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Short communication

# The effect of precipitant on co-precipitation synthesis of yttrium aluminum garnet powders

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## Abstract

Polycrystalline yttrium aluminum garnet ($Y_3Al_5O_{12}$, YAG) powders were prepared by the co-precipitation method from a mixed solution of aluminum and yttrium nitrates ($Y(NO_3)_3 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$) using ammonium carbonate ($(NH_4)_2CO_3$, AC) and ammonium hydrogen carbonate ($NH_4HCO_3$, AHC) as precipitants. The effect of precipitant and pH on the preparation of pure-phase YAG powders was mainly studied. Phase evolution of the precursors during calcination and sinterability of the resultant YAG powders were compared for the two precipitants. The composition of YAG precursor, the phase formation process of YAG and the properties of the powders were investigated by means of DTA–TG, XRD, and TEM. AC as precipitant could produce a hydroxide precursor, which transformed to a YAG and $Y_2O_3$ mixture at about 1300 K. AHC as precipitant could produce a loosely agglomerated carbonate precursor. The resultant YAG powders showed good dispersity and excellent sinterability. The precursor directly converted to pure YAG via $YAlO_3$ (YAP) phase at about 1300 K.

*Keywords:* Co-precipitation; Precursor powder; AHC; AC

## 1. Introduction

Yttrium aluminum garnet ($Y_3Al_5O_{12}$, YAG) has been well established as a laser host material [1,2], attributed to its relatively stable lattice structure and large thermal conductivity [3]. In addition, YAG also has great potential application in high-temperature engineering materials because of its better high-temperature strength as well as superior creep resistance [3]. Recently, many efforts have been made to synthesizing YAG transparent ceramics for solid-state laser applications, by which they were doped with transition and rare-earth metal elements [4–10], such as Nd [5], Yb [6], Ce [7], Eu [8], Cr [9], and Tb [10]. Owing to such a wide and diverse application potential for YAG-based materials, rapid synthesis methods for pure and homogeneously doped YAG powders are highly desirable [7,8,10–23].

The YAG-based materials are normally synthesized by a solid-state reaction method with $Y_2O_3$ and $Al_2O_3$ as raw materials, in which a relatively high temperature ($>1700$ K) and prolonged heating time are required [3,11]. However, the solid-state reaction method has some unavoidable disadvantages, such as the processing conditions fail to allow for easy control of microstructure, grain size or shape of the resulting powders. Moreover, the extensive ball milling leads to possible contamination and degeneration of luminescent property [3,11]. Recently, other wet-chemical methods [12] for producing YAG powders, such as the sol–gel method [8,13–14], hydrothermal synthesis [10,15], spray thermal decomposition [16] and metal-organic preceramic processing [17], have been used. Using these methods, homogeneous products achieve symmetrical mixing on the molecular level, lowering the crystallization temperature ($<1400$ K). Unfortunately, most of these chemical methods suffer from complex and time-consuming procedures and possible mismatch in the solution behavior of the constituents [8,10–17]. Compared with these methods, the co-precipitation method is a

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relatively simpler and more cost-effective way for powder synthesis [7,18–21], because precursor powders can be prepared on a large scale in water rather than in organic chemicals. However, the dispersion of the synthesized powder is not ideal. In order to achieve polycrystalline YAG ceramics with high density and high transparency, it is important to control the chemical composition and physico-chemical properties of the precursor [7,18–21]. Therefore, during the preparation of the precursor, the pH value of the precipitant needs to be controlled strictly to guarantee the uniform distribution of Al and Y elements [20–21]; in addition, the agglomeration problem, which takes place during the drying step, is practically difficult to completely avoid [7,18]. Obviously, the processes are very complex and hard to control.

In this work, the effects of precipitant and pH value on the co-precipitation method will be described. Ammonium hydrogen carbonate (AHC) was used to synthesize YAG powders from a mixed solution of aluminum and yttrium nitrates via the co-precipitation method. For comparison, ammonium carbonate (AC) was also used for powder synthesis under equivalent conditions. Phase evolution of the precursors and sinterability of the resultant YAG powders were investigated and compared between the two methods.

## 2. Experiments

$Y_3Al_5O_{12}$ compositions were prepared by the co-precipitation method in this study. As starting materials, weighted amount of 99.99% $Y(NO_3)_3 \cdot 6H_2O$ and $>99\%$ $Al(NO_3)_3 \cdot 9H_2O$ (A.R., Tianjin Fine Chemicals) with molar ratio of 3:5 for $Y^{3+}$:$Al^{3+}$ were first dissolved in 100 ml distilled water, and the concentrations of mother solution were 0.25 M for $Al^{3+}$. Then the mixtures were added dropwise into the precipitant solution at a speed of 2 ml/min and under vigorous stirring at room temperature (300 K). In this work, analytical grade AHC and AC were used as precipitating agents. The main difference between the two methods is the rate at which pH of the salt solution changes as a function of time, so the pH of the solution had been monitored. The precipitation processes were performed with a reverse-strike method, which is adding the mixed salt solution into the precipitant solution. In view of cation rich in the salt solution, this method has an advantage of higher cation homogeneity in the materials. Furthermore, the concentration of precipitant solution was expected to affect compositions of the resultant precipitate. Therefore, the concentration of precipitant solution was selected as 1.0 M, 200 ml, and was made by dissolving AHC or AC into distilled water. The precipitated slurry was aged for 24 h to achieve a sufficient reaction, and then the suspensions were filtered and washed repeatedly with distilled water and ethanol to remove residual ammonia and nitric ions. After washing, the resulted products were dried at 348 K for 12 h, and then the loose YAG precursors were obtained. Finally the precursors were sintering at 1073–1373 K in air atmosphere for 2 h. The preparation process is schematically shown in Fig. 1.

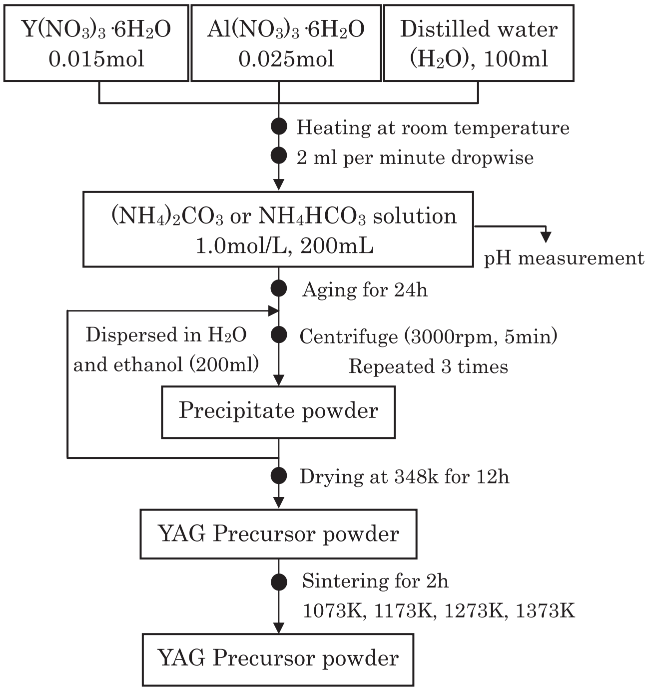

Fig. 1. Schematic representation of the preparation process of $Y_3Al_5O_{12}$ particles.

The thermal decomposition and crystallization behaviors were studied with the differential thermal analysis and thermogravimetry analysis (DTA–TG) at a heating rate of 10 K/min up to 1400 K in air. The pH of the suspension was monitored with a pH meter with an accuracy of 0.02 (PHS-3D, Leici, China). The phase identification was performed by using a conventional D/max X-ray diffractometer with Cu-$K\alpha$ radiation ($\lambda = 1.54056$ Å) in the range of $2\theta = 10$–$80°$. The morphologies of the powders annealed at different temperatures were observed by the transmission electron microscope (TEM, JSM-6360LV, JEOM, Japan). The elemental compositions were determined with a Link ISIS energy dispersive X-ray spectroscopy (EDS).

## 3. Results and discussion

### 3.1. X-ray diffraction (XRD) results

XRD spectra of the powders produced by the AC and AHC methods are shown in Figs. 2 and 3, respectively. No obvious diffraction peaks were observed when the particles were sintered at 1073 K (see Figs.2(b) and 3(b)). It can be concluded that the powders prepared by the two methods are amorphous below this temperature. Up to 1173 K, however, remarkable discrepancies concerning phase development were observed for the two precursors. For the powder produced by the AC method (Fig. 2), amorphous YAG peak was found at 1073 K with the presence of cubic $Y_2O_3$ crystallized peaks. At 1273 K and above, YAG phase was formed, but the $Y_2O_3$ cubic phase

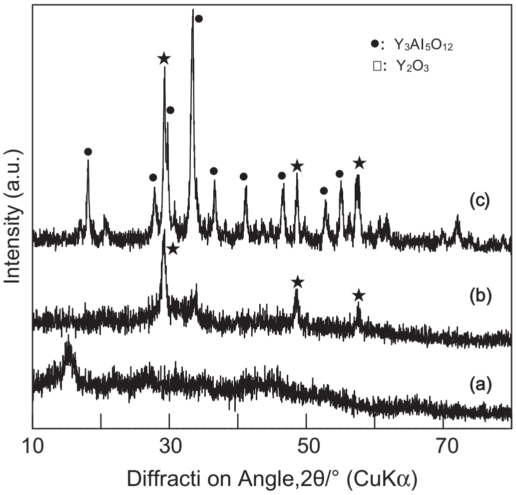

Fig. 2. XRD patterns of the dried powders synthesized with ammonium carbonate (AC) sintering for 2 h at (a) precipitate, (b) 1073 K, and (c) 1273 K.

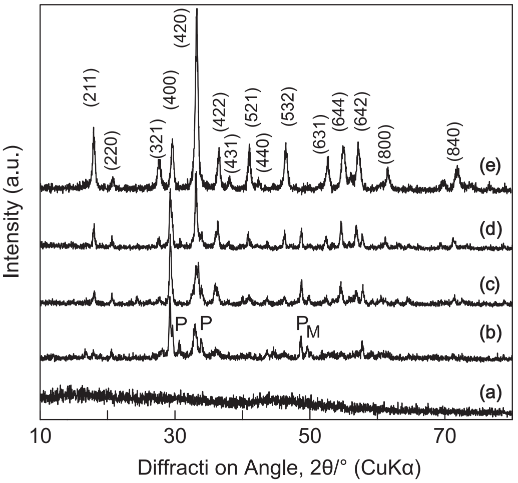

Fig. 3. XRD patterns of the dried powders synthesized with ammonium hydrogen carbonate (AHC) sintering for 2 h at (a) precipitate, (b) 1073 K, (c) 1173 K, (d) 1273 K, and (e) 1373 K. Note: "*P*" means YAP, "*M*" means YAM.

persisted and the intensity kept unchanged. This suggests that the precursor produced by the AC method contains excess $Y_2O_3$. It is considered that the segregation of $Al^{3+}$ could happen, resulting that the ratio of $Y^{3+}$ and $Al^{3+}$ deviates from 3:5 in co-precipitated powders. Thus, some $Y_2O_3$ phases appeared in the calcined powder.

The YAG powders synthesized by the AHC method, however, showed much better sintering ability than those by the AC method. To be crystallized as YAG, the precursor produced by the AHC method must be treated at 1073 K, with $Y_4Al_2O_9$ (YAM) and $YAlO_3$ (YAP) [7,11] forming intermediate phases (Fig. 3). Increasing the calcination temperature to 1173 K, strong cubic-YAG diffraction peaks can be observed in the XRD pattern shown in Fig. 3(c). Above this sintering temperature, continued refinement of peak shapes and intensities were observed, indicating higher cation homogeneity of the precursor and more rapid crystallite growth of the YAG powder. The full width at half maximum of X-ray diffraction peaks offers the information about crystallite size. The average crystallite size of the YAG powder heated to different temperatures was determined from the line broadening observed on (420) reflection peak shown in Fig. 4(b), which is concluded to be approximately 37 nm (1173 K, 2 h), 42 nm (1273 K, 2 h) and 81 nm (1373 K, 2 h).

### 3.2. Precipitation of the YAG precursor

In this work, AC and AHC were used as precipitating agents. For the AHC method, the chemical reactions of AHC hydrolysis are [19] as follows

$$NH_4HCO_3 + H_2O \leftrightarrow NH_4OH + H_2CO_3$$

For the AC method, the chemical reactions of AC hydrolysis are as follows

$$(NH_4)_2CO_3 + H_2O \leftrightarrow 2NH_4OH + H_2CO_3$$

And

$$NH_4OH \leftrightarrow NH_4{}^+ + OH^-$$

$$H_2CO_3 \leftrightarrow H^+ + HCO_3^-$$

$$HCO_3^- \leftrightarrow H^+ + CO_3^{2-}$$

It is important to keep a constant pH value by adding excess precipitating agent [10,13,20,21]. In this study, pH range variation with the dropwise time was observed for the two precipitant solutions during precipitation (Table 1). For the AHC process, pH of the AHC solutions showed weak alkalinity and decreased from an initial value of 7.86 to 7.56 at the completion of precipitation, and the resultant slurry had a constant pH of 7.58 during the aging period. Compared with AHC, the AC solution showed stronger alkalinity and had an

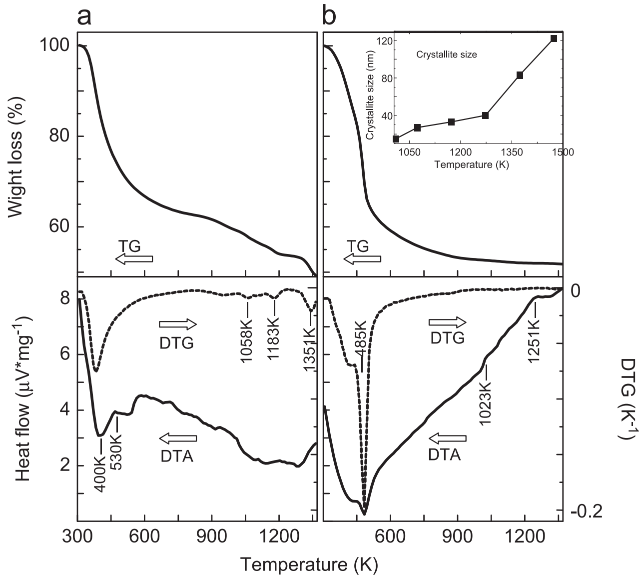

Fig. 4. DTA/TG traces of the YAG precursor powder synthesized with (a) ammonium carbonate (AC), (b) ammonium hydrogen carbonate (AHC) and the crystallite size as a function of calcinations temperature.

Table 1
The concentration change and the variation of pH.

| Precipitant | Concentration (M) | | pH | |
|---|---|---|---|---|
| | Initial | Final | Initial | Final |
| AC | 1.0 | 0.75 | 7.93 | 7.87 |
| AHC | 1.0 | 0.35 | 7.86 | 7.56 |

initial pH value of 7.93. During precipitation, pH decreased slightly from 7.93–7.87. The pH of AC solution was higher than that of AHC as shown in Table 1. Therefore, AC was in favor of cation complete precipitation. But as shown in Figs. 2 and 3, the precursor produced by the AC method contained excess $Y_2O_3$, indicating that the $[Al^{3+}]$ ions in the solution is not completely precipitated. In addition, it was adverse to form mono-dispersed powders using AC as precipitant. Therefore, we assume that the pH changes affect the composition of precursor produced [10,13,20,21], but it is not the pivotal factors.

As reported, for the synthesis of YAG precursor, Al-precipitate [21] and Y-precipitate [19,23] should be formed as hydrous aluminum and hydrous yttrium with amorphous structures, especially for the synthesis at low pH values. With aging, carbonate ions $[CO_3^{2-}]$ exchange moieties with $H_2O$ molecules, constricting the structures, and form better-crystallized precursors with the hydroxide ions. Thus, $[Al^{3+}]$ may be precipitated as gelatinous pseudo-boehmite AlOOH [10] or ammonium dawsonite $NH_4Al(OH)_2CO_3$ [22]. But for $[Y^{3+}]$, they may most likely be precipitated as normal carbonate of $[Y_2(CO_3)_3 \cdot nH_2O(n=2,3)]$ [19,21], depending on the concentrations of $[NH_4^+]$ and $[CO_3^{2-}]$ in the solution. The molar concentration changing with the dropwise time was observed during precipitation. For the AHC process, the solution concentration decreased from an initial value of 1–0.35 M, but the AC solution decreased slightly from 1 M to 0.69 M. For this reason, AC solution had much higher concentrations of $[NH_4^+]$ and $[CO_3^{2-}]$ compared with AHC. Constrainted by the amount of $(NH_4)_2CO_3$ presenting, the final product varies from AlOOH [10] to $NH_4Al(OH)_2CO_3$-$nH_2O$ in the Al-precipitate case [22], and from $Y_2(CO_3)_3$-$nH_2O$ to $Y(OH)CO_3$-$nH_2O$ in the Y-precipitate case. In addition, higher concentrations of $[NH_4^+]$ and $[CO_3^{2-}]$ would induce Al precipitate redissolution, and induce the yttrium compounds to reconstruct separately from the aluminum compounds. Thus, it is certain that the YAG powder precursor produced by the AC method is the carbonate compound which has the higher deviate from 3:5. To avoid the formation of gelatinous AlOOH [10], the precipitant was selected for the AHC solution and concentration was less than 1.5 M.

### 3.3. Thermal analysis and chemical analysis

Fig. 4 shows the TG–DTG–DTA curves of precursor powder prepared by the AC method and the AHC method, with a heating rate of 10 K/min from 300 K to 1400 K. The TG curve of YAG powder produced by the AC method indicates the overall weight loss beyond 50%. It can be explained by the removal of physically adsorbed water below 400 K with the 16.2% weight loss, the dehydration of hydroxides between 400 K and 600 K with 15.8% weight loss, and the decomposition of carbonates between 600 K and 1400 K with 18% weight loss. The TG curve indicates an overall 48.3% weight loss, which is higher than the value of 26.7% expected for the precursor of pure hydroxide, as shown in Fig. 4(b). It can be explained by the removal of physically adsorbed water or the basic salt of approximate formula $[Y_2(CO_3)_3 \cdot nH_2O$ $(n=2,3)]$, as discussed previously. For DTA curve below 400 K, the 9.8% weight loss and the slow decrease in endothermic peak are caused by dehydration of physically adsorbed water. The 31.8% weight loss between 400 K and 600 K is caused by the decomposition of carbonates and the release of ammonia in the precursor powders. At about 500 K, the DTG and DTA curves exhibit a sharp peak, indicating the fastest decomposition rate of the precursor powder at this temperature range. The 6.7% weight loss between 600 K and 1400 K was mainly due to the further decomposition of carbonate species. An exothermic peak at 1235 K can be attributed to crystallization and crystal growth of YAG. When the temperature is above 1300 K, there are no changes in TG and DTA curves, which suggests that the precursor powders completely transform to YAG cubic crystal phase. The XRD patterns (see Fig. 3) confirmed that the crystallization of YAG began below this temperature, because the exothermic peak in the DTA curve often lags after the crystallization.

### 3.4. Powder morphology

Fig. 5 shows the TEM images of the YAG powders produced by the AHC co-precipitation method, obtained at the conditions of (a) 1073 K, (b) 1173 K, (c) 1273 K, and (d) 1373 K for 2 h each. The precursor is loosely agglomerated and the resultant YAG powders show good dispersity and excellent sinterability. From Fig. 5(a), the morphology of particles was found to be mono disperses and amorphous YAG with size range 10–20 nm. Besides, the grain diameters are homogeneous and dispersibility is favorable. With the increase in of sintering temperature, the crystalline grain of YAG powders was enlarged and the crystallite shape was changed from irregular to regulation. From Fig. 5(d), it is observed that the crystal size of YAG powders is about 100 nm. However, prolonging calcination time and enhancing temperature will result in the aggregation of particles. Moreover, as shown by the high resolution TEM images in Fig. 5(c) and (d), the individual YAG crystallites appear to demonstrate a good crystallinity due to their clear lattice fringes.

The molar ratio of samples analyzed by energy dispersive X-ray spectroscopy (EDS) is shown in Fig. 6. The EDS patterns clearly indicated that, based on the Y, Al and O peaks [23], the final products were composed of

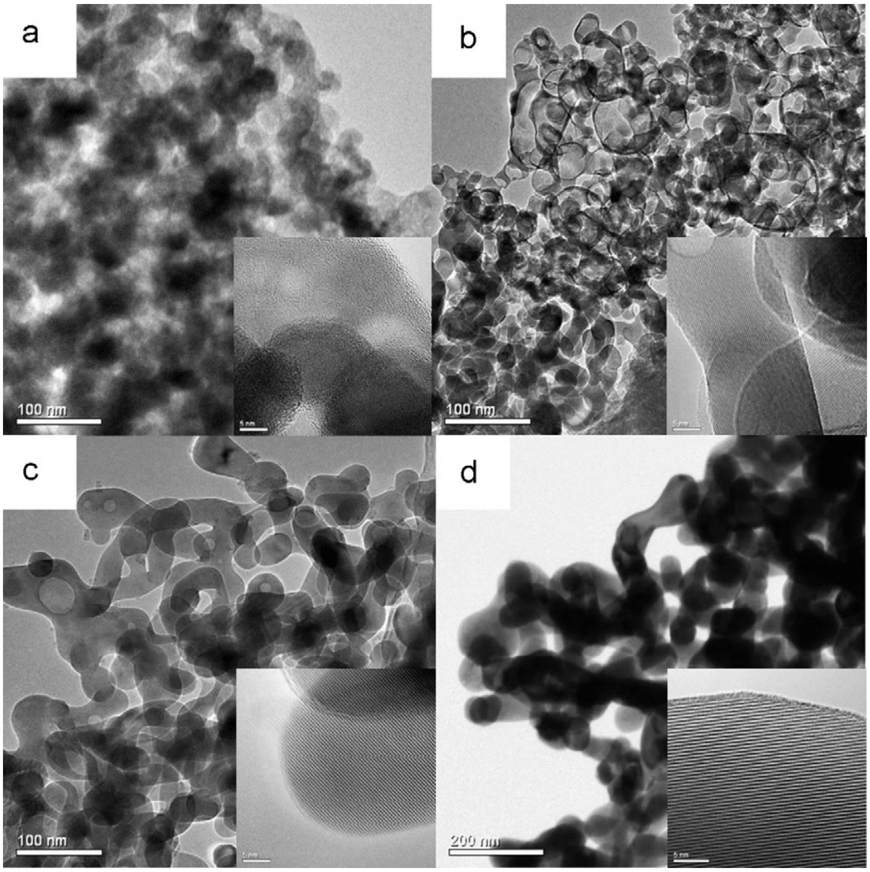

Fig. 5. The TEM and HRTEM images of the YAG precursor produced with AHC at the different sintering conditions: (a) 1073 K, (b) 1173 K, (c) 1273 K, and (d) 1373 K, 2 h.

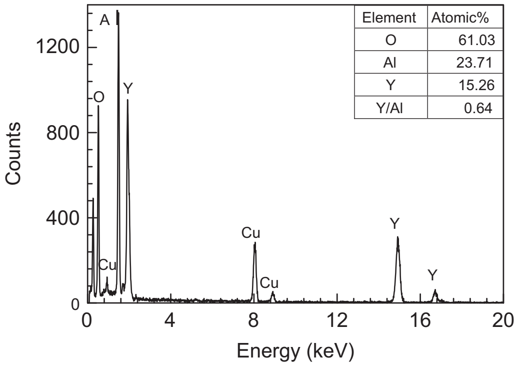

Fig. 6. EDS analysis of the component phases of the YAG precursor produced with AHC sintering at 1373 K for 2 h.

YAG, and the Cu peaks corresponding to base plate. But the precursor powders prepared by AHC have a slight deviate from 60% to 64%, because of the gelatinous AlOOH formation.

## 4. Conclusions

The polycrystalline YAG powders have been prepared by the co-precipitation method using AC and AHC as precipitants. It has been found that the use of AHC produced a carbonate precursor and the precursor directly converted to pure YAG cubic crystal phase via YAP phase, but the hydroxide precursor using AC as precipitant had transformed to a mixture with YAG and $Y_2O_3$ at about 1300 K. It is considered that the pH changing and the concentrations of $[NH_4^+]$ and $[CO_3^{2-}]$ in the precipitant solution affect the composition of precursor produced. EDS spectra show that the precursor powders prepared by AHC has a slight deviate from 60% to 64%, because of the gelatinous AlOOH formation.

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