipitate. The resulting clear supernatant was separated from the powder and analyzed by ICP-AES for aluminum and yttrium. The results are displayed in Fig. 7. The initial concentration of Al^{3+} and Y^{3+} are marked at time zero. It is clear that aluminum is precipitating first. At the time when a visible solid phase appeared, nearly all of the aluminum ions had precipitated. Alternate spectroscopic examination would possibly have provided more accurate information relative to early aluminum precipitation. Nevertheless, substantial yttrium ions were still present while nearly all of the aluminum had precipitated. The data in Fig. 7 support the concept of a sequential precipitation.

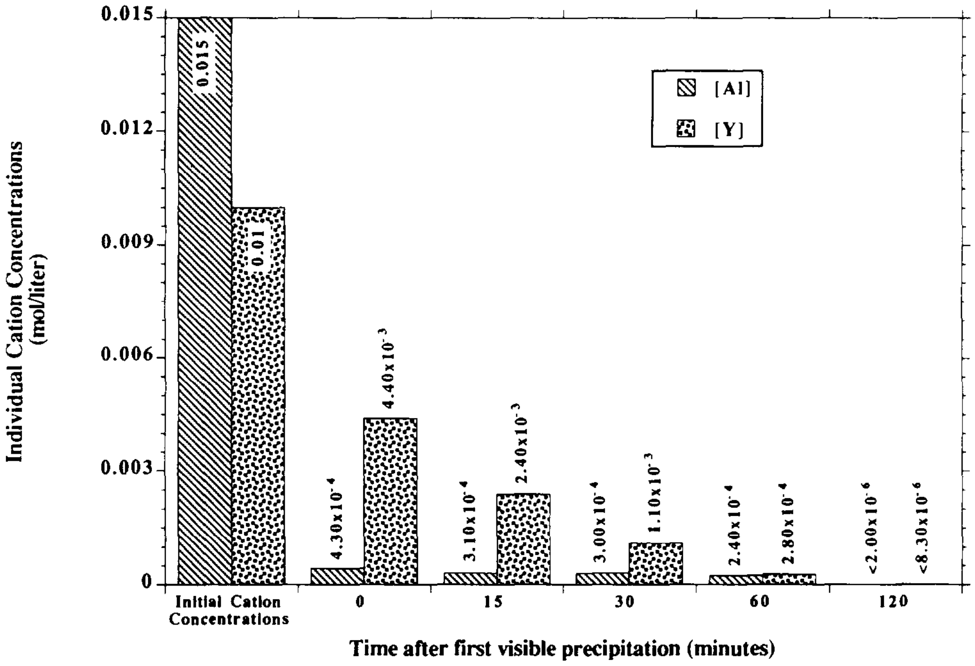

Fig. 7. [Al^{3+}] and [Y^{3+}] of samples drawn from precipitation solution at different times after the first visible sign of precipitation. Total starting cation concentration = 0·025 M.

4 Conclusion

Yttrium aluminum garnet precursor particles were synthesized by homogeneous precipitation via the thermal decomposition of urea in aqueous solutions. The precipitation of aluminum and yttrium ions by urea in the presence of nitrate ions produced a gelatinous solid phase. A hard mass was formed by drying the powders at 80°C in air. The precipitate was amorphous to X-rays, but crystallized to form single-phase YAG upon calcining to 850°C. The approximate chemical composition of the precipitate was $Al_5Y_3(OH)_{16}(CO_3)_4 \cdot 4H_2O$.

The powders obtained in this study were extremely fine grained, i.e. less than 100 nm. Their small size and intimate mixing, despite the apparent sequential precipitation process, yielded a highly reactive material that formed the desired single-phase yttrium aluminum compound at relatively low temperatures. Future studies will be aimed at disrupting the characteristic gel-like structure in order to obtain a processible powder that will take full advantage of the extremely small particle size.

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