Thermal Decomposition and Phase Evolution Behaviour of Precursors for YAG Prepared by Solution Combustion Technique

M.B. Kakade and S. Ramanathan
Materials Science Division
Bhabha Atomic Research Centre

and

B.B. Kalekar
Analytical Chemistry Division
Bhabha Atomic Research Centre

Abstract

Precursor powders for yttrium aluminum garnet (YAG) were synthesized by solution combustion reactions (nitrate – urea and nitrate – glycine reactions) and simple decomposition of nitrate solution. The TG - DTA studies of the precursors along with XRD analysis of typical heat-treated samples were carried out to understand the processes occurring at various stages during heating and optimize the calcination conditions to obtain phase pure YAG.

Precursors from all the reactions exhibited about 3 to 5 percent weight loss accompanied by an endotherm in the range of 30 to 300°C, corresponding to dehydration of absorbed moisture and traces of hydroxide. There were no further weight loss and heat effects noticed for the precursor from nitrate – urea reaction (precursor – A), indicating its chemical composition as YAG. This precursor was found to be pure crystalline YAG by XRD. The formation of crystalline YAG was attributed to the higher temperature due to flame formation during combustion. The precursor from nitrate – glycine reaction (precursor – B) exhibited a loss of weight of 5 percent accompanied by an exotherm in the range of 400 to 600°C and a loss of 12 percent accompanied by two shallow endotherms in the range of 900 to 1100°C. The processes occurring at these stages were characterized as burning away of the black carbonaceous contaminant and decomposition of a glycine complex of aluminum and yttrium respectively. The XRD studies showed that the precursor was amorphous up to 890°C and formed into a mixture of hexagonal YAP and cubic YAG phases at 930°C. The YAP phase appeared to be an intermediate that finally transformed into YAG. The precursor from simple decomposition of nitrates (precursor – C) exhibited a loss of weight of about 10 percent in the range of 300 to 500°C and the process was characterized as de-nitridation. Crystalline YAG formed directly from an amorphous oxide compound with no loss of weight but formation of two exotherms (one sharp and one shallow) in the temperature range of 850 to 1100°C. No noticeable intermediate phase was detected.

Introduction

Yttrium aluminum garnet (YAG) powders possessing controlled characteristics find a wide variety of applications in making transparent laser components, advanced engineering material and composites, phosphors, refractory coating etc. Formation of YAG by solid-state reaction requires temperature of the order of 1600°C and long duration. There are various solution based methods reported (such as simple decomposition of nitrates, sol – gel process, homogeneous and heterogeneous precipitation and solution combustion) in which YAG phase forms at a much lower temperature due to mixing of the reactants in molecular scale in solutions. The powders formed by
Combustion technique can be phase pure crystalline YAG or nano-crystalline compound containing volatiles which need to be calcined to form into phase pure YAG.

In solution combustion technique, from a very concentrated solution of the metal nitrates (oxidizer) and urea or glycine (fuel) a very porous mass of the oxide compound is formed due to the evolution of a large amount of gases. The heat evolved during combustion makes the reaction self-sustaining to form the compound. The stoichiometric amount of urea or glycine required for combustion can be calculated using the reported combustion reactions $^{9,12}$

$$2\text{M(NO}_3\text{)}_3 + 5\text{CO(NH}_2\text{)}_2 \rightarrow \text{M}_2\text{O}_3 + 5\text{CO}_2 + 10\text{H}_2\text{O} + 8\text{N}_2 \quad (1)$$

$$3\text{M(NO}_3\text{)}_3 + 5\text{NH}_2\text{CH}_2\text{COOH} \rightarrow 3/2\text{M}_2\text{O}_3 + 7\text{N}_2 + 10\text{CO}_2 + 25/2\text{H}_2\text{O} \quad (2)$$

where ‘M’ is the aluminum and yttrium ions in 5:3 ratio. $\text{M}_2\text{O}_3$ can be represented as $(Y_{3/8}\text{Al}_{5/8})_2\text{O}_3$. For every mole of $\text{M}_2\text{O}_3$ formed 23 and 20 moles of gases are evolved for reaction 1 and 2 respectively.

The simple decomposition of the aqueous solution of nitrates of aluminum and yttrium can be represented as

$$2\text{M(NO}_3\text{)}_3 \rightarrow \text{M}_2\text{O}_3 + 6\text{NO}_2 + 3/2\text{O}_2 \quad (3)$$

This reaction is endothermic and the number of moles of gases evolved per mole of $\text{M}_2\text{O}_3$ formed is 7.5. Acidic nitrogen dioxide gas polluting the atmosphere is evolved in this reaction which is not present in combustion reactions.

However the exothermicity, fast reaction kinetics and evolution of large amount of gases make the combustion reaction violent and pose problems in scaling up of the process. One way of exercising control over the reaction kinetics is by way of using the fuel for which the heat of combustion is sufficient but not excessively too high (e.g., reaction 2 is less exothermic than reaction 1).

A study of the thermal decomposition by thermal analysis (TG - DTA) and phase evolution by XRD of the precursors formed by these reactions is essential in optimizing calcination conditions for formation of phase pure YAG and brings out the advantages and limitations of each reaction. A comparative study of the above aspect has been carried out for the precursors formed by solution combustion reactions (nitrate - urea, nitrate - glycine reactions) and simple decomposition of nitrates.

**Experimental**

Aqueous stock solutions of aluminum nitrate (1.9 M) and yttrium nitrate (1.1 M) required for YAG composition (batch size ~40 grams) were mixed and concentrated to a viscous liquid (metal ion concentration ~ 10 M) by evaporation at 70°C in an air oven for three batches. Urea (urea/nitrate ion molar ratio ~5/6) and glycine (glycine/nitrate ion molar ratio ~5/9) were dissolved in two batches of the concentrated liquid of nitrates in two pyrex beakers. The precursors were formed by heating the viscous solutions in the beakers gently on a laboratory assembled nicrome wire heater till the combustion reaction set in accompanied by the evolution of a large amount of gaseous product with heat (called precursor - A and B respectively). The third batch of the nitrate solution in the beaker was decomposed on the same heater till evolution of reddish fumes of nitrogen dioxide subsided (precursor - C). The as formed precursors - A, B and C were dry ground separately in a planetary mill (M/s. Fritsch) for half an hour to form into a homogeneous powder mass. The powders thus obtained were subjected to TG - DTA studies in Netzsch Thermal Analyser (Model STA 409) in air for volatile loss and heat effects (heating rate - 10°C/min.). XRD studies were carried out for typical heat-treated precursors in a Philips X-ray diffractometer for phase formation. The average crystallite size was determined by the line broadening method (peak corresponding to 420 reflection) using the Scherrer formula.

**Results and Discussion**

**Formation of precursors**

The precursors were formed by conducting the combustion and decomposition reactions on a
heater in open, as the heat output of the heater could be easily controlled so that the reaction did not become excessively vigorous and the gases evolved could easily escape. In case of formation of precursor by solution combustion reaction using urea as fuel (precursor-A), as the temperature reached gradually about 200°C, the viscous liquid foamed vigorously with the evolution of a larger amount of bubbles of gaseous product of fuel - oxidizer reaction (CO₂, N₂, H₂O). This was accompanied by the formation of a bright flame (maximum flame temperature recorded by using two color pyrometer was 1600°C) and a porous sponge-like solid. Also in case of formation of precursor using glycine as fuel (precursor-B), as combustion set in above 200°C, a large amount of gas was evolved but no flame formed. The reaction was smooth without any spilling. The combustion was slower and controlling the process for larger batch size was easier. In case of formation of precursor by simple decomposition of nitrates (precursor-C), the solution decomposed smoothly with the evolution of bubbles of reddish brown nitrogen dioxide gas (major acidic pollutant to the atmosphere) forming compact granules of aggregated powder. The precursors - A and C were white while precursor -B was black and contaminated with carbonaceous material. The black color was attributed to segregation of some amount of glycine and its charring due to the lower reaction temperature (~600°C). This was confirmed by the formation of a black product in the initial stage of decomposition of the aqueous solution of pure glycine, which burned off above 600°C. Concentrating the solution of aluminum nitrate and yttrium nitrate before adding urea was necessary to avoid loss of urea by the side reaction - hydrolysis of urea in water above 80°C.

\[
\text{CO(}\text{NH}_2\text{)}_2 + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 2 \text{NH}_3 \quad (3)
\]

Combustion set in only when the liquid reactant became viscous.

**Characterization of precursors**

*TG-DTA and XRD studies* : The TG - DTA pattern for the precursor -A is given in Fig.1. It exhibited a shallow broad endotherm accompanied by 3 percent loss in weight in the range of 25 to 300°C. This could be attributed to the process of dehydration of absorbed moisture and traces of structural hydroxide in the powder. There were no heat or weight loss effects above 300°C indicating the completion of YAG formation in this combustion reaction due to the higher temperature of the flame. The XRD studies showed that the as formed precursor was well-crystallized YAG phase with an average crystallite size of about 280Å (Fig.2).

*Fig.1 TG - DTA pattern for precursor -A*

*Fig.2 XRD pattern for the as formed precursor -A*

The TG-DTA pattern of the precursor -B is shown in Fig.3. It exhibited a broad endotherm accompanied by a loss of weight of 5 percent in the temperature range of 25 to 300°C, attributed...
to the dehydration of absorbed moisture and traces of structural hydroxide in the powder. It showed a broad exotherm accompanied by a loss of weight of 5 percent in the temperature range of 400 to 600°C which could be attributed to the burning of the carbonaceous material (free carbon). This was confirmed by the burning off of the black product formed in the initial stages of decomposition of pure glycine in this temperature range. There were two shallow endotherms in the temperature range of 900 to 950 and 1000 to 1050°C accompanied by a total weight losses about 12 percent. The EGA analysis data showed that the gas evolved corresponding to these endotherms to be carbon dioxide. The flat TG curve above 1100°C indicated completion of all volatile losses at this temperature.

The XRD patterns of the as formed precursor and that heated to different temperatures decided from TG – DTA studies are shown in Fig.4. The as formed precursor and that heated to 890°C were amorphous, that heated to 930°C was a mixture of hexagonal YAP and cubic YAG and that heated to 1050°C was pure cubic YAG. Based on XRD studies on isothermal heat treated samples prepared by nitrate - glycine reaction, Hess et al. reported that an intermediate YAP phase formed which subsequently transformed into the stable YAG phase. This is in agreement with the present observation. The total-carbon analysis data by vacuum fusion technique of the precursor was 8 weight percent which was attributed to both the carbonaceous material existing below 600°C and the carbon dioxide evolved in the range of 900 to 1100°C. The important finding of this study is that the amorphous precursor formed by combustion is not chemically pure YAG compound and it releases substantial amount of volatiles not only in the initial stages but also during crystallization, an aspect which has not yet been reported. The loss in weight (carbon dioxide) at the crystallization stage shows that the precursor heated to 890°C is a glycine complex of aluminum and yttrium.

The formation of hexagonal YAP as an intermediate showed the closeness of its structure to that of the amorphous glycine complex. The kinetically favored YAP phase formed that finally transformed into the thermodynamically stable cubic YAG. The ease of formation of YAG phase from the YAP phase showed that the chemical composition of the YAP phase was Y₃Al₅O₁₂ (i.e., it is a solid solution of Al₂O₃ in Al₂O₃) and not a mixture of Al₂O₃ and Al₂O₃.

The TG-DTA pattern of the precursor –C formed by the simple decomposition of nitrates is shown in Fig.5. It exhibited an endotherm in the range of 25 to 300°C accompanied by a weight loss of...
3 percent, attributed to the loss of absorbed moisture and traces of structural hydroxide in the powder. Another endotherm occurred in the range of 300 to 500°C accompanied by a weight loss of about 10 percent, which could be attributed to the decomposition of left over nitrate in the precursor. There was a gradual loss of weight of about 3 percent in the temperature range of 500 to 800°C with no detectable heat effect. There were two exotherms in the temperature range of 870 to 950°C (sharp) and 950 to 1050°C (very shallow) accompanied by very little loss in weight at these stages. This indicated the chemical composition of the precursor before and after the exotherms was the same i.e., YAG.

The XRD patterns for the precursor and that heated to different temperatures are shown in Fig 6. The as formed precursor and that heated to 820°C were amorphous. Crystallization to pure YAG set in around 870°C and progressed upon further heating. The average crystallite size values for the precursor heated to 870 and 950°C were exactly the same (~280Å) while that for the precursor heated to 1050°C is 350Å. This observation showed that in the temperature range of 870 to 950°C only the progress of crystallization from amorphous precursor took place while further growth of crystallites occurred in the range of 950 to 1050°C. As the crystallite size increased in the range of 950 to 1050°C, the shallow exotherm around 1000°C could be attributed to further growth of crystallites. Thus well-crystallized YAG formed from precursor - C above 1050°C. The point to be noted was crystalline YAG formed directly from amorphous oxide compound of the same chemical composition without any detectable intermediate phase.

The crystallization of pure YAG phase in all these precursors at a temperature around 1100°C established the presence of compositional homogeneity of metal atoms in all the precursor intermediates.

**Conclusions**

Chemically pure crystalline YAG formed in nitrate - urea reaction. However the reaction is too vigorous with flame formation. The preparation of precursor of YAG powder by nitrate - glycine reaction is a versatile one for scaling up. The reaction yields amorphous precursor that upon subsequent heat treatment exhibits volatile loss in stages due to dehydration, carbon burning, and crystallization. Loss of volatiles during crystallization is an interesting observation in this study which has not been reported so far. The formation of YAG phase from the amorphous precursor takes place via the formation of an intermediate YAP-like structure. These powders are the softest agglomerates...
that could be easily ground. Simple decomposition of nitrates yields amorphous precursor. Upon further heat treatment, it evolves volatiles in stages due to dehydration and de-nitridation. Crystalline YAG phase forms directly from the amorphous oxide compound without any loss of volatile.

It can be said that the combustion synthesized powder from nitrate - glycine reaction needs to be calcined just like the one formed by simple decomposition of nitrates. But the powder agglomerates formed by this reaction (nitrate - glycine reaction) is expected to be the softest due to the evolution of large amount of gases and just required amount of heat. The nitrate - urea combustion reaction results directly in the formation of YAG but difficult for scaling up due to flame formation. The study of thermal decomposition and phase evolution for all these precursors established the calcination condition to form chemically pure and crystalline YAG phase.

Acknowledgements

The authors thank Mr. B. R. Ambekar of Applied Chemistry Division and Mr. E. K. Unnikrishnan of Analytical Chemistry Division for their help in carrying out the XRD and carbon analysis studies respectively. The authors acknowledge the help of Dr. P.V. Ravindran in the interpretation of the TG-DTA data. Also they thank Dr. P.K. De, Head Materials Science Division and Dr. S. Banerjee, Director Materials Group for their keen interest in this work.

References


This paper was awarded the Second Prize at the 13th National Symposium on Thermal Analysis, held at BARC, Mumbai, during January 21-23, 2002
About the authors …

Mr M.B. Kakade joined BARC in 1984 after doing M. Sc. from Karnataka University, Dharwar. He has worked on ceramic material processing which includes sintering of magnesia, alumina, spinel, sillimanite grog and zircon wares. At present, he is working on synthesis and characterisation of zinc chromate, yttrium aluminium garnet and lanthanum strontium manganite powders by solution combustion technique for various applications.

Dr S. Ramanathan joined BARC in 1976 through 19th batch of Training School and works on processing of advanced ceramic materials. He worked on the development of thoria – yttria solid oxide electrolyte for oxygen sensor applications and obtained Ph D in Materials Science from IIT Mumbai. He worked on synthesis of controlled morphology sub-micron sized oxide powders by homogeneous precipitation technique and impervious oxidation resistant and porous catalytic coatings by sol – gel technique. Presently, he is working on the formation of ceramic shapes by liquid based fabrication techniques (slip and tape casting). He has about forty-five publications in Indian and International journals.

Mr Bhupesh B Kalekar graduated from University of Pune and joined Analytical Chemistry Division of BARC in 1998 after completion of one year training course in Analytical Chemistry. He works on thermal analysis to study the decomposition mechanism and kinetics of solid-state reactions.