



# Investigations on vacuum sintered ytterbium-doped YAG ceramic: a laser–host material

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**Abstract.** Laser–host ceramics are a new class of materials and have proved to be a good alternative to the single-crystals. They can be produced in large size with higher concentration of activator ions having more homogeneity which is difficult to achieve with the conventional single-crystal growth technology. Ytterbium (Yb)-doped yttrium aluminium garnet (YAG) is a very attractive laser–host material because of its broad emission band, low quantum defect, no excited state absorption or up-conversion loss and wide range of tunability. In the present work, 10 atm% Yb-doped YAG transparent ceramic was fabricated using nano-powder technology and vacuum sintering. Single-phase nano-powders of Yb:YAG were synthesized by a co-precipitation method and thereafter sintered under vacuum at 1750°C for 5 h. The as-sintered ceramic samples are of dark greenish colour which is attributed to the reduction of Yb<sup>3+</sup> to Yb<sup>2+</sup> during vacuum sintering. However, after annealing in air at 1350°C for 8 h they retain their natural colour attributed to the transformations from Yb<sup>2+</sup> to Yb<sup>3+</sup>. The transmission spectra of the as-sintered polished ceramics show the presence of broad absorption bands near 250, 380, 480 and 630 nm due to the electronic transitions in the Yb<sup>2+</sup> ion. These bands disappear after annealing in air. The well-established bands due to transitions in Yb<sup>3+</sup> were observed between 900 and 1000 nm.

**Keywords.** Optical ceramics; Yb:YAG; sintering.

## 1. Introduction

Ytterbium (Yb)-doped yttrium aluminium garnet (Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>; YAG) is a well-known laser–host material. Its broad emission band, low quantum defect, no excited state absorption or up-conversion loss and wide range of tunability make it ideal for high power operations, such as thin-disk lasers. Currently, Yb:YAG is available as a single crystal or transparent ceramic for laser–host applications [1]. Ceramics are new types of laser gain hosts and have proved to be a good alternative to the single-crystal host. They can be produced in large size with higher concentration of Yb<sup>3+</sup> ions having more homogeneity which cannot be achieved with the conventional single crystal growth technology. Above that ceramics show better mechanical properties due to their polycrystalline nature. Despite these remarkable advantages, the production of high quality (i.e. low loss) transparent ceramics is non-trivial due to the presence of numerous scattering centres. The issues also arise from the fact that the optical quality of YAG-based ceramics highly depends on compositional heterogeneity. YAG is often described as a ‘line compound’ in reference to the Al<sub>2</sub>O<sub>3</sub>–Y<sub>2</sub>O<sub>3</sub> phase diagram; recent studies have estimated the width of the phase domain to be on the order of 0.1 mol% [2]. Any departure from stoichiometric composition leads to the formation of scattering centres

(secondary phases and pores) which significantly affect the transparency. For ytterbium (Yb)-doped YAG materials, an additional issue arises due to the multivalent nature of ytterbium. Ytterbium mainly exists as the Yb<sup>3+</sup> ion (+3 valance) as required for the Yb:YAG solid state laser. However, under a reducing atmosphere or in the presence of impurity with +4 valance, Yb<sup>3+</sup> easily converted to the Yb<sup>2+</sup> ion (+2 valance) [3]. This divalent Yb-ion strongly degrades the laser efficiency of Yb:YAG due to the presence of strong absorption in the visible-near-infrared (NIR) range. The fabrication of high quality transparent ceramic requires precise control over the starting particle size and morphology, composition and sintering parameters. The aim of present work is to investigate the effect of vacuum sintering on the transmission spectrum of Yb (10 atm%)-doped YAG ceramic.

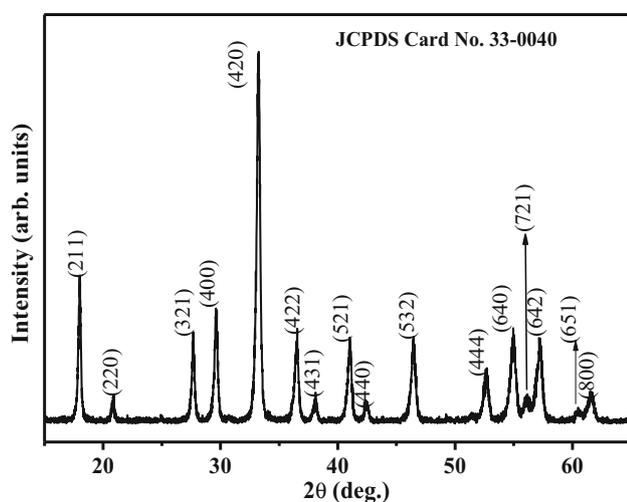
## 2. Experimental

Nano-powder of (Y<sub>0.90</sub>Yb<sub>0.10</sub>)<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> was synthesized by a co-precipitation method using Y(NO<sub>3</sub>)<sub>3</sub> · 6H<sub>2</sub>O, Al(NO<sub>3</sub>)<sub>3</sub> · 9H<sub>2</sub>O and Yb<sub>2</sub>O<sub>3</sub> as raw materials. Ammonium bicarbonate (AHC) was used as a precipitant. Nitrate solution of yttrium and aluminium was prepared by dissolving the required

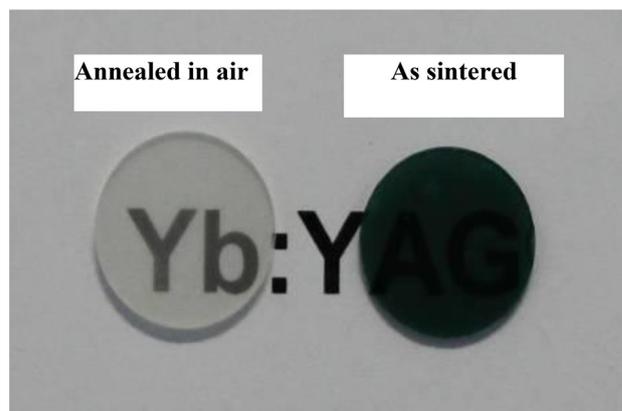
amount of metal nitrates in 200 ml of distilled water at room temperature. The nitrate solution of Yb was prepared by dissolving  $\text{Yb}_2\text{O}_3$  in nitric acid at  $70^\circ\text{C}$ . Thereafter, the required amount of Yb-nitrate solution was mixed with already prepared nitrate solution of yttrium and aluminium. The mixing of the solutions was carried out for 1 h and the final pH of the metal nitrate solution is  $\sim 1.40$ . The AHC precipitant solution ( $\sim 1.6$  M) was prepared by dissolving the required amount of AHC in 450 ml distilled water. The pH of the AHC solution was found to be  $\sim 8$ . The nitrate solution of Al, Y and Yb-ions was added drop-wise into 1.6 M AHC solution at room temperature under constant stirring. The pH of the AHC solution was continuously monitored during the addition of nitrate solution. With the addition of nitrate solution, the pH of AHC solution decreases monotonously. This decrease in the pH indicates a steady depletion of AHC, which means that the precipitation process continues. The pH of the AHC solution decreases from its initial value of  $\sim 8$  to  $\sim 7.5$  after the complete addition of nitrate solution. Thereafter, the pH increases as the ageing proceeds. The increase in pH is attributed to the decomposition of carbonic acid and the consuming process of  $\text{NH}_4^+$  to leave more  $\text{OH}^-$  ions in the solution [4]. The precipitates were stirred for 3 h and then washed four times with distilled water. The washed powder was dried at  $\sim 90^\circ\text{C}$  for 12 h and crushed in a mortar pestle. The dried powder was calcined at  $1175^\circ\text{C}$  for a dwell time of 8 h to obtain single-phase Yb:YAG powders. The calcined powder was compacted by cold isostatic pressing at 250 MPa and thereafter sintered at  $1750^\circ\text{C}$  for 5 h under vacuum ( $\sim 2 \times 10^{-6}$  mbar). The sintered samples were polished and subjected to optical analysis.

### 3. Results and discussion

Figure 1 shows the powder diffraction profile of calcined powder. It shows a single-cubic phase (JCPDS card no. 33-0040) formation with no signature of the impurity phase. However,

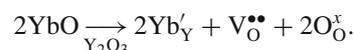


**Figure 1.** X-ray diffraction profile of calcined Yb:YAG powder.



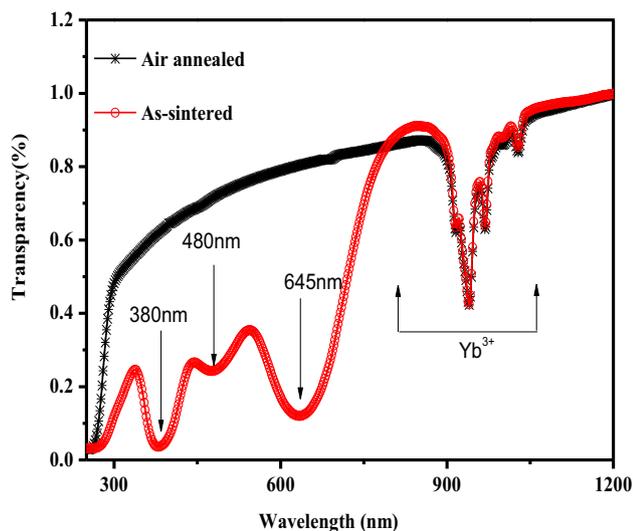
**Figure 2.** Photographs of the air-annealed and as-sintered Yb:YAG ceramic.

to ensure the pure single phase formation the Yb:YAG powder was calcined twice at  $1175^\circ\text{C}$  with intermediate ball milling using zirconia ball and alcohol as milling media. The lattice parameter was calculated by standard software and found to be  $12.02 \text{ \AA}$  for calcined powder. Figure 2 shows the photograph of air-annealed and as-sintered polished ceramic samples. The dark greenish colour in the as-sintered sample is attributed to the formation of colour centres and most likely consisting of oxygen vacancies. Since the ceramics were sintered under vacuum conditions, thus the formation of oxygen vacancies is inevitable. The reduction of  $\text{Yb}^{3+} \rightarrow \text{Yb}^{2+}$  during sintering leads to the formation of oxygen vacancies to satisfy the charge imbalance as shown below:



According to the above equation, oxygen vacancies (point defects) were formed due to charge differences between divalent Yb-ions and  $\text{Y}^{3+}$  cations in YAG. It has been explained by Chen *et al* [5] that free electrons exist in the vacuum-sintered Yb:YAG ceramic. These free electrons trapped around oxygen vacancies, in association with  $\text{Yb}^{2+}$  ions, generate the  $\text{Yb}^{2+}-\text{F}^+$  composite colour centres responsible for the green colour of the vacuum sintered ceramics. The greenish colouration disappears completely after annealing the crystals in air at  $1350^\circ\text{C}$  for 8 h (figure 2).

Figure 3 shows the normalized transmission spectra of the as-sintered and annealed ceramic sample. The as-sintered sample shows the presence of broad absorption bands centring around 650, 480, 380 and 270 nm in addition to well-known absorption peaks between 900 and 1050 nm. The absorption bands below 700 nm are assigned to  $4f \rightarrow 5d$  electronic transitions in a divalent Yb ion i.e.,  $\text{Yb}^{2+}$  [6,7] and the narrow lines between 900 and 1050 are well-known for  ${}^2\text{F}_{7/2} \rightarrow {}^2\text{F}_{5/2}$  transition in  $\text{Yb}^{3+}$ . The presence of  $4f \rightarrow 5d$  electronic transitions due to  $\text{Yb}^{2+}$  suggests that oxygen defects generated during vacuum sintering would lead to the reduction of  $\text{Yb}^{3+}$ -ions to  $\text{Yb}^{2+}$ -ions for charge compensation. After annealing



**Figure 3.** Transmission data for the air-annealed and as-sintered Yb:YAG ceramic.

under air these bands disappear as a result of crossover from  $\text{Yb}^{2+}$  to  $\text{Yb}^{3+}$  during annealing. A sharp decrease in the transmittance is observed near 200 nm is due to the valance band-to-conduction band electronic transition in the host i.e., YAG.

#### 4. Conclusions

Transparent Yb-doped YAG ceramic was fabricated using nano-powder technology and a vacuum sintering technique. The as-sintered ceramic samples are greenish in colour which turns into conventional whitish colour after annealing at 1350°C in air for 8 h. The greenish colour for the as-sintered samples was attributed to the reduction of  $\text{Yb}^{3+}$  to  $\text{Yb}^{2+}$

during vacuum sintering. The transmission spectra of the as-sintered samples show the presence of broad absorption bands centring around 650, 480, 380 and 270 nm in addition to well-known narrow absorption peaks between 900 and 1050 nm for Yb-doped materials. The absorption bands below 700 nm are assigned to  $4f \rightarrow 5d$  electronic transitions in the divalent Yb ion i.e.,  $\text{Yb}^{2+}$  and the narrow lines between 900 and 1050 are well-known for  ${}^2F_{7/2} \rightarrow {}^2F_{5/2}$  transition in  $\text{Yb}^{3+}$ . The presence of  $4f \rightarrow 5d$  electronic transitions due to  $\text{Yb}^{2+}$  suggests that oxygen defects generated during vacuum sintering would lead to the reduction of  $\text{Yb}^{3+}$ -ions to  $\text{Yb}^{2+}$ -ions for charge compensation. After annealing under air these bands disappear as a result of crossover from  $\text{Yb}^{2+}$  to  $\text{Yb}^{3+}$  during annealing.

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