

Novel microwave assisted synthesis of highly doped phase pure Nd:YAG nanopowder

L. KIRANMALA*, M. REKHA, M. NEELAM

Chemistry Division, Laser Science and Technology Centre, DRDO, Metcalfe House, Delhi-110054, India

For the first time, the studies on 2 to 10 at.% neodymium (Nd^{3+}) ion doped Yttrium Aluminum Garnet (Nd:YAG) nanopowders obtained by microwave assisted citrate nitrate gel combustion synthesis is described in this work. This paper reports on high doping of Nd^{3+} ions with retaining the cubic garnet structure of YAG as evidenced from XRD, except the case of 8 at.% doped Nd:YAG. Phase pure YAG formation with 8 at.% Nd^{3+} doping was explored by using urea and alanine as alternative to citric acid complexing agents. Complete crystallization of YAG as a result of 2 hour thermal treatment at 900 °C under oxygen supply was studied by using Fourier Transform Infra-Red Spectroscopy (FTIR) and X-Ray Diffraction (XRD) techniques. With an increase in the dopant concentration a red shift in the FTIR peaks was observed. Using the XRD data, the cell parameter of Nd^{3+} (2 to 6 and 10 at.%) YAG was found to increase with an increase in the dopant concentration. The average primary particle size calculated using Scherrer's equation was ~25 nm which was additionally supported by Transmission Electron Microscopy (TEM) results yielding particle sizes in the range of ~25 to 30 nm for all the cases.

Keywords: *high doping, Nd:YAG, microwave assisted sol-gel process, cell parameter*

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1. Introduction

Neodymium doped YAG is an important laser material. The laser output is directly related to the level of lasing medium (Nd^{3+}) doped in the host (YAG). For high power laser applications, the fabrication of YAG laser materials doped with a high concentration of Nd^{3+} has been an area of great importance and a subject of extensive research. Moreover, highly doped YAG ceramics is promising for high power microchip laser application. The absorption coefficient of 4.8 at.% Nd^{3+} is 4.8 times larger compared to 1 at.% Nd:YAG single crystal [1]. So the higher the Nd^{3+} concentration the larger is the optical absorption and gain co-efficient which has led to the development of high power miniature and microchip lasers [2]. In single crystals grown by Czochralski method more than 1 % of Nd^{3+} cannot be doped homogeneously without deteriorating the lasing properties [3]. Furthermore, in single crystals, the higher doping can also lead to cracking. Using flux method, higher Nd^{3+} concentrations up to 4.5 at.% can be achieved but it takes a long growth

time, yielding very small crystals not suitable for practical applications [4]. Recently, polycrystalline Nd:YAG ceramic laser materials have received great attention due to their certain advantages [5]. One very important advantage is the ease of higher doping in ceramics as compared to single crystals. For fabrication of ceramics the initial Nd^{3+} doped YAG powder can be achieved by different routes such as solid state reactions and wet chemical reactions. Starting from the solid state reaction, by vacuum sintering technique, up to 8.2 at.% Nd^{3+} doped YAG ceramics have been fabricated [6].

Doping of Nd^{3+} up to 24 at.% has been reported by co-precipitation route. But Nd^{3+} doping larger than 5.7 at.% caused impurities of YAM and YAH in the garnet structure which retained even after heat treatment of precursor at 1050 °C. Further investigation at temperatures higher than 1100 °C was suggested to be carried out for higher doping of Nd^{3+} in YAG [2].

By conventional sol-gel process only up to 4 at.% Nd^{3+} doped YAG has been reported using 1,2-ethanediol [7]. By a novel microwave assisted gel combustion process, 2 at.% Nd^{3+} ion doping was achieved [8]. The advantage of using a microwave

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

assisted process is the fact that the energy interacts at molecular level, leading to homogeneous reaction, enhanced reaction kinetics and bulk nucleation. This may be due to better microwave absorption by the precursors leading to effective utilization of the reaction enthalpy to increase the reaction rate [9]. For the first time the studies on synthesis of highly doped (up to 10 at.%) phase pure Nd:YAG by this method are reported.

2. Experimental

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 the starting materials. The metal precursors were taken in the molar ratios of $Y_{2.94}Nd_{0.06}Al_5$, $Y_{2.88}Nd_{0.12}Al_5$, $Y_{2.82}Nd_{0.18}Al_5$, $Y_{2.76}Nd_{0.24}Al_5$ and $Y_{2.70}Nd_{0.30}Al_5$ for 2, 4, 6, 8 and 10 at.% Nd^{3+} respectively. Citric acid was used as the chelating agent. The total amount of cations to citric acid was taken in the ratio of 1:1. The nitrate-citrate sol prepared in deionized water was ultrasonically stirred for 2 h and kept in the oven at 80 °C for 16 h. The gels obtained were combusted in a domestic microwave oven operating at 2.45 GHz which was modified to exhaust the evolved gases. These microwave combusted powders were used as the precursor powders, which were calcined at 900 °C for 2 h under oxygen supply.

Fourier Transform Infra-Red Spectroscopy (FTIR) was carried out by Bruker, (Vector 22) to identify the temperature of formation of Y–O and Al–O bonds. X-Ray Diffraction (XRD) studies were carried out with the help of Philips X-Ray Diffractometer, PW 3020 in 2θ range from 20 to 80° for characterization of phase purity, particle sizes and cell parameters. Nd^{3+} doping was characterized by EDX using Scanning Electron Microscope (Zeiss EVO Series, EVO 50). Transmission Electron Microscopy (TEM) studies were done on FEI Philips Morgagni 268. The TEM specimens were prepared on copper grids by dispersing the powder ultrasonically in acetone.

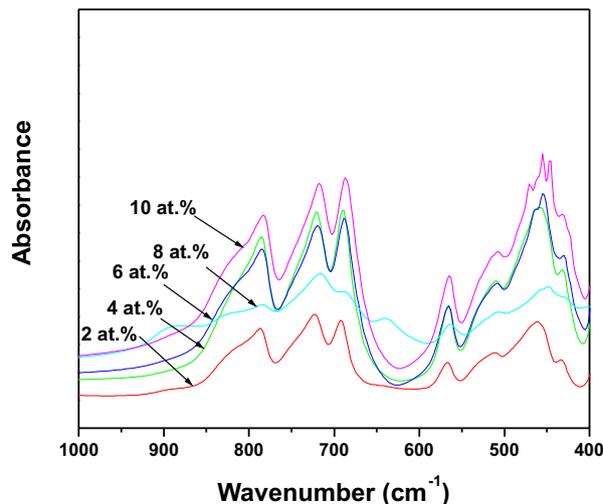


Fig. 1. FTIR of YAG doped with different Nd^{3+} concentrations.

3. Results and discussion

FTIR spectra of Nd^{3+} 2 to 10 at.% doped YAG powders (Fig. 1) treated at 900 °C for 2 h revealed vibrational bands in the region of 400–800 cm^{-1} corresponding to those of metal–oxide (M–O) bond in YAG [10]. At 8 at.% Nd^{3+} , incomplete formation of M–O bond was indicated in the FTIR spectrum. As incorporation of Nd^{3+} is a function of time and temperature during a calcination process [11], the powder was further calcined at 1100 °C for 2 h under flowing oxygen. Still complete calcination did not take place. This was further evidenced by XRD.

There was a slight shift in the peak positions towards lower wavenumber as we increased the dopant concentration. This is an indication that the dopant occupies the lattice positions in the cubic structure [12].

The XRD of YAG (Fig. 2) calcined at 900 °C for 2 h showed the characteristic peaks (JCPDS 33-40) in all the powders, up to 6 at.% Nd^{3+} doping. However, the XRD of 8 at.% Nd^{3+} doped YAG showed extra peaks at $2\theta = 26.7^\circ$, 30.6° and 43.8° which correspond to Y_4AlO_9 , YAM phase. This can be attributed to the fact that neodymium is much larger than yttrium (0.102 and 0.114 nm for Y^{3+} and Nd^{3+} , respectively). Therefore, the higher the Nd^{3+} concentration, the longer the diffusion time leading to

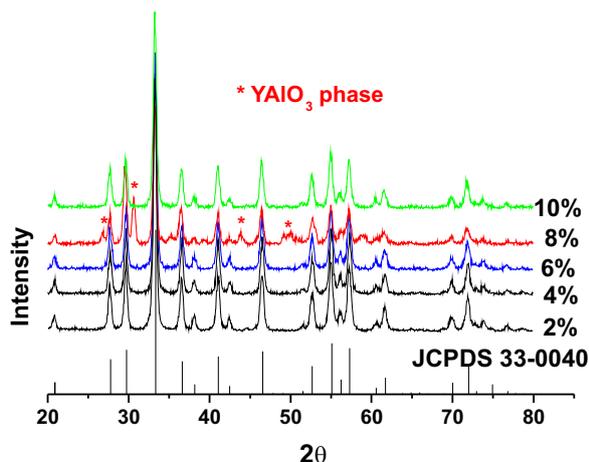


Fig. 2. XRD depicting complete crystallization to phase pure YAG.

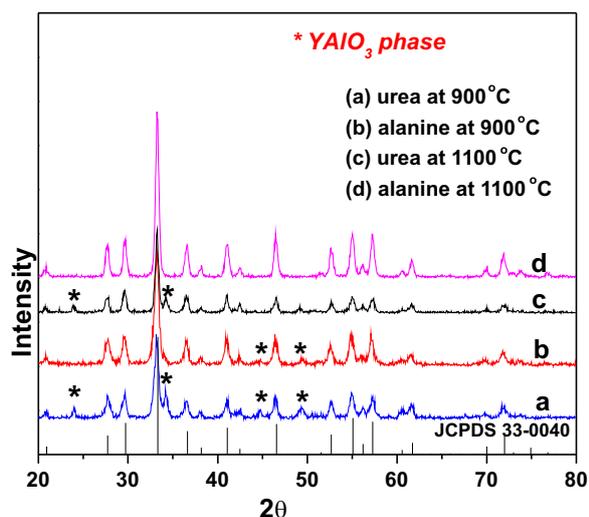


Fig. 3. XRD of 8 at.% Nd^{3+} doped YAG using other complexing agents.

higher temperature for crystallization of cubic phase of YAG [13, 14]. But these extra peaks sustained even after heating the powder further at 1100 °C for 2 h. However, phase purity was again observed in case of 10 at.% Nd^{3+} doping after annealing at 900 °C for 2 h.

To explore this discrepancy in the case of 8 at.% Nd^{3+} doping, urea and alanine were used in place of citric acid in the molar ratio of metal nitrate to complexing agent 1:2.5 and 1:0.5 for urea and L-alanine, respectively. But phase purity could not be achieved in both the cases as the YAP and YAH phases were

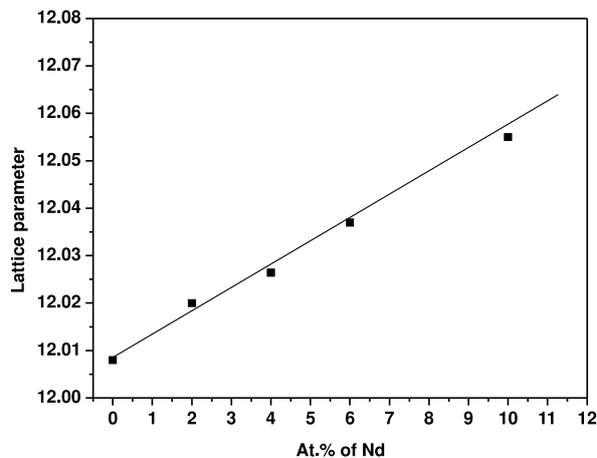


Fig. 4. Lattice parameter variation with dopant concentration.

present in the powders calcined at 900 °C for 2 h. However, with L-alanine, the phase pure YAG was formed at 1100 °C for 2 h. But in case of citric acid and urea complexing agent even on the treatment at 1100 °C for 2 h, the phase purity could not be achieved. The metal nitrate to total carbon content ratio was found to be 1:6 for citric acid, 1:2.5 for urea and 1:1.5 for L-alanine. The carbon content was the lowest in case of L-alanine and phase purity was achieved after 2 hour treatment at 1100 °C. It is possible that the presence of excess carbon trapped in case of citric acid and urea prevented the formation of phase pure YAG even after the thermal treatment at 1100 °C for 2 h. This different behavior in case of 8 at.% Nd^{3+} doping needs further exploration.

The cell parameters of the powders were calculated with the help of diffraction angles and interplanar spacing from the XRD data using the least square method. The cell parameter, a of cubic YAG is 12.008 Å (JCPDS 33-40). Since the effective radius of Nd^{3+} is greater than that of Y^{3+} , the value of cell parameter also increased continuously with the increase in dopant concentration from 2 at.% to 6 at.% and then at 10 at.% (Fig. 3). The absence of any extra peak in the XRD graphs confirms that the compounds are phase pure and Nd^{3+} is uniformly distributed in the desired lattice structure. The particle size was calculated using Scherrer's equation [15]:

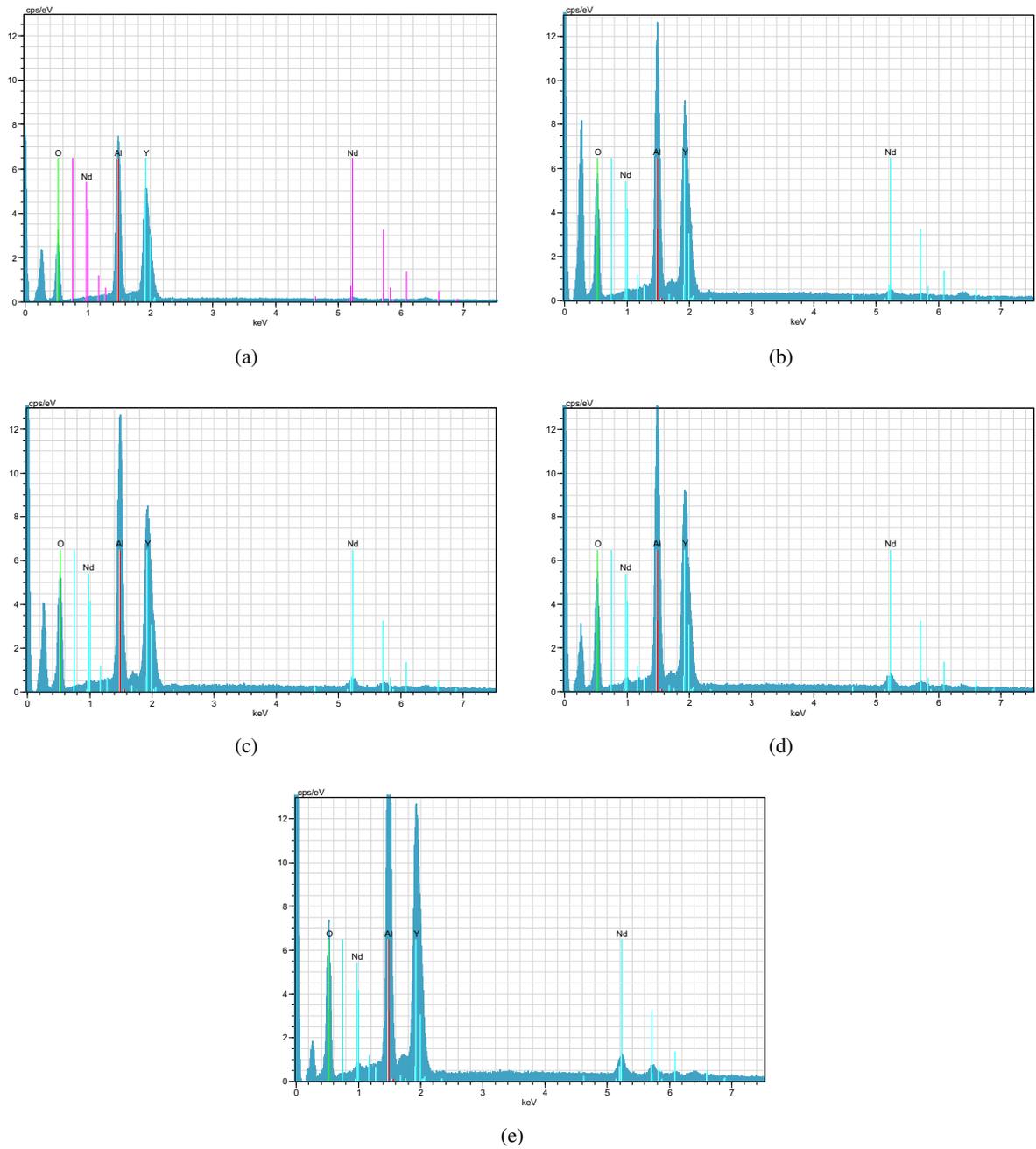


Fig. 5. EDX spectra of YAG doped with Nd^{3+} a) 2 at.% , b) 4 at.% , c) 6 at.% , d) 8 at.% , e) 10 at.%.

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

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 a characteristic of the

instrument. The primary particle size of the samples was in the range of 25 to 30 nm.

On the EDX spectra (Fig. 4) an increase in the area under the peaks of Nd with the increase in dopant concentration was observed. A typical transmission electron micrograph (Fig. 5) showed the particle sizes in the range of 25–50 nm.

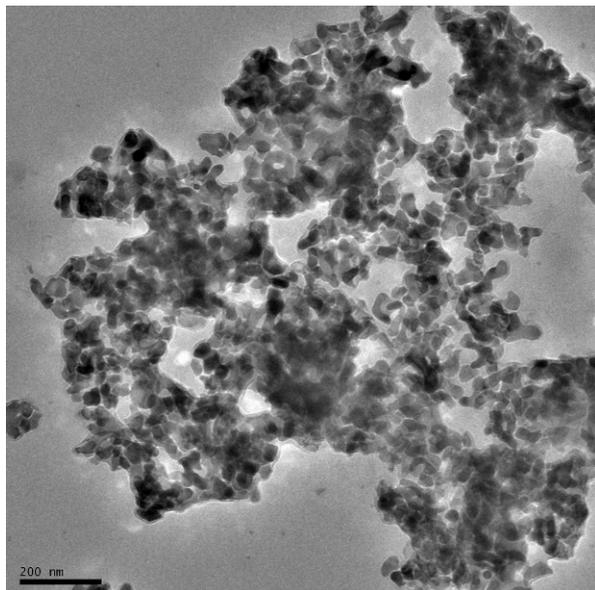


Fig. 6. Typical TEM of Nd:YAG nanopowder.

4. Conclusions

- The microwave assisted gel combustion yielded phase pure YAG with a high concentration of neodymium as compared to reported 4 % and 5.7 % for conventional sol-gel and coprecipitation techniques, respectively, indicating efficiency of microwave assisted route to obtain high neodymium ion doping.
- The cell parameter increased continuously for 2, 4, 6 and 10 at.% Nd³⁺ doping using citric acid complexing agent, as also evidenced by EDX.
- For 8 at.% Nd³⁺ doping, phase purity was obtained after 2 hour treatment at 1100 °C using alanine complexing agent. Thus the microwave assisted synthesis method is simple and robust for obtaining phase pure YAG with high concentration of neodymium ions.

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