

# Sol–gel preparation and optical characterization of $\text{Tb}_x\text{Y}_{3-x}\text{Al}_5\text{O}_{12}$

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Received 31 May 2005; accepted 3 November 2005

Available online 28 November 2005

## Abstract

$\text{Tb}^{3+}$  doped Yttrium Aluminum Garnet (Tb: YAG) is a very promising optical material. This article reports synthesis of Tb doped YAG polycrystalline powder by sol–gel method. The sample was heat treated at different temperatures for characterization purpose. The powder was characterized by X-ray diffraction analysis (XRD), Scanning electron microscopy (SEM), Photoluminescence (PL) studies and Raman Spectroscopy.  $^5\text{D}_4 \rightarrow ^7\text{F}_j$  transitions were observed due to presence of  $\text{Tb}^{3+}$  in the YAG structure. Phonon band and few inter manifold transitions in  $^7\text{F}_6$  and  $^7\text{F}_5$  have been observed. Raman active  $\text{A}_{1g}$ ,  $\text{E}_g$ ,  $\text{T}_{2g}$  modes have been successfully identified in the phonon band at room temperature Raman measurements.

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**Keywords:** Sol–gel preparation; Characterization

## 1. Introduction

Yttrium Aluminum Garnet [ $\text{Y}_3\text{Al}_5\text{O}_{12}$ , (YAG)] based phosphors doped with rare earth ions (Eu, Tm, Tb, Ce) find important applications in fabrication of optical devices. It is advantageous to study properties of  $\text{Re}^{3+}$  ions in YAG structures as it has relatively stable lattice and large heat conductivity [1]. In view of their high temperature chemical stability, Tb: YAG is expected to replace the existing sulphide based materials that are commonly used as main component in cathode ray tubes [2]. These phosphors also have characteristic narrow band emission that makes it suitable for contrast enhanced display applications in high ambient illumination conditions. Furthermore Tb activated YAG phosphors has luminescence properties that are fairly sensitive to temperature variations and shows little tendency to saturate at high current excitations.

Synthesis of Tb: YAG has been realized in many different ways. Van der Weg and Vantol [3] synthesized Tb: YAG by co-precipitation of hydroxides from nitrate solutions by annealing at 1275 °C in Nitrogen atmosphere. YAG phosphors were also synthesized using sol–gel method but achieved crystalline phase at relatively high temperatures greater than 1200 °C.

Choe et al. [4] demonstrated a novel method for YAG: Tb phosphor synthesis using alkoxide derived sol–gel process at about 900 °C. In the present work Tb: YAG is synthesized starting from metal oxides and nitrates using citrate–nitrate sol–gel method and characterize it using optical techniques. The sol–gel synthesis of metal oxides is based on the polymerization of inorganic molecular precursors in aqueous solution or metal alkoxide in non-aqueous media.

## 2. Experimental

Aluminum nitrate ( $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , analytical grade), Yttrium oxide ( $\text{Y}_2\text{O}_3$ , 99.9% pure), Terbium Oxide ( $\text{Tb}_4\text{O}_7$ , 99.9% pure) and hydrated citric acid ( $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ , analytical grade) were used as starting materials in the present synthesis. Citrate ion served as chelating agent to metal cation and fuel for combustion. Yttrium oxide (.00375 mol) was first dissolved in conc. nitric acid. Terbium oxide (.000125 mol) digested in conc. nitric acid was added to the above solution and stirred for 3 h at 60–65 °C. Aluminum nitrate (.0125 mol) dissolved in distilled water was further added to this solution and the resulting mixture was again stirred for 3 h at same temperature. The mole ratio of Tb:Y was 1:15. In the following step solution of citric acid in distilled water was added and stirred again for 3 h at same temperature. After concentrating the solution under

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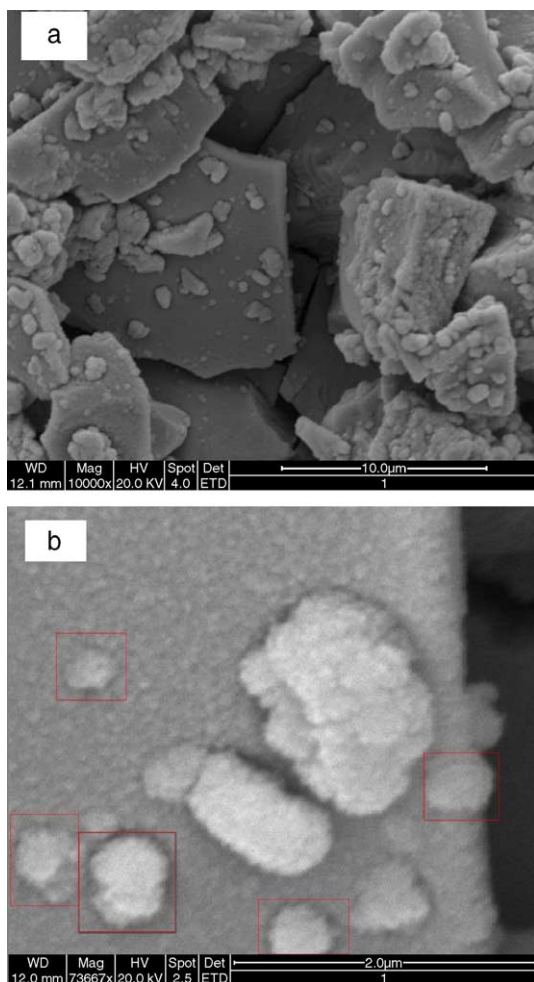


Fig. 1. (a) SEM micrograph showing coexistence of large plate like agglomerations along with smaller grains. (b) Shows SEM micrograph of submicron scaled grains (marked in red). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

constant stirring the solution was finally put on water bath and a transparent sticky gel was obtained. The gel was then oven dried at about 150 °C and auto combustion took place accompanied by brown fumes. Finally a fluffy yellowish precursor remained. The precursor was then treated at 800, 900, 1100 and 1400 °C in air.

X-ray measurements were done for verification of crystallinity and formation of Tb: YAG. The particle size and morphology was examined using scanning electron microscopic images. The photoluminescence of the synthesized Tb: YAG sintered at different temperatures was taken at room temperature. Raman spectrum of the powdered sample was measured by excitation using Argon ion laser source operating at wavelength of 514.5 nm. The laser power used was 5 W. Raman spectrum was collected using SPEX 1877E triplemate spectrometer attached with liquid N<sub>2</sub> cooled CCD in 90° reflection geometry mode. The spectrum was recorded at room temperature.

### 3. Results and discussion

X-ray diffraction data was acquired for the sample sintered at 800, 900, 1100 and 1400 °C for 10 h. The data was taken using Cu-Kα radiation in the range  $2\theta = 15^\circ$  to  $75^\circ$ . The 100% intensity was observed at  $2\theta = 33.7^\circ$  for the sample sintered at 1100 °C. The X-ray spectra recorded was in accordance with the data reported by Choe et al. [4]. Thus formation of single phase Tb: YAG was confirmed.

The textural properties of the calcined sample at 1100 °C for 10 h were investigated by SEM. The Tb: YAG solids are composed of grains with no regular shape. Fig. 1a shows coexistence of large plate like agglomerations with smaller spherically shaped grains. The large variation in grain size is accounted due to agglomeration due to large exposure time of the sample and high temperatures. Existence of submicron scaled grains of the order of 200–300 nm can be verified from the SEM image in Fig. 1b.

Photoluminescence properties of Tb<sub>x</sub>Y<sub>3-x</sub>Al<sub>5</sub>O<sub>12</sub> ( $x = .1875$ ) annealed at 800, 1100 and 1400 °C were studied at room temperature

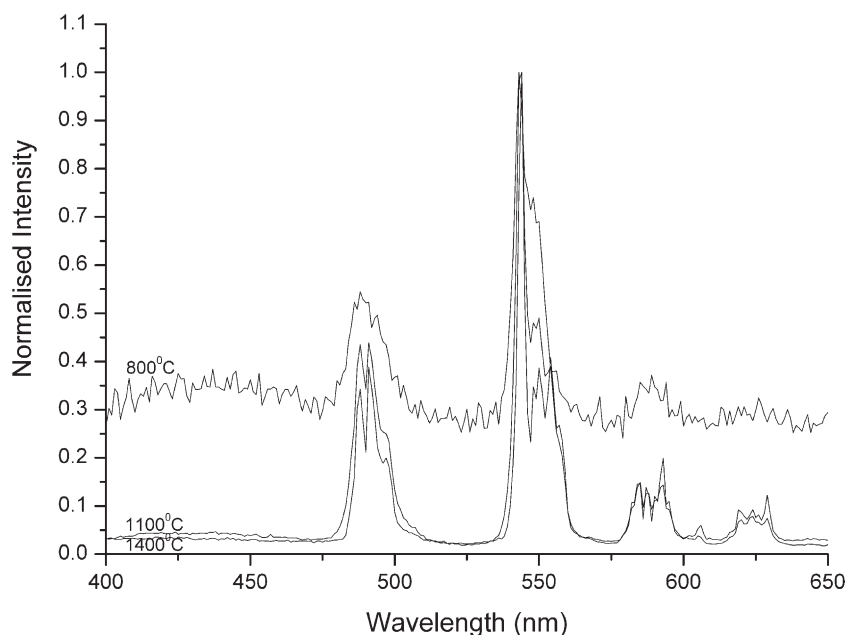


Fig. 2. Photoluminescence spectra of Tb: YAG samples sintered at 800, 1100 and 1400 °C.

using 350 nm excitation. The  $\text{Tb}^{3+}$  luminescence arises due to transition from low energy states,  $^7F_j$  ( $j=6, \dots, 0$ ) and excited states  $^5D_4$  and  $^5D_3$  leading to luminescence and associated to  $^5D_3 \rightarrow ^7F_j$  and  $^5D_4 \rightarrow ^7F_j$  transition [5] of the stark components in the blue and green spectral range. The  $^5D_4$  level is separated from  $^7F_0$  by  $\sim 14,000 \text{ cm}^{-1}$  and  $^5D_3$  states further up. The luminescence characteristics of Tb: YAG phosphor particles have been reported to depend on morphology of the particles such as size, shape, crystallinity, defects etc by Kang et al. [6]. The intensity of rare earth luminescence in aluminum garnets doped with trivalent rare earth ions also depends in a nonlinear way on the concentration of  $\text{Tb}^{3+}$  ions. It has been reported by Van der Weg et al. [7] that at very low doping concentrations  $x \sim 10^{-3}$  the phenomenon of photoluminescence is mainly governed by the absorption of incident radiation where as the

process of cross relaxation is unimportant, 1/6th of excitation ends up in  $^5D_4$  level and 5/6th in the  $^5D_3$  level. At higher concentration the cross relaxation process rearranges the energy in favor of  $^5D_4$  emission. It is clearly evident from the recorded data shown in Fig. 2 that for the doping concentration used ( $x=.1875$ ) the process of cross relaxation over takes the phenomenon of photoluminescence arising from the absorption of the incident radiation. Hence the observed PL spectrum in the green region beyond 480 nm is assigned due to  $^5D_4 \rightarrow ^7F_j$  transition. In depopulation of  $^5D_3$  states to  $^5D_4$  states, the energy difference is absorbed by a transition into the ground state manifold  $^7F_6 \rightarrow ^7F_1$  in the neighboring Tb ion. Robbins et al. [8] has concluded that this process in Tb: YAG can be described by electric dipole–dipole interaction.

The local site symmetries of rare earth ions in crystals can be characterized by electronic Raman spectroscopy. The  $\text{Tb}^{3+}$  ions occupy

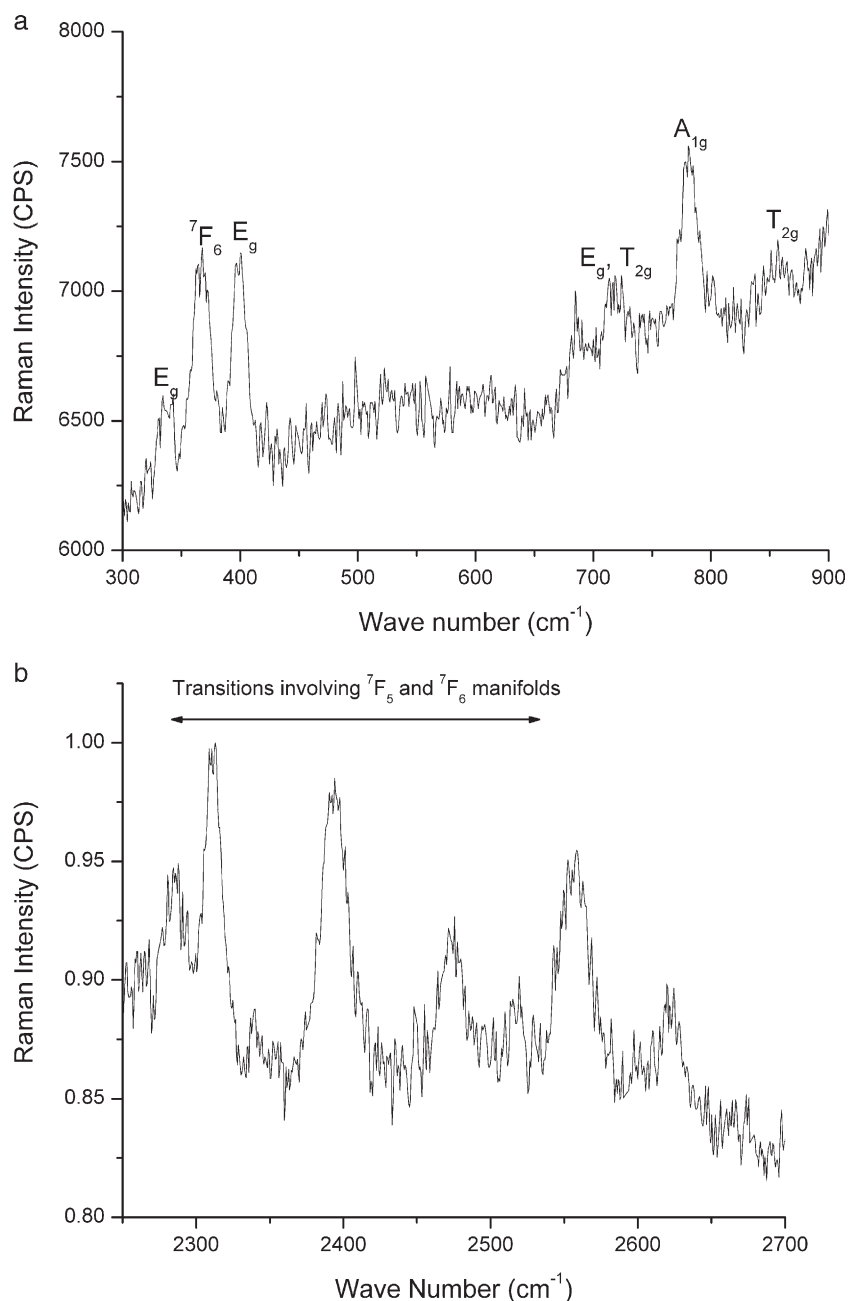


Fig. 3. (a) Raman spectrum of Tb: YAG sample showing  $^7F_6$  intermanifold transition and  $A_{1g}$ ,  $E_g$ , and  $T_{2g}$  Raman active modes at room temperature. (b) Raman Spectra of Tb: YAG sample showing transitions involving  $^7F_6$  and  $^7F_5$  manifolds.

sites having  $D_2$  symmetry as a result of this the  $(2J+1)$  fold degeneracy of LSJ manifold is completely removed and the energies of 49  $^7F_j$  crystal field states are separated into levels lying up to  $6000\text{ cm}^{-1}$  from zero field position. From the data reported on the splitting of  $^7F_j$  manifolds of  $\text{Tb}^{3+}$  in YAG by Gruber et al. [9] we can easily assign the first peak around  $370\text{ cm}^{-1}$  in Fig. 3a to be due to within one of the  $^7F_6$  intermanifold electronic transition of  $\text{Tb}^{3+}$  ion. In cubic symmetry  $A_{1g}$ ,  $E_g$ ,  $T_{2g}$  modes are Raman active and  $T_{1u}$  modes are IR active. Based on these investigations of Hurrel and Porto [10] and the data reported by them acquired at 90 K we can clearly see one strong and one weak scattering  $A_{1g}$  modes, two strong and one very weak scattering  $E_g$  mode, one strong and one weak scattering  $T_{2g}$  modes around 783, 373, 340, 403, 714, 719 and  $857\text{ cm}^{-1}$ . The very weak  $714\text{ cm}^{-1}$  scattering  $E_g$  mode and strong 719  $T_{2g}$  scattering mode are not well resolved in the measurements reported in this article. No shift in frequency at room temperature measurement of phonon spectra is observed and the results are well within the error limits reported by Hurrel and Porto. For ions in crystals, admixture can occur between wave function of opposite parity, either directly via crystal field or indirectly by vibronic coupling. Such mixing introduces odd parity associated with excited electronic states with even parity wave functions of the low lying  $^7F_{6,5,\dots,0}$  states of  $\text{Tb}^{3+}$ . The admixture of states can cause intensity borrowing and can give rise to transition from  $^7F_6 \rightarrow ^7F_{5,4,\dots,0}$  [11] peaks corresponding to these transitions involving  $^7F_6$  and  $^7F_5$  manifolds are clearly evident have been indicated in Fig. 3b.

#### 4. Summary and conclusion

Submicron sized Tb: YAG polycrystalline powder has been synthesized using sol–gel techniques following citrate–nitrate procedure. Formation of garnet structure of Tb: YAG is confirmed by the X-ray data analysis. The sample synthesized was sintered at different temperatures and

characterized using optical techniques. Luminescence spectra arising from  $^5D_4 \rightarrow ^7F_{j=6,5,\dots,0}$  transitions were observed at room temperature. Existence of  $^7F_6$  and  $^7F_5$  inter-manifold transitions was confirmed. A few of strong, weak and very weak scattering  $A_{1g}$ ,  $E_g$ , and  $T_{2g}$  Raman active modes could be observed at room temperature Raman measurements.

#### Acknowledgement

I would like to acknowledge my friends, Dr. Bansilal's lab SL211, IIT-Kanpur and DIT grant DIT/CELT/20030292 through which I was employed in this lab.

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