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Sol Freeze Dry Nd:YAG Nanopowder Synthesis and Sinterability Studies

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ABSTRACT

Citrate nitrate sol freeze dry synthesis of 2 atomic % neodymium ion doped Yttrium Aluminium Oxide (Nd:YAG) nanopowders was explored for the first time. Sol was prepared by dissolving nitrates of Al^{3+}, Y^{3+} and Nd^{3+} keeping molar ratio to be 5: 2.94: 0.06. Total metal ion to citric acid ratio was optimised at 1 is to 0.25. Sol was freeze dried at -80 °C for 48 h. Dried mass thus obtained was calcined at 1000 °C for 2 h to give phase pure Nd:YAG as characterised by FTIR and XRD. Particles were in the size range of 35 nm - 50 nm with close to spherical morphology as observed by TEM. Nanopowder was compacted and sintered at 1700 °C for 5 h under 10^{-6} mbar followed by hot isostatic press at 1750 °C for 4 h under 200 MPa, to give 71 per cent transmission at 1064 nm indicating synthesis of well sinterable Nd:YAG nanopowders.

Keywords: Freeze dry, Nd:YAG, transparent ceramic, vacuum sintering, HIP, Nd:YAG nanopowder, sinterability

1. INTRODUCTION

Nd:YAG laser ceramic has some important advantages over single crystals such as large size fabrication, possibility of producing multilayer ceramic structure and low cost production[1,2]. It is particularly useful for high temperature and high energy applications. When doped with rare earth ions (Nd^{3+}), it is the most widely explored and used solid state laser material till date[3,4]. Worldwide research for the synthesis of highly sinterable Nd:YAG nanopowder is going on tremendously exploring different types of methods for developing transparent ceramics. To name a few, Nd:YAG synthesis has been reported using methods like co-precipitation[5-7], sol-gel[8], spray drying[9], homogeneous precipitation[10], freeze drying[11,12], microwave assisted combustion[13], etc.

Freeze drying is a very good technique for synthesis of multi component compounds with an accurate control of stoichiometry with high surface area, since it involves sublimation for elimination of water from frozen solution containing cations in stoichiometric ratios[14]. Freezing the sol make cations mobility difficult and thus prevent cation segregation leading to high cation homogeneity. Since water is directly removed by sublimation during freeze drying solid bridge formation is prevented, leading to well dispersed powder formation[15]. Some reports are there in the literature for the synthesis of Nd:YAG by freeze drying starting from organo-metallic precursors[12] and carbonate precipitates[16] and fabrication of transparent ceramics.

In the present study freeze drying synthesis of Nd:YAG nanopowders from sol of simple metal nitrates with citric acid is reported for first time. Sinterability of these nanopowders was also explored and transparent ceramic with 71% transmission at 1064 nm was obtained. By citrate nitrate and other sol gel route YAG and Nd:YAG nanopowder synthesis has been reported[17-20] with no description of transmission value.

2. EXPERIMENT

Yttrium nitrate, $Y(NO_3)_3.6H_2O$ (99.9 per cent, Alfa Aesar), Aluminum nitrate, $Al(NO_3)_3.9H_2O$ (99.999 per cent, Alfa Aesar), Neodymium nitrate, $Nd(NO_3)_3.6H_2O$ (99.9 per cent purity Alfa Aesar) and Citric acid anhydrous (99.5+ per cent purity Alfa Aesar) were used as the starting materials. The metal nitrates were taken in the molar ratio of Nd^{+3}:Y^{3+}:Al^{3+} as 0.06: 2.94: 5 to give 2 atomic per cent neodymium ion doped Yttrium Aluminium Garnet ($Nd_{0.06}Y_{2.94}Al_5O_{12}$). Sol was prepared by dissolving metal nitrates along with citric acid, used as the complexing agent, keeping the metal nitrate to citrate ratio as 1: 0.25, in high purity water of resistivity >5 MΩ-cm purified by Millipore Elix 10 water purifier. Sol thus prepared was treated in two ways. A part of it was freeze dried at very low temperature of -80 °C for 48 h in freeze drier (Virtis pilot scale lyophilizer) and another part was dried in conventional oven at 80 °C - 110 °C for 40 h. Metal nitrates are often used as starting materials due to their high solubility and low decomposition temperature. But it is very difficult to freeze the nitrate sol[14]. Metal nitrate-citrate sol underwent freeze drying at -80 °C for 48 h compared to reported at -20 °C for 20 h for organmetallic sol. The freeze dried swollen solid mass and oven dried gel thus obtained were calcined at 1000 °C for 2 h to give Nd:YAG nanopowder. Calcination temperature has been optimised in previous work[21]. The whole process is illustrated in the flow chart.

Evolution of the crystalline phases was monitored by X-Ray Diffraction (XRD) on X'PERT PRO PANalytical PW 3050/60 Standard Resolution Goniometer, keeping 2θ range from 15° to 75°. The crystallite size was determined by using the well known Scherrer's equation. Particle size range and morphological studies were carried out on transmission electron microscope (TEM, 200 kV, JEOL TEM-2100) by preparing samples on copper grids. Both the powders were

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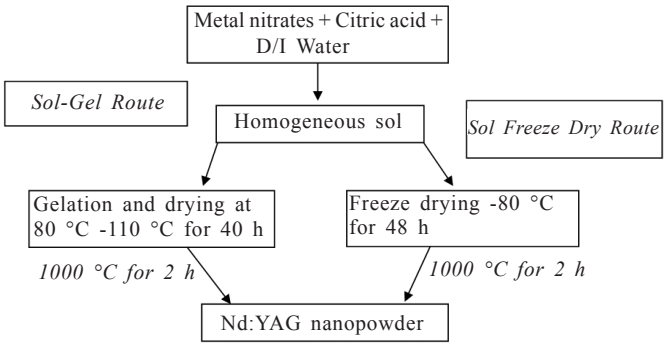


uniaxially pressed in a 13 mm diameter steel die lined with tungsten carbide at 34 MPa and isostatically pressed at 300 MPa. The green compacts were sintered at 1700 °C for 5 h under vacuum 1.1X10^{-6} mbar in a furnace with tungsten and molybdenum mesh heaters at 600 °C/h heating and cooling rates. Vacuum sintered pellets were then hot isostatically pressed at 1750 °C for 4 h at 200 MPa. The sintered specimen was analysed for retention of phase purity by XRD. Ceramics were post sintered at 1300 °C for 5 h, polished and gold coated to observe microstructure using scanning electron microscope (SEM) LEO-1430. Transmission studies of samples was done on Cary 5000 UV-VIS-NIR spectrophotometer.

The emission spectra of specimens were recorded using 808 nm 3 W diode laser as the excitation source and the emission was coupled to a monochromator (Acton SP2300) attached with an InGaAs detector. The spectral measurements were carried out at room temperature within the spectral region of 900 nm - 1200 nm with 0.1 nm resolution.

3. RESULTS AND DISCUSSION

The powders obtained by sol-gel (SG) route and freeze dry (FD) route after calcination at 1000 °C for 2 h were found to be highly crystalline and phase pure on peak indexing the XRD data with the standard JCPDS as shown in Fig. 1. The main peak is centered at 2θ = 33.35° and corresponds to a crystal plane with Miller indices of [420] characteristic of YAG[22].

Particle size was calculated using Scherrer's[23] Eqn (1).

$$t = \frac{0.9\lambda}{\cos\theta\sqrt{\beta_{sample}{}^2 + \beta_{inst}{}^2}} \quad (1)$$

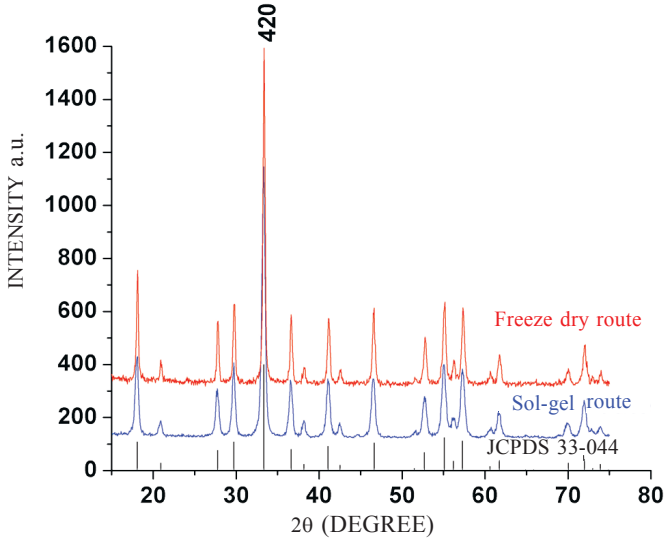
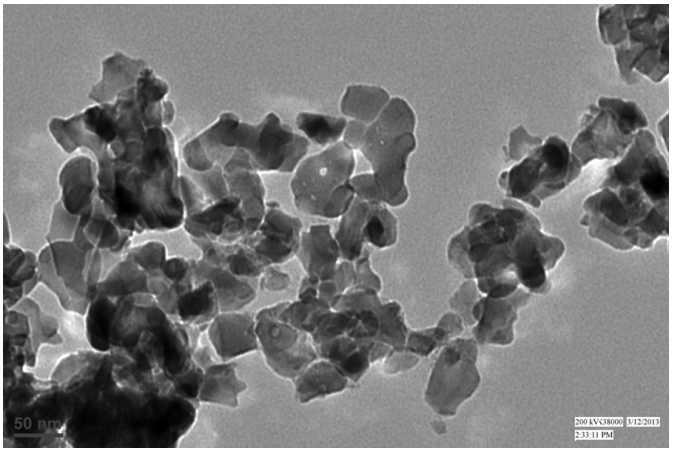
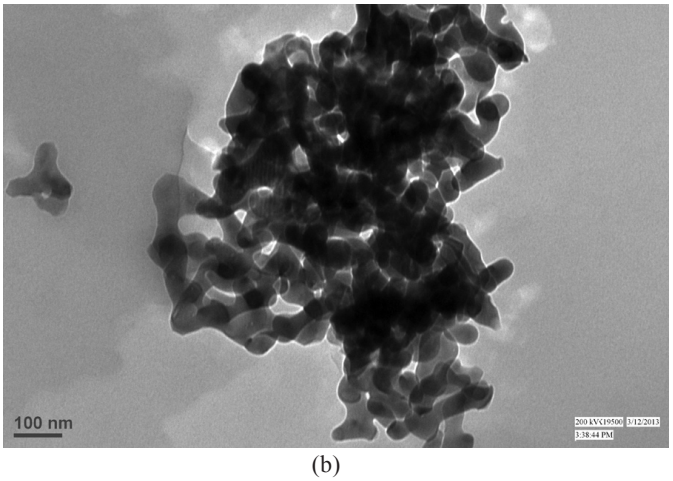


Figure 1. XRD of Nd:YAG nanopowder on calcination at 1000 °C for 2 h.

where t is the crystallite diameter, λ=1.54056Å, θ is the diffraction angle, β_{sample} is the FWHM of the diffraction peak and β_{inst} is characteristic of the instrument. The particle size calculated by applying Scherer's equation was found to be 30 nm. By TEM the particle size range was 35 nm - 50 nm in both the cases as shown in Fig. 2. The freeze dry route resulted into particles with close to spherical and very uniform morphology. This is a characteristic consequence of freeze dry synthesis due to the elimination of water by sublimation leading to uniform porous structure[14]. On the other hand sol-gel route synthesised nanopowder showed non uniform and polyhedral morphology as observed by TEM. After vacuum sintering at 1700 °C for 5 h under vacuum 1.1x10^{-6} mbar, opaque ceramics were obtained in both the cases with densities ~90-93%. The densities were determined by Archimedes principle using density kit of Mettler Toledo XS205DU. The sintered ceramics were hot isostatically pressed at 1750 °C for 4 h under 200 MPa Argon pressure and achieved 71% transmission at 1064 nm for freeze dried nanopowder compared to translucent ceramic from citrate nitrate sol-gel route as shown in Fig. 3. The green compacts were repeatedly sintered at different sintering schedules from 1600 °C to 1700 °C under vacuum (1.1 x 10^{-6} mbar) from 5 h to 10 h followed by Hot Isostatic Press treatment from 1650 °C to 1750 °C under 200 MPa for 2 h - 4 h. Finally heat treatment schedule mentioned above gave 71 per cent transmission at 1064 nm. Optimisation of sintering schedule is still underway to increase transmission from 71 per cent to 84 per cent, which is theoretical transmission[24].

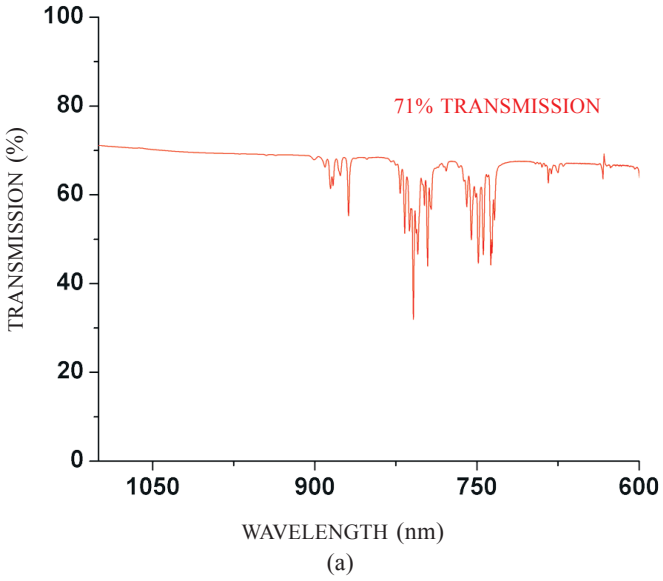


(a)



(b)

Figure 2. TEM of Nd:YAG nanopowders obtained by (a) Sol-Gel route and (b) Freeze dry route.



(b)

Figure 3. (a) Transmission of sintered ceramics and (b) actual photographs of samples.

SEM of the polished and gold coated surface of freeze dry route transparent ceramic as shown in Fig. 4 after annealing at 1300 °C for 5 h revealed grain size upto 15 µm - 20 µm. Phase purity has been retained as observed by XRD is as shown in Fig. 5. This indicated formation of highly sinterable Nd:YAG nanopowder from freeze dry route.

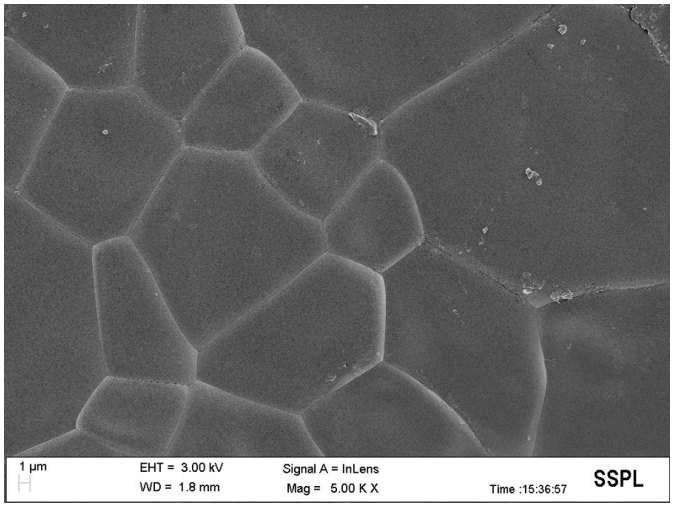


Figure 4. SEM of sintered ceramics of FD Route nanopowder.

Room temperature emission spectra of freeze dry route Nd:YAG transparent ceramic measured under 808 nm excitation as shown in Fig. 6, shows strongest flourescence emission of Nd^{3+} ions at 1064 nm corresponding to $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition.

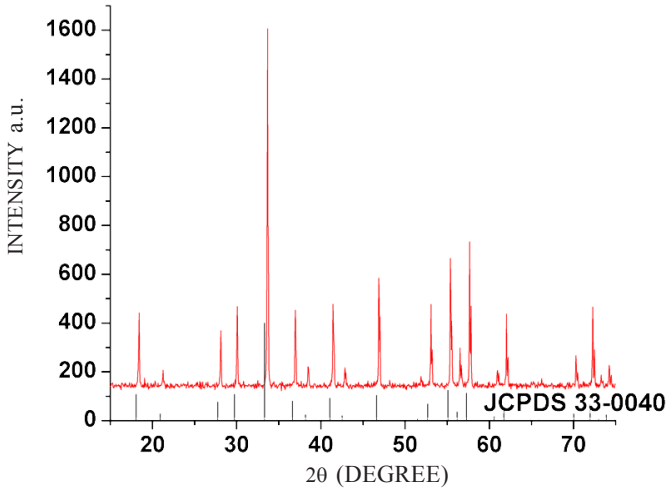


Figure 5. XRD of sintered ceramics of FD Route nanopowder.

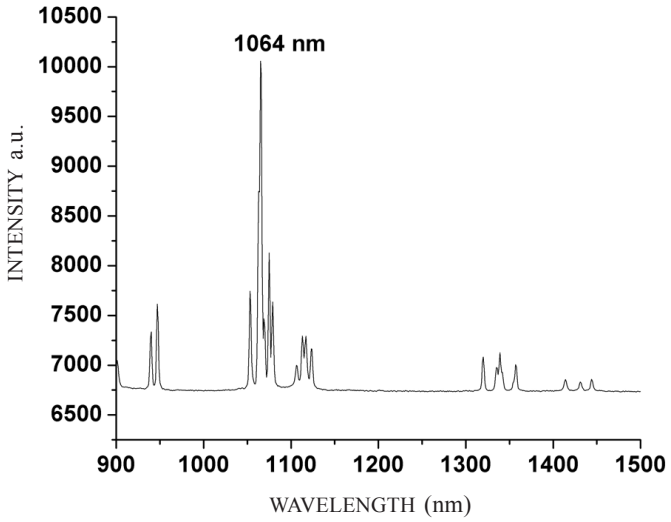


Figure 6. Emission spectra of Nd:YAG transparent ceramics from FD Route.

4. CONCLUSION

A very simple citrate nitrate sol freeze dry synthesis of Nd:YAG nanopowder was explored and compared with nitrate citrate sol-gel route leading to formation of uniform homogeneously uniform, non agglomerated Nd:YAG nanopowders in case of freeze dry route. Sintering at low temperature of 1700 °C for mere 5 h under vacuum 1.1×10^{-6} mbar followed by hot isostatic press at 1750 °C for 4 h under 200 MPa Argon pressure led to 71 per cent transmission at 1064 nm, indicating high sinterability of nanopowders from sol freeze dry route. Phase purity was retained from powder to ceramic all through the sintering process.

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