Defence Science Journal, Vol. 64, No. 5, September 2014, pp.490-494, DOI : 10.14429/dsj.64.5409

Nd:GGG Nanopowders by Microwave Gel Combustion Route and Sinterability Studies

Kiranmala Laishram[*], Rekha Mann, Richa Sharma[@], Dinesh Bhardwaj[@], Suman Shakya[#], and Neelam Malhan

Laser Science and Technology Centre, DRDO, Delhi-110 054, India
[@]Amity Institute of Applied Sciences, Amity University, Noida, India
[#]Department of Physics, Indian Institute of Technology Delhi, India
[*]E-mail: kiranmala@lastec.drdo.in

ABSTRACT

Synthesis of $Nd_{0.03}Gd_{2.97}Ga_5O_{12}$ (Nd:GGG) nanopowder was carried out by microwave-assisted nitrate-citrate gel combustion technique. Various nitrate-to-citrate ratios from stoichiometric-to-fuel lean were explored. Gels were combusted by microwave heating and the combusted powders were calcined at 900 ^{O}C for 2 h. Fourier Transform Infra-red Spectroscopy (FTIR) and X-ray Diffraction (XRD) of calcined nanopowders showed phase pure Nd:GGG formation, from stoichiometric-to-fuel lean nitrate-to-citrate ratio of 1 to 0.416. Particles in the size range of 150 nm - 200 nm were obtained for stoichiometric ratio. Highly uniform, spherical morphology, with size range 90 nm - 100 nm, were obtained in fuel lean ratio of 1 to 0.416. Sintering of these nanopowders at 1550 °C for 2 h in air resulted in retention of phase purity as observed by XRD. Grain growth of less than 2 µm, for fuel lean ratio of 1 to 0.416, indicated formation of highly sinterable Nd:GGG nanopowders.

Keywords: Phase pure GGG, citrate-nitrate, microwave combustion, XRD

1. INTRODUCTION

Nd:GGG has potentially very important applications in solid state high capacity laser[1,2] due to its excellent optical and mechanical properties[3]. GGG has high refractive index (n=2) and transparency in visible-to-far IR, making it a very useful material for solid state lasers. Nd-GGG has high fracture strength, good chemical stability, high thermal conductivity, large rare earth doping ratio, and is easy to grow[4]. This material is a better substitute to the most widely used solid state laser Nd:YAG due to certain reasons[5]. However laser quality single crystal Nd:GGG is very difficult to grow due to certain reasons[6-8]. But with the development of ceramic technology, Nd:GGG transparent ceramic for laser applications is a challenge and new research trend for the materials scientists worldwide[9,3]. To achieve high density and transparent polycrystalline Nd:GGG, fine powders without or only with slight agglomeration are necessary[10]. GGG synthesis by co-precipitation has been reported using 2 per cent additional Ga^{3+} ions to compensate the loss of Ga^{3+} ions during washing and high temperature calcinations to GGG[8,11,12].

Synthesis of GGG for several gel combustion routes using citric acid have been reported[13,14]. But detailed explorations of nitrate-citrate ratios to give highly sinterable nanopowders have not been reported. There are several reports on synthesis of Nd:YAG[15] and Nd:Yttria[16] nanopowders by citrate/alanine nitrate microwave gel combustion route, but there is no report on synthesis of GGG/Nd:GGG nanopowders by microwave gel combustion route. Further sintering studies of Nd:GGG nanopowders with reference to retention of phase purity has not been explored. The ratio of complexing agent-to-metal cations is an important parameter because it decides the amount of organics to be removed during calcinations, which in turn affects the ceramic properties[17,18].

In the present work, synthesis of Nd:GGG nanopowders using different nitrate-to-citrate molar ratios by microwave gel combustion technique is being reported for the first time. The effects of different nitrate-to-citrate ratios on phase evolution, size and shape of the Nd:GGG particles were studied.

2. EXPERIMENTAL

Four sets of sols were prepared by taking Nd_2O_3, Gd_2O_3 and Ga_2O_3 in their stoichiometric ratios of $Nd_{0.03}Gd_{2.97}Ga_5$ and dissolved in HNO_3 and then mixed with citric acid to obtain metal nitrate-to-citrate ratios of 1: 0.208, 1: 0.416, 1: 0.833, and 1: 1.666. The ratios 1: 0.208, 1: 0.416 and 1: 0.833 are fuel lean and 1: 1.666 is stoichiometric by equivalence theory[19]. These reaction mixtures were kept in an ordinary oven for gelation at 110 °C for 10 h. Gels were further treated in domestic microwave modified for exhaust gases, operating at 2.45 GHz, with output power of 900 W**.** The gel underwent drying and subsequent rapid combustion within 5 min - 10 min for 10 gm batch in the microwave oven, giving fluffy powder precursors. The precursors formed were calcined at 900 °C for 2 h. Compaction of the powders was carried out by uniaxial

Received 17 December 2013, Revised 23 April 2014, Online published 22 September 2014

press at 34 MPa followed by cold isostatic press at 300 MPa. The compacts were sintered at 1550 °C for 2 h in air.

FTIR spectra were recorded on FTIR Spectrometer (Bruker, model Vector 22) using KBr matrix. XRD was carried out on PANalytical X'pert Pro from 2θ value 15° to 75° for characterisation of phase purity. Diffused reflectance measurement on Nd:GGG nanopowders was carried out on an ultraviolet–visible-near infrared (UV–VIS-NIR) spectrophotometer (Varian Cary 5000). Transmission electron microscopy (TEM) was done on 200 kV, JEOL TEM-2100. Scanning electron microscopy (SEM) of the gold-coated surface of ceramic was carried out on Zeiss EVO 40. 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 a *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. Dynamic light scattering (DLS) analysis was done by taking approx- 0.1 gm sample dispersed in 15 ml ethanol and sonicated for 15 min, using Nanoplus Zeta/nano particle analyzer.

3. RESULTS AND DISCUSSION

FTIR spectra of microwave combusted precursors (Fig.1) showed weak absorption bands between 850 cm^{-1} and 900 cm^{-1} caused by the CO_3^{2-} produced during the process. The absorption peaks between 1350 cm^{-1} to 1400 cm^{-1} resulted from vibration of *C-O* and *C-C* bond. Broad absorption bands between 400 cm^{-1} and 800 cm^{-1} were observed which indicate that Nd:GGG formation has not taken place. FTIR spectra of the microwave precursor calcined at 900 °C for 2 h (Fig.2) showed characteristic peaks of Nd:GGG at 671 cm^{-1}, 615 cm^{-1}, and 578 cm^{-1} [20,3] for nitrate-to-citrate ratio of 1: 0.416, 1: 0.833, and 1: 1.666 but not for 1:0.208 which consists of least ratio of citric acid.

From XRD (Fig. 3) pattern of the samples calcined at 900 °C for 2 h, it can be seen that for nitrate-to-citrate ratio of 1: 0.416, 1: 0.833, and 1: 1.666 the positions of diffraction peaks are in accordance with those of standard GGG-PDF 880-574. But the diffraction peaks in nitrate-to-citrate ratio of 1:0.208 do not agree with those of standard GGG with additional peaks of Gd_2O_3. It may be due to the evaporation of Ga_2O_3 during combustion because of less complexation of fuel with Ga^{2+} ions, leading to disturbance in the 3:5 ratio of Gd^{3+}:Ga^{3+} ions,

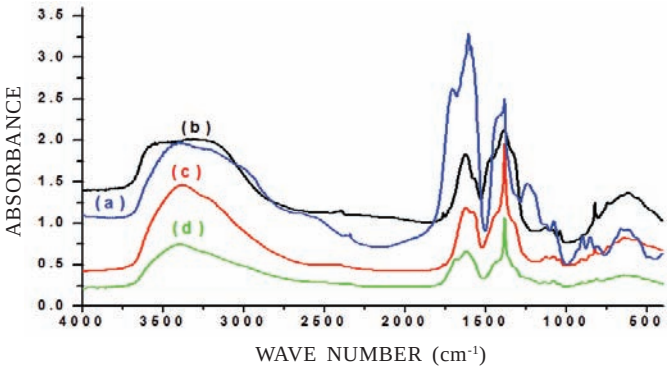


Figure 1. FTIR of microwave precursors with nitrate-to-citrate ratios (a) 1.666, (b) 0.833, (c) 0.416, (d) 0.208.

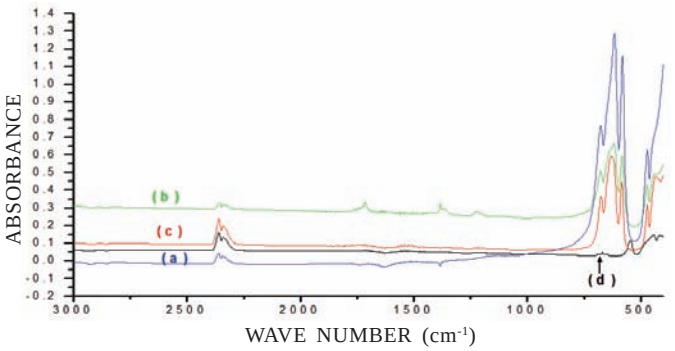


Figure 2. FTIR after calcination at 900 °C for 2 h with nitrate-to-citrate ratios (a) 1.666, (b) 0.833, (c) 0.416, (d) 0.208.

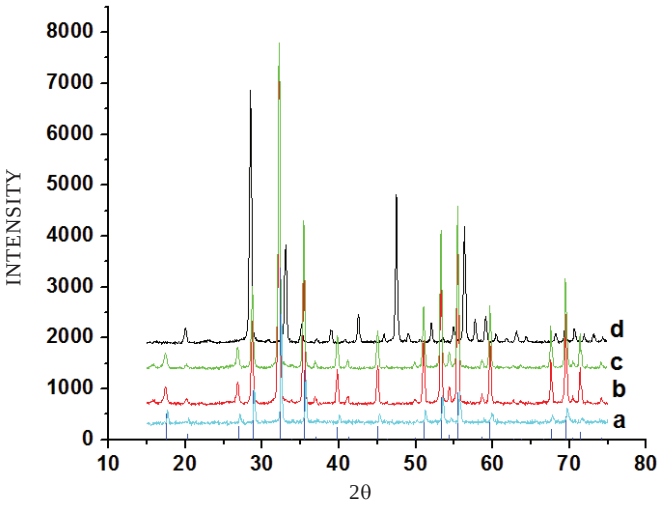


Figure 3. XRD after calcination at 900 °C for 2 h with nitrate-to-citrate ratios (a) 1.666, (b)0.833, (c) 0.416, (d) 0.208.

resulting in non-formation of phase-pure GGG. Considering the cubic symmetry of Nd:GGG the lattice parameter, *a*, was calculated by least square method using the following equation:

$$a = d_{hkl}(h^2 + k^2 + l^2)^{1/2}$$

The lattice constant for Nd:GGG, as calculated, was found to be 12.3876 Å which is larger than 12.3835 Å for undoped GGG[21]. This indicates substitution of gadolinium by neodymium. The lattice parameter increases because neodymium ion has bigger size than gadolinium ion[22]. Diffused reflectance spectra of Nd:GGG in Fig. 4 showed all the transitions peaks of neodymium ion in GGG[23].

Room temperature emission spectra of Nd:GGG nanopowder measured under 808 nm excitation in Fig. 5 shows strongest flourescence emission of Nd^{3+} ions at 1062 nm corresponding to $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition[24].

TEM images of calcined Nd:GGG powders at 900 °C with nitrate-to-citrate ratio 1: 1.666, 1: 0.833, and 1: 0.416 were shown in Figs 6(a) to 6(c). It was observed that particle size in stoichiometric ratio is between 200 nm - 300 nm with a strong necking between the particles. In case of fuel lean ratios, the size of particle has reduced up to 80 nm - 100 nm in 1:0.416.In citrate-to-nitrate ratio of 1: 0.416, particles are relatively well

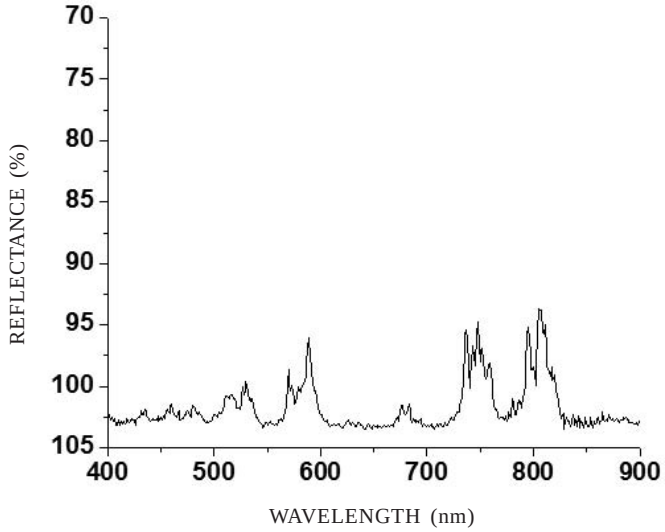


Figure 4. Diffused reflectance spectra of Nd:GGG after calcination at 900 °C for 2 h with nitrate-to-citrate ratio 1:0.416.

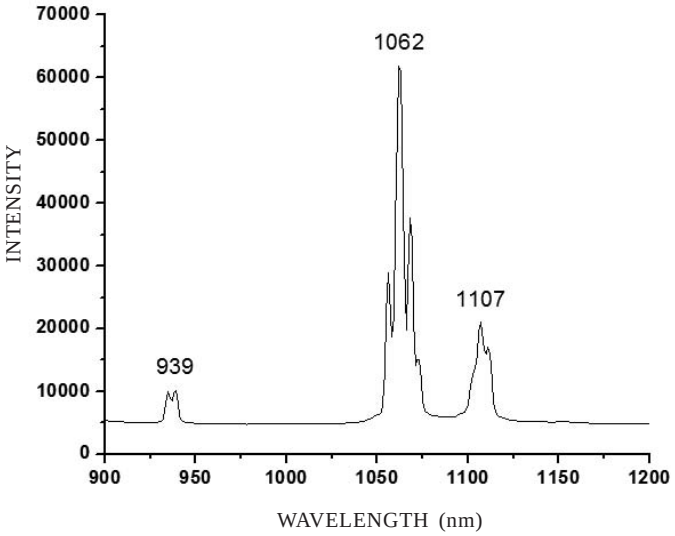
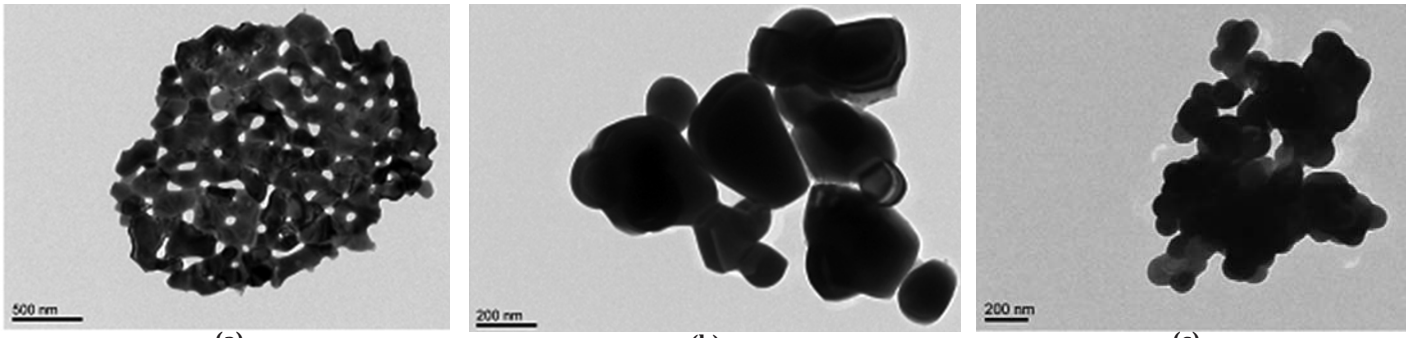


Figure 5. Photoluminescence of Nd:GGG nanopowder.



(a) (b) (c)

Figure 6. TEM of Nd:GGG after calcination at 900 °C for 2 h with nitrate-to-citrate ratio (a) 1.666, (b) 0.833, (c) 0.416.

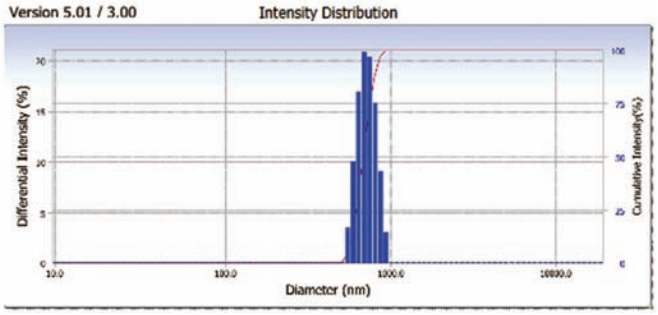


Figure 7. DLS showing agglomerate distribution.

and uniformly distributed, which is favourable for transparent ceramic fabrication. For stoichiometric nitrate-to-citrate ratio, large amount of carbon produced during microwave combustion led to big particle size during calcinations due to more localized heat compared to fuel lean ratios. Within fuel lean citrate-to-nitrate ratios, only for 0.416 best particle morphology and size range were obtained, indicating optimised ratio. Thus, metal nitrate-to-fuel ratio has direct influence on particle size. From DLS analysis, the agglomerate size was found to be less than 1 μm, indicating that nanosized particles of 80 nm - 100 nm tend to agglomerate due to van der Waals forces. Thus the agglomerate size has uniform distribution that led to uniform sintering as observed from SEM of sintered ceramics.

Compaction and subsequent air sintering at 1550 °C for 5 h in air of phase pure Nd:GGG nanopowders with varied nitrate-to-citrate ratio of 1: 1.666, 1: 0.833, and 1: 0.416 showed good and homogeneous compaction with least porosity as observed by SEM in Fig.8. SEM showed highly homogeneous and least grain growth of less than 2 μ in case of nitrate-to-citrate ratio 1: 0.416. It complements with the TEM analysis in which this ratio showed smaller size and narrow size range, making these particles highly sinterable. XRD of the air-sintered ceramics showed phase purity retention as depicted in Fig. 9.

4. CONCLUSION

A detailed study on the phase purity and particle morphologies of Nd:GGG was carried out taking different ratios of metal nitrates-to-citric acid. Formation of phase pure Nd:GGG took place, from stoichiometric citrate-to-nitrate ratio up to fuel lean ratio of 1 : 0.416. However best particle properties, with regard to narrow particle size range and close to spherical and uniform particle morphology were achieved for citrate-to-nitrate ratio of 0.416. Least grain growth on air sintering at 1550 °C for 2 h was observed for citrate-to-nitrate ratio of 0.416. These highly sinterable powders are expected to give transparent ceramics.

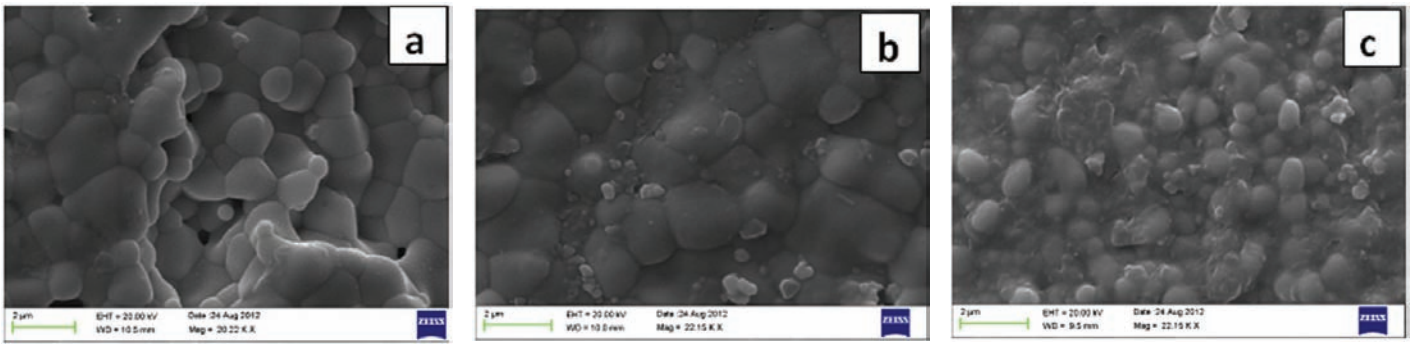


Figure 8. SEM after air sintering at 1550 °C for 2 h of Nd:GGG nanopowders compact with nitrate-to-citrate ratios (a) 1.666, (b) 0.833, (c) 0.416.

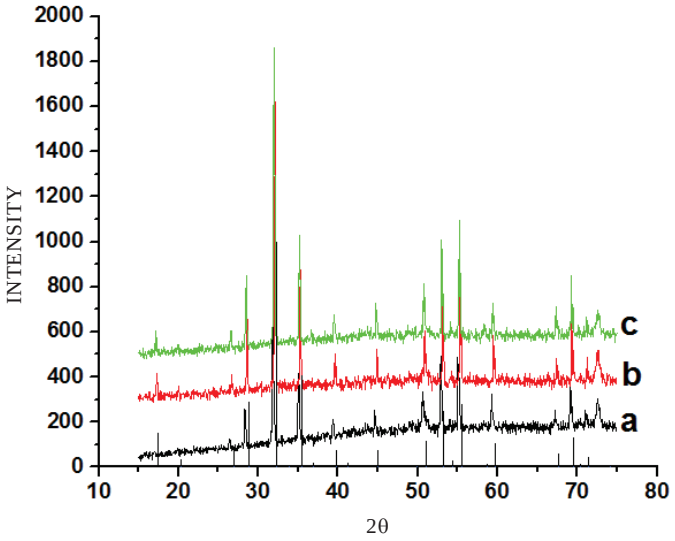


Figure 9. XRD after air sintering at 1550 °C for 2 hrs of Nd:GGG nanopowders compact with nitrate-to-citrate ratios (a) 1.666, (b) 0.833, (c) 0.416.

ACKNOWLEDGEMENTS

Authors thank Director, Laser Science and Technology Centre, DRDO, Delhi , for his encouragement and support to carry out this work. Further we extend our thanks to AIRF-JNU, Delhi, for their timely help during characterization and Dr G. Vijaya Prakash of IIT-Delhi for providing the emission measurement facilities.

REFERENCES

1. Liu, J.H.; Han, Y.H. & Zhao, Y.D. A diode-pumped Nd^{3+}-doped Gadolinium Gallium garnet quasi-three-level laser at 933 nm. *Laser Physics*, 2013, **23**(11), 5002. doi: 10.1088/1054-660X/23/11/115002
2. Liu, Hongliang; Jia, Yuechen; Chen, Feng & Aldana, Javier R. Vázquez de. Continuous wave laser operation in Nd:GGG depressed tubular cladding waveguides produced by inscription of femtosecond laser pulses. *Opt. Mater. Express*., 2013, **3**(2), 278-283. doi: 10.1364/OME.3.000278
3. Wang, Guisu; Li, Xia & Geng, Yanling. Preparation of gadolinium gallium garnet polycrystalline powders for transparent ceramics. *J. Alloys Comp.*, 2010, **505**(1), 213-216. doi: 10.1016/j.jallcom.2010.06.031
4. Xueyan, Tian; Xiyan, Zhang; Yinzhu, Li & Peizhi, Yang. Synthesis and spectral properties of Nd^{3+}: $Gd_3Ga_5O_{12}$ nanopowder for transparent laser ceramics. *J. Rare Earths*, 2006, **24**(4), 443-446. doi: 10.1016/S1002-0721(06)60140-3
5. Yao, Yan-ping & Liu, Jing-he. Preparation of Nd- doped Gadolinium- Gallium garnet laser ceramic powder by sol-gel method. *Optoelec. Lett.*, 2006, **2**(4), 288-291. doi: 10.1007/bf03033662
6. Li, Xianxue; Hu, Zhang-Gui & Li, Jiangtao. Nanostructured GGG powders via gel combustion. *Sci. Optical Mater.*, 2007, **29**(7), 854-857. doi: 10.1016/j.optmat.2006.01.010
7. Sun, Dunlu; Zhang, Qingli; wang, Zhaobing; Su, Jing; Gu, Changjiang, Wang, Aihua & Yin, Shaotang. Co-precipitation synthesis and sintering of nanoscaled Nd:$Gd_3Ga_5O_{12}$ polycrystalline material. *Mater. Sci. Eng., A* 2005, **392**(1-2), 278-281. 10.1016/j.msea.2004.09.057
8. Luo, Zhenlin; Lu, Menglin; Bao, Jun; Liu, Wenhan & Gao, Chen. Co-precipitation synthesis of gadolinium gallium garnet powders using ammonium hydrogen carbonate as the precipitant. *Mater. Lett.* 2005, **59**(10), 1188-1191. doi:10.1016/j.matlet.2004.12.025
9. Yu, F.P.; Yuan, D.R.; Duan, X.L.; Guo, S.Y.; Wang, X.Q.; Cheng, X.F. & Kong, L.M. A simple process to synthesize sphere- shaped gadolinium gallium garnet nanoparticles for transparent ceramic. *J. Alloys Comp.*, 2008, 465(1-2), 567-570. doi:10.1016/j.jallcom.2007.11.008
10. Dexin, Huang; Xuejian, Zhang; Jinghe, Liu & Dan, Zhang Nanostructured Yb:GGG polycrystalline powders via gel combustion method. *J. Rare Earths*, 2009, **27**(3), 402-405. doi: 10.1016/S1002-0721(08)60260-4
11. Dexin, Huang; Xuejian, Zhang; Jinghe, Liu & Dan, Zhang. Synthesis of Polycrystalline Yb:$Gd_3Ga_5O_{12}$ nanopowders by homogeneous precipitation method. *J. Wuhan University of Technology-Mater. Sci. Ed.*, 2010, **25**(1), 123-125. doi: 10.1007/s11595-010-1123-7
12. Dong, Yanmin: Sun, Jing; Yu, Wensheng; Li, Weihang & Teng, Fei. Preparation and properties of Nd,Yb:GGG polycrystalline nanopowders. *J. Adv. Ceram.*, 2012, 1(4), 296-300. doi: 10.1007/s40145-012-0030-0
13. Gluchowski, P.; Hreniak, D. & Strek, W. Spectroscopic properties of Cr^{+3} doped $Gd_3Ga_5O_{12}$ nanoceramics. *In* the 9th Laser Ceramic Symposium Institute of Low temperature and Structure Research PAS, Wroclaw, Poland, 2-6 Dec 2013, Korea.

14. Li, Xianxue; Hu, Zhang-Gui & Li, Jiangtao. Nanostructured GGG powders via gel combustion. *Opt. Mat.*, 2007, **29**(7), 854-857. doi: 10.1016/j.optmat.2006.01.010
15. Saladino, Maria Luisa; Nasillo, Giorgio; Martino, Delia Chillura & Caponetti, Eugenio. Synthesis of Nd:YAG nanopowder using the citrate method with microwave irradiation. *J. Alloys Compds.* 2010, **491**(1-2), 737-741. doi: 10.1016/j.jallcom.2009.11.054
16. Mangalaraja, R.V.; Moujon, J.; Hedstrom, P.; Camurri, Carlos P.; Ananthakumar, S. & Oden, M. Microwave assisted combustion synthesis of nanocrystalline yttria and its powder characteristics. *Power Technology*, 2009, **191**(3), 309-314. doi:10.1016/j.powtec.2008.10.019
17. Sumio, S. Handbook of sol gel science and technology. Kluwer Academic Publications. 2005,1.
18. Vaqueiro, P. & López-Quintela, M.A. Influence of complexing agents and pH on yttrium-iron garnet synthesized by the sol-gel method. *Chem. Mater*., 1997, **9**(12), 2836-2846. doi: 10.1021/cm970165f
19. Jain, S.R.; Adiga, K.C. & Pai, Verneker V.R. A new approach to thermochemical calculations of condensed fuel-oxidizer mixtures. *Combustion Flame*, 1981, **40**, 71. doi: 10.1016/0010-2180(81)90111-5
20. Panga, Maolin & Lin, Jun. Growth and optical properties of nanocrystalline $Gd_3Ga_5O_{12}$:Ln (Ln = Eu^{+3}, Tb^{+3}, Er^{+3}) powders and thin films via Pechini sol–gel process. *J. Cryst. Grow.*, 2005, **284**(1-2), 262–269. doi: 10.1016/j.jcrysgro.2005.07.007
21. Makino, Hiroshi; Nakamura, Susumu & Matsumi, Koichi. Lattice parameter variations in Czochralski grown Gadolinium Gallium garnet single crystals. *Jpn. J. Appl. Phys.*, 1976, **15**(3), 415-419. doi: 10.1143/JJAP.15.415
22. Lipinska, L.; Ryba-Romanowski, Rzepka, A.; Ganschow, S.; Lipinski, R.; Diduszko, R. & Pajaczkowska, A. Preparation and characterization of Nd doped gadolinium gallium garnet nanopowders and crystals. *Cryst. Res. Technol*., 2009, **44**(5), 477-483. doi:10.1002/crat.200800315
23. Qureshi, Mohammad, Chen, Hsin-Yu & Lu, Chung-Hsin. Synthesis and photoluminescent properties of neodymium-ion doped perovskite oxides. *Solid State Comm*., 2007, **142**(1-2) 85–88. doi: 10.1016/j.ssc.2007.01.021
24. Jing, Sun; Fenming, Zeng; Jianli, Li; Yiing, Cao; Yuchun, Wan & Jinghe, Liu. Synthesis of Nd:GGG ultrafine polycrystalline powders by sol-gel method. *J. Rare Earths*, 2005, **23**(1), 188-190.

CONTRIBUTORS

Ms Kiranmala Laishram obtained her MSc (Physical Chemistry) from Manipur University in 2002. She is working as Scientist 'D' at Laser Science and Technology Centre (LASTEC), Delhi. Her areas of interest are : Material characterization techniques, laser materials, and nonmaterial-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, Delhi, 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 published 5 technical reports.

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

Mr Dinesh Bhardwaj completed his BSc (Industrial Chemistry) from University of Delhi, in 2010 and MSc (Industrial Chemistry) from Amity University, in 2012. Presently working as a Project Fellow in Organic Hybrid Solar Cell Division of National Physical Laboratory, CSIR.

Ms Richa Sharma completed her BSc (Industrial Chemistry) from University of Delhi, in 2010 and MSc (Industrial Chemistry) from Amity University, in 2012. Working as a Project Assistant at the Amity University and also pursuing PhD at the Amity Institute of Applied Sciences.

Ms Suman Shakya completed her MTech (Nanotechnology) from Aligarh Muslim University in 2010. Currently pursuing her PhD from Nanophotonics Laboratory at Department of Physics, Indian Institute of Technology Delhi, New Delhi.