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# FORMATION OF YAG FROM COPRECIPITATED YTTRIUM ALUMINIUM HYDROXIDES

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## Abstract

Thermal decomposition of the amorphous coprecipitate of yttrium and aluminium hydroxides forming yttrium aluminium garnet has been investigated employing thermal analyses, X-ray diffraction and IR spectroscopy. On heating, the coprecipitate progressively loses water forming a stable but highly disordered hydroxy garnet which crystallizes at ~1180 K and decomposes to YAG at ~1290 K. Nucleation of the crystalline phase appears to begin at ~800 K.

**Keywords:** yttrium aluminium hydroxides, coprecipitated, hydroxy garnet

## Introduction

Yttrium aluminium garnet (YAG) single crystals being hosts for neodymium and chromium lasers, synthesis of the high purity polycrystalline compound for crystal growth has received considerable attention. Pure YAG ($Y_3Al_5O_{12}$) free from impurity phases cannot be prepared by conventional solid state methods due to the existence of other stable phases in the $Y_2O_3$–$Al_2O_3$ system [1–6]. Hence coprecipitated hydroxides of yttrium and aluminium which form a convenient precursor, have been employed for preparation of YAG. De With and Van Dijk [7, 8] used the coprecipitate to obtain sintered high density samples of YAG. However, Glushkova *et al.* [9] found that the YAG formed from the hyroxides precursor contained other impurity phases. Gowda [10] reported the preparation of phases-pure YAG and other Y/Al oxides by the sol-gel process. Vrolijk and associates [11] studied the conditions for preparing yttrium aluminium hydroxides coprecipitate (YAHC) with minimum particulate agglomeration. Recently Apte *et al.* [12] studied the preparation of YAG from

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YAHC formed by direct and reverse precipitation from mixed nitrate solutions of yttrium and aluminium by ammonia.

Though preparation of YAG through the YAHC precursor has been studied, the mechanistics of its formation as well as the nature of the precursor have not been yet delineated. Our preliminary studies [13, 14] indicated that the precursor is a complex hydroxide and not a mixture of hydroxides. Results of detailed investigations to characterize YAHC and formation of YAG therefrom, are discussed here.

## Experimental

Preparation of the YAHC precursor was carried out as follows: standardized solutions of Analar grade nitrates of yttrium and aluminium were prepared; required quantities of the solutions were weighed and mixed such that the cationic ratio. Y/Al equalled 3/5. The hydroxides were precipitated at 360 K by slow ad-

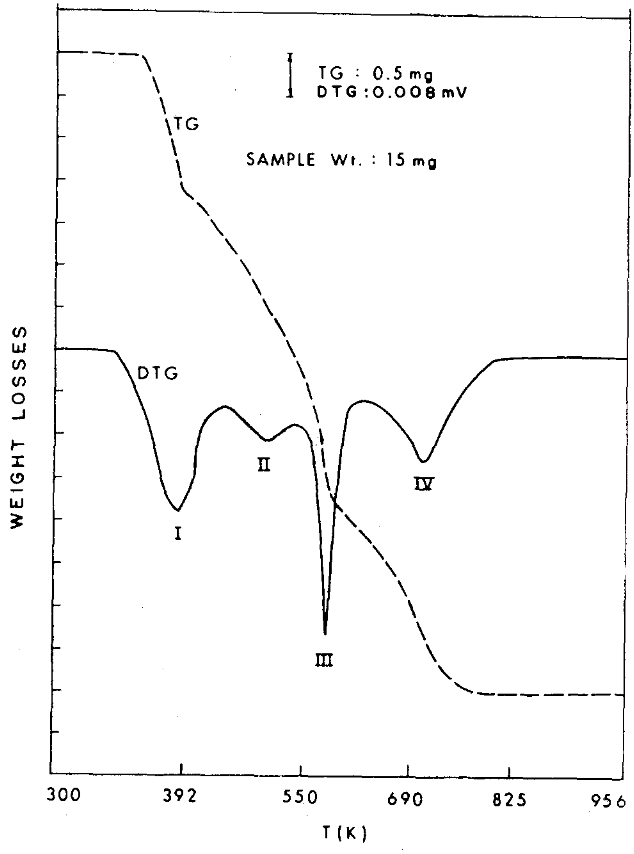

Fig. 1 TG and DTG plots of YAHC from 300 to 950 K

dition of dilute ammonia (25% v/v) with constant stirring. On completion of precipitation at *pH*~10 the slurry was left standing for a few hours and filtered. The precipitate was washed thoroughly with very dilute ammonia and dried overnight at 398 K. Hydroxides of yttrium and aluminium were also prepared by the same procedure.

Thermogravimetric (TG) and differential thermogravimetric (DTG) analyses of the samples were carried out on an Ulvac Sinku Riko 7000 analyzer. Netzsch Thermal Analyser STA 409 was employed for determining the weight losses above 1200 K. X-ray diffraction (XRD) patterns of the samples were taken on a Philips wide angle goniometer using Ni-filtered CuK$_\alpha$ radiation. Their infra red spectra were taken on a Pye Unicam 9512 spectrophotometer. The samples were dispersed in Nujol and spectra were recorded in the region 400 to 4000 cm$^{-1}$.

## Results and discussion

The thermal decomposition of YAHC takes place in several steps, as depicted in Figs 1 and 2, thereby demonstrating that the hydroxyl groups and water molecules in the complex are not equivalent among themselves and their stabilities are different. In spite of drying the samples at 398 K they hold considerable amount of free water as seen in the figures. The weight losses from ambient to 625 K show relatively larger deviations from sample to sample due to the differences in their free and labile water contents. After the loss of free

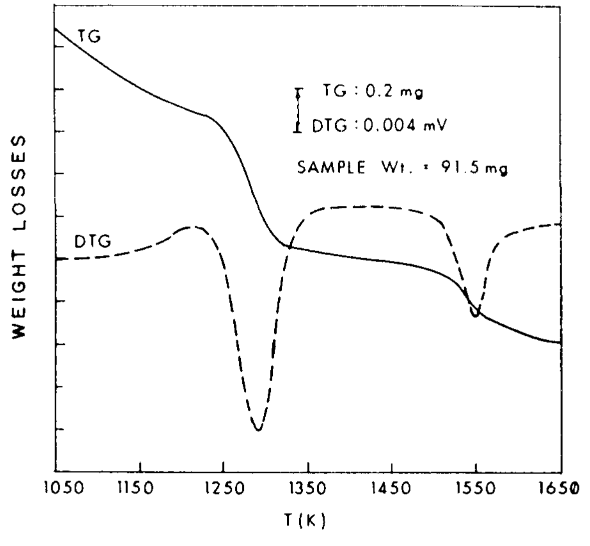

Fig. 2 TG and DTG of YAHC at higher sensitivity (TG 2.5 times and DTG twice higher than in Fig. 1) between 1050–1450 K

water five weight losses in the temperature intervals of 432 to 548 K, 548 to 625 K, 625 to 796 K, 1225 to 1350 K and above 1500 K with peaks at 518, 578, 715, 1290 K are noted in the plots though the one at 518 K is not distinguishable in the TG. Labile water from the complex is lost in two steps between 432 and 625 K leaving an intermediate which on decomposition at 715 K produces a highly disordered hydroxy garnet undergoing crystallization at 1180 K, as seen by the exothermic peak in the DTA. At 1290 K the hydroxy garnet decomposes to the YAG which is found to loose oxygen above 1500 K becoming nonstoichiometric.

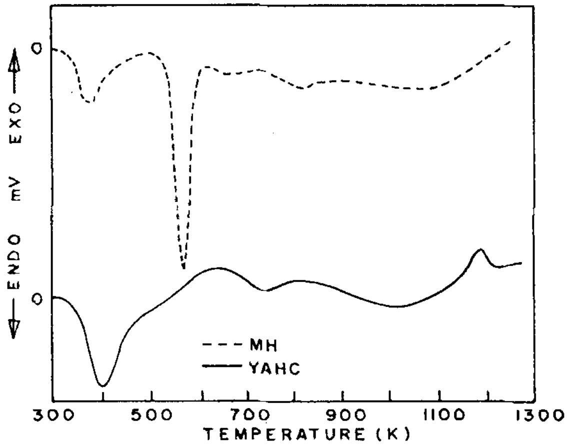

Fig. 3 DTA of YAHC and MH samples between 300 and 1300 K

DTA data of the YAHC and a mixture of yttrium and aluminium hydroxides taken in 3/5 molar ratio (referred hereafter as MH) between 300 and 1300 K, are given in Fig. 3. The exothermic peak of the YAHC at 1180 K due to the crystallization of the hydroxy garnet and the strong endothermic peak observed in the MH samples at 575 K due to the decomposition of $Y(OH)_3$ to its oxyhydroxide [14, 15] are the dominant differences between the two sets of data. The absence of an endothermic peak corresponding to the major weight loss of the YAHC at ~578 K is very significant. A prominent exothermic hump between 575 and 675 K in the DTA immediately following this weight loss leads us to infer that a highly exothermic molecular rearrangement take place in the solid concomitant with this weight loss.

Representative XRD patterns of the YAHC heated at 625, 900, 1095 and 1290 K between 2θ of 15° and 60° are shown in Fig. 4. It is noted that up to ~900 K the samples are highly amorphous. Diffractograms of the hydroxy garnet, at $900<T<1180$ K, exhibit a broad band, in the region of 27°–34° enveloping the dominant (420), (400) and (321) reflections of YAG, as seen in Fig. 4–B&C. This is considered to signal the onset of short range order in the

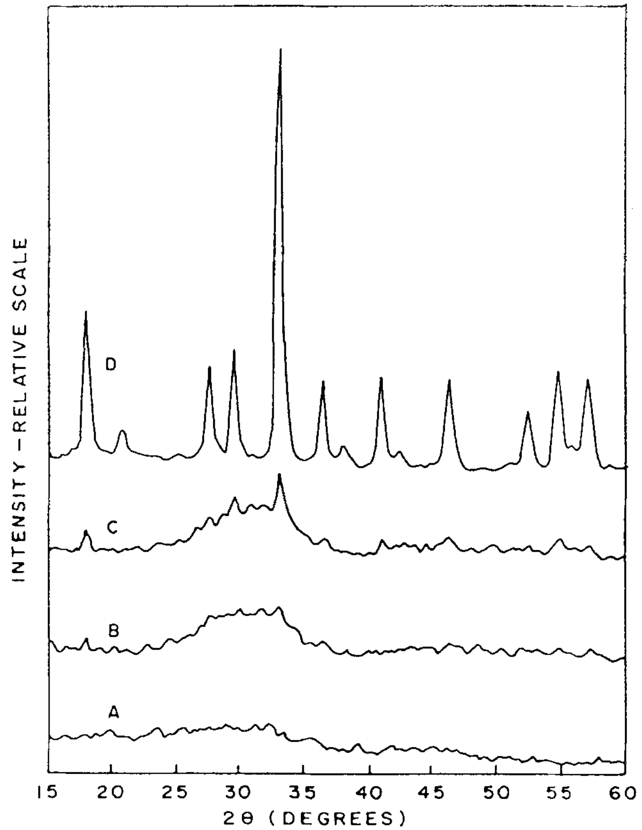

**Fig. 4** X-ray diffractograms of YAHC samples heated to: A=625 K, B=900 K, C=1095 K and D=1290 K, between 15° and 60°

solid, initiating nucleation of the crystalline phase. The fully crystalline phase [16] appears only above 1180 K.

The possibility of the YAHC having any structural relation to the crystalline layered double hydroxide complexes [17] is eliminated by its very amorphous nature.

The DTA and XRD results provide direct evidence that the YAHC is a complex hydroxide unlike inferred by Apte *et al.* [12]. No trace of formation of the hydroxides or oxides of yttrium or aluminium, at any temperature during the decomposition of the YAHC is observed in the diffractograms, whereas in the MH samples reflections due to various oxides/oxyhydroxides of the cations, depending on the thermal treatments of the samples, are found in the MH samples.

Infrared spectra of the samples show good agreement with the thermoanalytical and XRD results. Spectra of samples heated at different temperatures along with those of the pure hydroxides of yttrium and aluminium are repro-

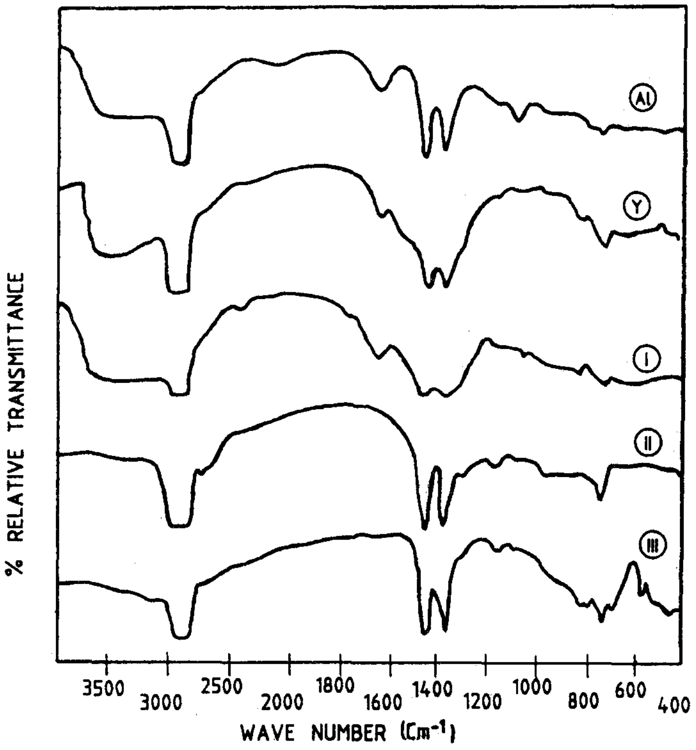

**Fig. 5** Typical IR spectra of aluminium hydroxide (Al) and yttrium hydroxide (Y) dried at 398 K and YAHC samples heated: I at 398 K, II at 900 K and III at 1290 K respectively

duced in Fig. 5. The spectra prominently exhibit the absorption peaks due the stretching and bending of the OH group. Complete loss of free and labile water from YAHC takes place around 625 K as shown by the sizable diminition in the intensities of the bands at 1600–1700 and 3020–3800 cm$^{-1}$ and loss of bound water from the complex at 715 K is marked by their extinction. Only when structural water is lost from the hydroxy garnet at 1290 K, characteristic absorption peaks of pure YAG appear in the 400 to 800 cm$^{-1}$ region of the spectrum. [The categorization of the hydroxyl groups (and water molecules) of YAHC as free, labile, bound and structural is meant only to identify the different entities.]

Based on the experimental data the thermal decomposition of YAHC is schematically formulated as given in Table 1. Since the hydroxy garnet losses small amount of water with increasing temperature, as seen in Fig. 2, it is shown as nonstoichiometric in the Table.

Our results are generally in agreement with those of the previous workers. The yttrium aluminium gels prepared by Gowda [10] were amorphous up to

**Table 1** Thermal decomposition data of YAHC

| Empirical formulae | Mass loss/% | | $T_{Decomp.}$/K (DTG peak) | Water/OH species lost |
|---|---|---|---|---|
| | Observed | Calculated | | |
| $Y_3Al_5(OH)_{24}{\cdot}23H_2O$ | – | – | 395 | Free water |
| $Y_3Al_5(OH)_{24}{\cdot}16H_2O$ | 10.5±1.0 | 10.3 | 518 | Labile water |
| $Y_3Al_5(OH)_{24}{\cdot}9H_2O$ | 21.0±1.0 | 20.6 | 578 | Labile water |
| $Y_3Al_5(OH)_{24}{\cdot}0.5H_2O$ | 33.0±0.5 | 33.1 | 715 | Bound OH |
| $Y_3Al_5O_{11-x}(OH)_{2+2x}$ ($x$~0.5) | 49.5±0.2 | 49.3 | 1290 | Structural OH |
| $Y_3Al_5O_{12}$ | 51.5±0.1 | 51.5 | 1550 | – |
| $Y_3Al_5O_{12-d}$ (d~0.075) | 51.6±0.1 | 51.6 | – | – |

1073 K while Apte *et al.* [12] noted that the YAHC crystallize only at temperatures >1200 K depending on the atmosphere in which the samples were heated. Though their DTA–TG data showed perceptible weight losses after the crystallization these were not investigated and hence the formation of the hydroxy garnet phase as a stable intermediate was overlooked.

## Conclusion

The present investigations show that the amorphous coprecipitate of yttrium and aluminium hydroxides (in 3/5 molar ratio) formed from their nitrate solutions is a complex hydroxide and not a mixture of hydroxides of the cations. YAHC decomposes to YAG by elimination of water in several steps. A hydroxy garnet having a highly disordered crystal structure and stable in the temperature range of 800 to 1290 K and crystallizing at 1180 K is formed as an intermediate. On decomposition of the hydroxy garnet at 1290 K, pure YAG is obtained, which becomes nonstoichiometric at temperatures above 1500 K.

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