

Studies of Process Parameters on Scale up of Nd:YAG Nanopowder Synthesis by Sol-gel Process

Kiranmala Laishram^{1*}, Rekha Mann¹, Neelam Malhan¹, and Ravi Kumar Gupta²

¹Laser Science and Technology Centre, Delhi-110 054, India

²Directorate of Public Interface, DRDO Bhawan, Delhi-110 001, India

*E-mail: kiranmala@lastec.drdo.in

ABSTRACT

Scale up of process from 6 g to 200 g batch for preparation of phase pure Neodymium doped Yttrium Aluminum Garnet (Nd:YAG) nanopowder by sol-gel process using nitrate-citrate route was carried out. Optimisation of process parameters was done to resolve problems associated with large batch such as evolution of large amount of acidic fumes, increased gelation and drying time and incomplete calcination. The problem of exhaust of excess acidic fumes with size scale up was handled by passing ammonia and optimized pH of the sol. Process of drying the sol was optimised for large batch size. On scaling up from 6 g to 200 g batch incomplete crystallization was observed on calcination under conditions optimized for 6 g batch. The causes of incomplete calcination with size scale up was identified and resolved to achieve completely crystalline particles in the range of ~25 nm to 50 nm.

Keywords: Phase-pure Nd:YAG, sol-gel process, nitrate-citrate sol, XRD, calcination

1. INTRODUCTION

Neodymium doped YAG ($Y_3Al_5O_{12}$) is an important solid-state laser material. Nd:YAG lasers have defence applications as rangefinders, target designators, and target interrogators. Fabrication of polycrystalline Nd:YAG lasers comparable to single crystals has been reported in the literature¹. Fabrication of laser quality Nd:YAG ceramics by solid state reaction from oxide precursors has been reported². Using YAG nanopowder synthesized by sol-gel method, fabrication of transparent YAG ceramics has been reported³.

For achieving transparent ceramics the starting nanopowder should have some ideal characteristics such as sub-micron particle size (<100 nm), narrow size distribution and homogeneity throughout the bulk⁴. To carry out detailed studies from nanopowders to ceramics there is always a need to synthesize a large batch in one go to prevent batch to batch variation in nanopowders properties.

We report the scale up of the synthesis of phase pure Nd:YAG from 6 g to 200 g by nitrate-citrate sol-gel process. The evolution of a large amount of hazardous nitrous fumes was one of the major problems during scaling up. Another problem faced was significant increase in the gelation time, drying time and incomplete crystallization. In the present work optimisation of conditions on scale up to 200 g batch are being discussed.

2. EXPERIMENTAL WORK

Yttrium nitrate, $Y(NO_3)_3 \cdot 6H_2O$ (99.9 % purity Alfa Aesar), Neodymium nitrate, $Nd(NO_3)_3 \cdot 6H_2O$ (99.9 % purity Alfa Aesar) Aluminum nitrate, $Al(NO_3)_3 \cdot 9H_2O$ (99.9 % purity Alfa Aesar) and Citric acid anhydrous (99.5+ % purity Alfa Aesar)

were used as received. Two sols were prepared by taking stoichiometric amounts of nitrates corresponding to the molar ratio of $Y_{2.94}Nd_{0.06}Al_5$ for 6 g and 200 g YAG respectively, which corresponds to 2 at.% of Nd for both the batches. Citric acid was used as the chelating agent. The total cation to citric acid was taken in the ratio of 1:1. The process route is given in the flow chart as shown in Fig. 1. The nitrate-citrate sol in millipore water was prepared by ultrasonic stirring. The pH of the sols was adjusted to 1 by passing NH_3 gas. Gelation took place at 80 °C within 16 h. Drying of the gel was carried out from 110 °C to 150 °C in an oven modified for scrubbing ammonium nitrates in dil. NaOH soln. For 6g batch the precursor powder was calcined at 900 °C for 2 h. And calcination of precursor was carried out at 900 °C for 2 h with flow of oxygen @ 4 litres/min.

Fourier transform infra-red spectroscopy (FTIR) was carried out by Bruker, (Vector 22) to identify the temperature at which Y-O and Al-O bond formation was taking place. X-ray diffraction (XRD) was carried out with the help of Philips X-Ray Diffractometer, PW for characterisation of phase purity and particle size. Nd³⁺ doping was characterised by EDX using scanning electron microscope (ZEISS EVO Series, EVO 50). Transmission electron microscopy (TEM) was done on FEI Philips Morgagni 268. The TEM specimens were prepared on copper grids by dispersing the powder ultrasonically in acetone.

3. RESULTS AND DISCUSSION

The amount of water required to dissolve the solid reactants is an important parameter in scaling up the process as it is directly related to the consumption of electricity and time in gelation and drying in sol-gel process. Taking 6 g batch

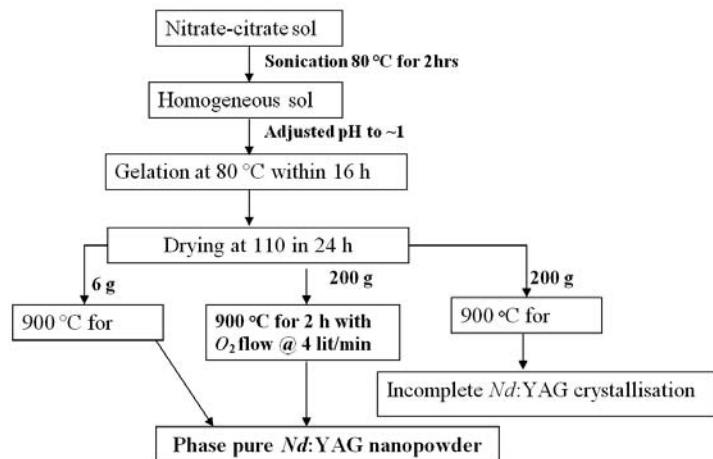


Figure 1. Flow chart of process route.

itself the water content was optimised by taking different w/w solid to total content percentage starting from 30 per cent, 40 per cent, and 50 per cent to 60 per cent till the solid contents dissolved easily without causing saturation. All these mixtures led to similar results in terms of phase purity and particle size. So 60 per cent was optimised for the larger batch as it was least time consuming during the process.

For 6 g batch total solid content was ~61 g and for 200 g it was ~2033 g. For 6 g batch from preparation of sol to drying of the gel reaction was carried out in a 1 litre beaker and optimised gelation and drying parameters as given in the process flow chart. For 200 g batch 5 litre beaker was taken for the same process but gelation and drying did not take place under those optimised parameters of 6 g batch. Gel was not formed at 80 °C even within 48 h and drying also took place only in 3 days (72 h). The consumption of time and power on size scale up upto precursor stage was three times that of 6 g batch. To solve this problem the surface area of the apparatus was increased by transferring the sol into trays and carried out the process in the same oven under the optimised parameters of 6 g batch.

Further with increase in the batch size the increased continuous evolution of acidic fumes was tackled by converting the acidic byproducts into ammonium salt by passing NH_3 to the sol. On passing NH_3 even in slight excess [$pH > 2$] precipitation occurred which is supposed to create inhomogeneity in sol-gel

processes. So pH was optimised to 1 to prevent precipitation.

FTIR spectra depicted complete formation of YAG on scale up from 6 g batch to 200 g batch. FTIR was done of gels (Fig. 2) treated from 150 °C to 900 °C. In the spectrum of the gel at 150 °C there was no peaks in the M-O region, the bands at $\sim 1562\text{ cm}^{-1}$ and $\sim 1384\text{ cm}^{-1}$ can be assigned to the ionized carboxylates and carbonates resulting from the rupture of citrate network⁵ and intensities of these peaks reduced significantly at 500 °C along with a broad band in the M-O region. At 750 °C the intensities of the peaks corresponding to the organic residues had further reduced and that in the M-O region had become more prominent. At 900 °C, the broad band in the region of $800\text{ cm}^{-1} - 400\text{ cm}^{-1}$ is replaced by several peaks at 784 cm^{-1} , 719 cm^{-1} , 688 cm^{-1} , 566 cm^{-1} , 511 cm^{-1} , 455 cm^{-1} and 428 cm^{-1} which may be attributed to the M-O vibrations in YAG⁶. The broad peak at $\sim 3300\text{ cm}^{-1}$ in b, c, and d (Fig.2) corresponds to adsorbed moisture on the powders which may be removed by treating the powder at $\sim 100\text{ °C}$ before sampling for FTIR analysis.

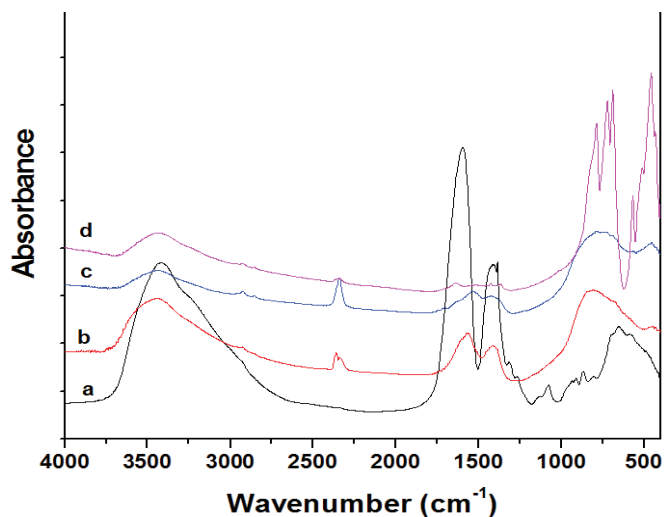


Figure 2. FTIR of YAG precursor treated at different temperatures (a) 150 °C, (b) 500 °C for 26 h, (c) 750 °C for 15 h, and (d) 900 °C for 2 h.

For 6 g batch XRD patterns of Nd:YAG (Fig.3) calcined at 800 °C/4 h showed the characteristic peaks (JCPDS 33-40) but the background intensity was very high indicating incomplete

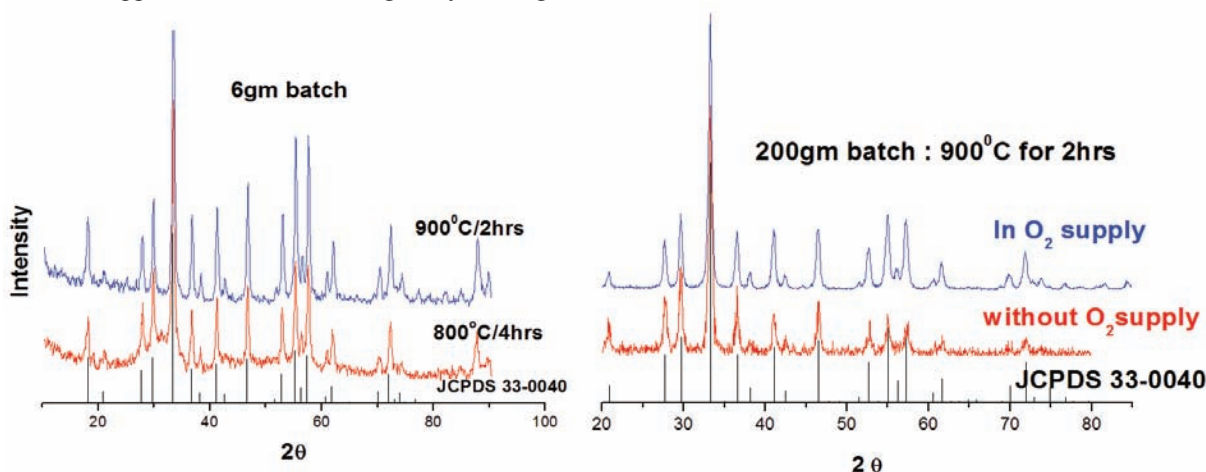


Figure 3. XRD depicting complete crystallisation to phase pure YAG.

crystallization. At 900 °C for 2 h complete crystallization to phase pure *Nd*:YAG was observed. But for 200 gm batch, on treatment at 900 °C for 2 h in the same furnace, due to the large amount of precursor, the atmospheric oxygen present inside the furnace chamber was not sufficient to burn out all the organic residues present in the precursor. Hence crystallization was not complete and presence of oxygen deficient phase i.e. $YAlO_3$ (at $2\theta = 44^\circ$) was indicated in XRD pattern. However on treatment at 900 °C with flow of oxygen at the rate of 4 lit/min complete crystallization to phase pure cubic *Nd*:YAG structure was obtained. Particle size was calculated using Scherrer's equation⁷.

$$t = \frac{0.9\lambda}{(\beta_{sample}^2 - \beta_{inst}^2)^{1/2} \cos \theta}$$

where t is the crystallite diameter, $\lambda = 1.54056 \text{ \AA}$, θ is the diffraction angle, β_{sample} is the FWHM of the diffraction peak and β_{inst} is characteristic of the instrument. Three strong peaks were chosen (at $2\theta = 29.6^\circ$, 33.3° and 46.5°) to calculate the particle size. The average primary particle size was $\sim 25 \text{ nm}$ for both the batches. The lattice parameter, a of cubic YAG is 12.008 \AA ⁸. For 2 at.% Nd doped YAG the lattice parameter was calculated to be 12.020 . This increase in lattice parameter is indicative of Nd^{3+} replacing Y^{3+} because the effective radius⁹ of Nd^{3+} is greater than that of Y^{3+} .

From EDX spectrum presence of *Nd* in the powder was detected for both the batches. Fig. 4 depicts the EDX spectrum which is representative of both the batches. When rare earth elements are involved the EDX is reliable for only qualitative analysis and accurate quantitative analysis of *Nd*:YAG has never being discussed in the literature. In the extensive work on *Nd* doping upto 24 at.% elemental composition is discussed only by the increase in the peak of *Nd* in EDX graphs and increase in lattice parameter¹⁰. TEM (Figs 5 & 6) showed particle size in the range of 25 nm-50 nm for both 6 g as well as 200 g batch indicating efficiency of scale up without distortion in particle morphology and size.

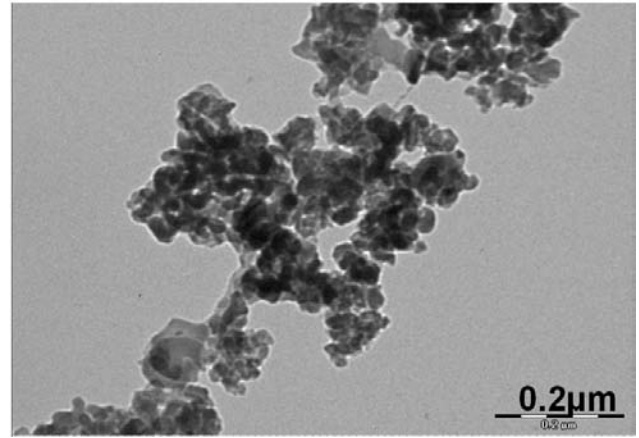


Figure 5. TEM of *Nd*:YAG nanopowder of 6 g batch.

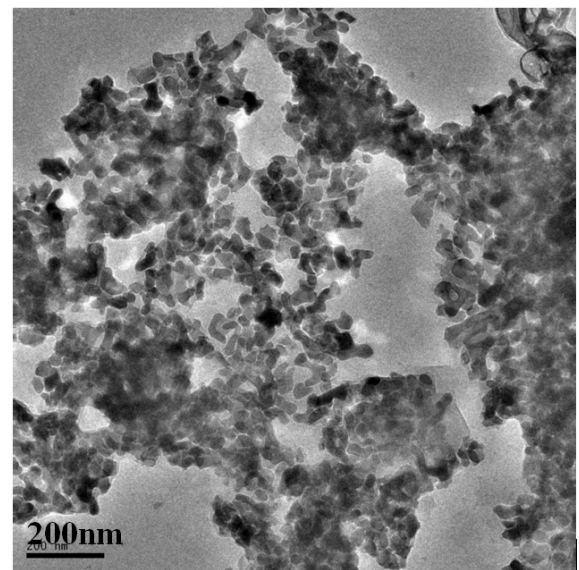


Figure 6. TEM of *Nd*:YAG nanopowder of 200 g batch.

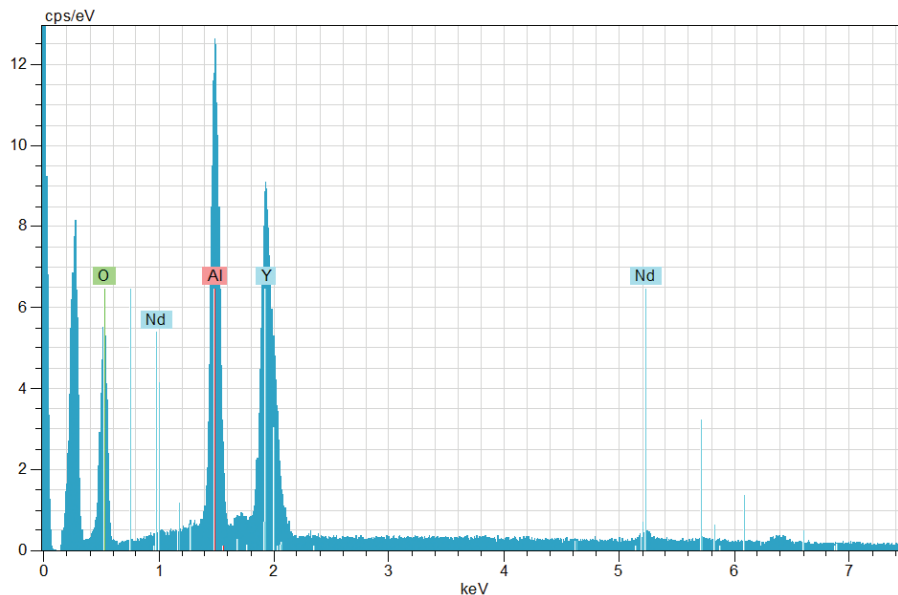


Figure 4. EDX showing presence of *Nd*.

4. CONCLUSION

A laboratory scale large batch (200 g) of phase pure Nd:YAG was synthesized by sol-gel process using nitrate-citrate sol.

- Phase pure Nd:YAG was obtained for both 6 g and 200 g batch at 900 °C for 2 h under oxygen supply.
- XRD and FTIR confirmed the formation of phase pure product in both the batch sizes.
- Particle sizes obtained were in the range of ~25 nm - 50 nm by TEM.

By taking into consideration above discussion it can be concluded that the method has been optimised for large scale synthesis of Nd:YAG efficiently.

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REFERENCES

1. Jiang, L.; Yusong, W.; Yubai, P.; Wenbin, L.; Liping H. & Jingkun G. Fabrication, microstructure and properties of highly transparent Nd:YAG laser ceramics. *Optical Materials*, 2008, **31**(1), 6-17.
2. Akio, I.; Toshiyuki, K.; Kiichiro, K. & Kunio, Y. Fabrication and optical properties of high-performance polycrystalline Nd:YAG ceramics for solid-state lasers. *J. Am. Ceram. Soc.*, 1995, **78** (4), 1033-040.
3. Robert, F.; Dariusz, H.; Witold, L.; Wieslaw, S.; Hubert, M.; Ewa, G.; Stanislaw, G. & Piotr, M. Method of preparation and structural properties of transparent YAG nanoceramics. *Optical Materials*, 2007, **29**(10), 1252-257.
4. Johanne, M. Synthesis of Yd:Y₂O₃ nanoparticles and fabrication of transparent polycrystalline yttria ceramics. Lulea University of technology, France. 2005 (PhD Thesis).
5. Vaqueiro P, Lopez-Quintela MA. Influence of complexing agents and pH on Yttrium-Iron garnet synthesized by the sol-gel method. *Chemistry of Materials*, 1997, **9**(12), 2836-841.
6. Hofmeister AM, Campbell KR. Infrared spectroscopy of Yttrium Aluminum, Yttrium Gallium, and Yttrium Iron garnets. *J. Appl. Phys.*, 1992, **72**(2), 638-46.
7. Cullity, B.D. & Stock, S.R. Elements of X-ray diffraction. Ed 2nd, Addison-Wesley, MA, London. 1978
8. JCPDS 33-40.
9. Kiranmala, L.; Rekha, M. & Neelam, M. Novel microwave

assisted synthesis of highly doped phase pure Nd:YAG nanopowder. *Mater. Sci. Poland*, 2012, **29**(3), 184-88.

10. Caponeti, E.; Saladino, M.L.; Serra, F. & Enzo, S. Coprecipitation synthesis of Nd:YAG nano-powders: The effect of Nd dopant addition with thermal treatment. *J. Mater. Sci.*, 2007, **42**, 4418-27.

Contributors



Ms Kiranmala Laishram obtained her MSc (Physical Chemistry) from Manipur University in 2002. She is working as Scientist 'C' at Laser Science and Technology Centre (LASTEC), Delhi. Her areas of interest are material characterisation techniques, laser materials, and nanomaterial-synthesis and applications. She has published 22 research papers in the journals and conferences, and 5 technical reports.



Dr (Mrs) Rekha Mann obtained her MSc and MPhil (Organic Chemistry) from Kurukshetra University, and PhD (Applied Chemistry) from Delhi College of Engineering, Faculty of Technology, Delhi University in 2003. Presently she is working as Scientist 'D' at LASTEC, Delhi. Her areas of interest are nanomaterial synthesis and processing, laser materials, organic synthesis, and polymer materials. She has published 24 research papers in the journals and conferences, and 5 technical reports.



Ms Neelam Malhan obtained her MSc (Physical Chemistry) from University of Delhi and MTech (Modern Methods for Chemical Analysis & Control) from IIT, Delhi in 1979. Presently she is working as Scientist 'F' at LASTEC, Delhi. Her areas of interest are: Development of high purity grade oxide materials & catalyst for laser applications, analytical techniques for material characterization, nanomaterial synthesis, ceramic processing & sintering, polycrystalline laser ceramics Nd-doped YAG & Nd-doped Yttria for SSL applications. She has published 20 research papers in the journals and conferences.

Mr Ravi Kumar Gupta obtained his MSc (Organic Chemistry) from Delhi University in 1978, DIIT (High Polymers & Rubbers) from IIT Kharagpur in 1979. Presently, he is working as Scientist 'G' at Directorate of Public Interface, DRDO Bhawan. His areas of interest are: Heat-resistant polymers, polymers, organic and polymeric laser materials, polycrystalline laser materials, and synthesis and characterisation of nanomaterials.