

Nitrate-citrate Sol-gel Synthesis of Phase Pure Nd^{3+} -doped Nanocrystalline Yttrium-aluminum-garnet

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ABSTRACT

Phase pure nanopowders of undoped and neodymium (Nd^{3+})-doped yttrium-aluminum-garnet (YAG) was synthesised by sol-gel process using nitrate-citrate gel method. Complete crystallisation of YAG was studied using Fourier transform infra-red spectroscopy (FTIR) and x-ray diffraction (XRD). Complete phase formation took place at 900 °C for 2 h. The average primary particle size calculated was ~25 nm. Transmission electron microscopy (TEM) showed particles in the range of ~25 nm to 30 nm. Nd -dopant concentration levels of 2 and 4 atomic per cent were studied. Using XRD data the cell parameters of Nd (0, 2 and 4 atomic per cent):YAG were calculated and it was found to increase with increase in dopant concentration.

Keywords: Phase-pure YAG, sol-gel process, Nd -doping, cell parameter

1. INTRODUCTION

Rare earth-doped $Y_3Al_5O_{12}$ (yttrium-aluminum-garnet (YAG)) is an important solid-state material due to its interesting optical and mechanical properties^{1,2}. Single crystals of YAG doped with neodymium ion are used as gain medium in solid-state lasers³. The single crystals of YAG require complex methods of synthesis. However, polycrystalline Nd:YAG powders can be compacted and sintered to give transparent ceramics¹. Synthesis of YAG nanopowders by various methods has been reported such as sol-gel^{4,5}, coprecipitation^{6,7}, spray pyrolysis⁸ and combustion⁹ technique. Synthesis by solid-state reaction involves lengthy high temperature treatment yielding phase impurities. Due to the formation of intermediate metastable phases such as $Y_4Al_2O_9$ (YAM), hexagonal $YAlO_3$ and orthorhombic $YAlO_3$, other than Al_2O_3 and Y_2O_3 in the yttria-alumina system, phase pure YAG is not easy to obtain¹⁰.

The author earlier reported the synthesis of phase pure YAG nanopowders by nitrate-citrate sol-gel route⁵. Highly doped YAG ceramics are promising materials for high power microchip laser application¹¹. However, in single crystals grown by Czochralski method, more than 1 per cent of Nd^{3+} cannot be doped homogeneously without deteriorating the lasing properties¹². The author in the paper report synthesis of YAG nanopowders doped with 2 and 4 atomic per cent neodymium ion. The benefit of present method is high neodymium ion doping by citrate nitrate sol-gel process during which chemical homogeneity of the system is maintained throughout the process.

2. EXPERIMENTAL WORK

Yttrium nitrate, $Y(NO_3)_3 \cdot 6H_2O$ (99.9 per cent purity

Alfa Aesar), neodymium nitrate, $Nd(NO_3)_3 \cdot 6H_2O$ (99.9 per cent purity Alfa Aesar) aluminum nitrate, $Al(NO_3)_3 \cdot 9H_2O$ (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 precursors were taken in the molar ratios of $Y_{2.94}Nd_{0.06}Al_5$ and $Y_{2.88}Nd_{0.12}Al_5$ for 2 atomic per cent and 4 atomic per cent Nd respectively. Citric acid was used as the chelating agent. The total cation to citric acid was taken in the ratio of 1:1. The nitrate-citrate sol in millipore water was prepared by ultrasonic stirring. Gelation took place at 80 °C for 16 h. Drying of the gel was carried out from 110 °C to 150 °C in 24 h. This precursor powder was calcined at different temperatures up to 900 °C.

Thermo-gravimetric analysis (TGA) of the precursor was carried out in air at a heating rate of 10 °C/min from room temperature to 1300 °C by Perkin Elmer Diamond Simultaneous TGA/DTA. 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 using Philips x-ray diffractometer, PW 3020 in 2θ range from 15° to 80° for characterisation of phase purity, particle size, and cell parameters. 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. Nd^{3+} doping was characterized by EDX using scanning electron microscope (ZEISS EVO Series, EVO 50).

3. RESULTS AND DISCUSSION

TGA of the xerogel shows total weight loss of ~65 per cent (Fig.1) with maximum weight loss taking place up to 600 °C.

The strong exotherm at 421.46 °C along with weight loss depicted by TGA corresponds to decomposition of the citrate network. A small exotherm corresponding to weight loss at ~ 890 °C indicates crystallisation of YAG⁴. Further after 900 °C the weight loss was almost negligible, indicating that reactions involving weight loss is over by this temperature.

FTIR spectra of 0, 2, and 4 atomic per cent Nd doped

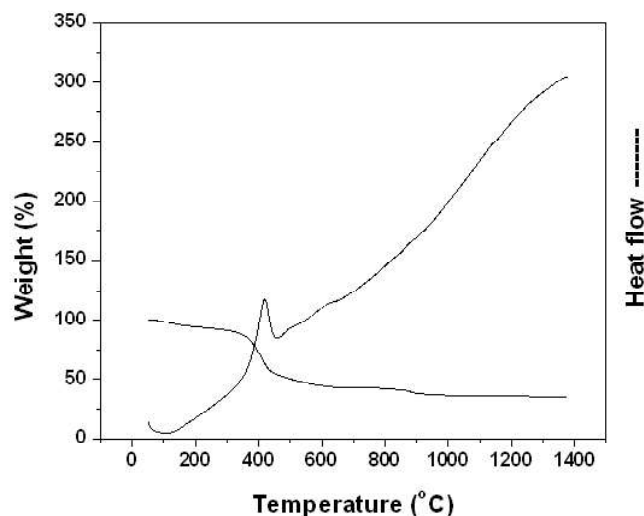


Figure 1. TG-DTA of YAG precursor.

YAG calcined at 900 °C for 2 h are shown in Fig. 2. The metal-oxide (M-O) bonds in YAG show vibrational bands in the region of 400-800 cm^{-1} . Peaks were seen at 786 cm^{-1} , 721 cm^{-1} , 690 cm^{-1} , 565 cm^{-1} , 512 cm^{-1} , 458 cm^{-1} and 432 cm^{-1} which may be attributed to the M-O vibrations in YAG¹³. Formation of YAG at this temperature of 900 °C for 2 h as indicated by FTIR peaks well corresponds to the crystallisation peak of YAG as observed at ~ 890 °C in results of TG-DTA. With Nd^{3+} doping, slight shifts in peak position of M-O bonds characteristic of YAG towards

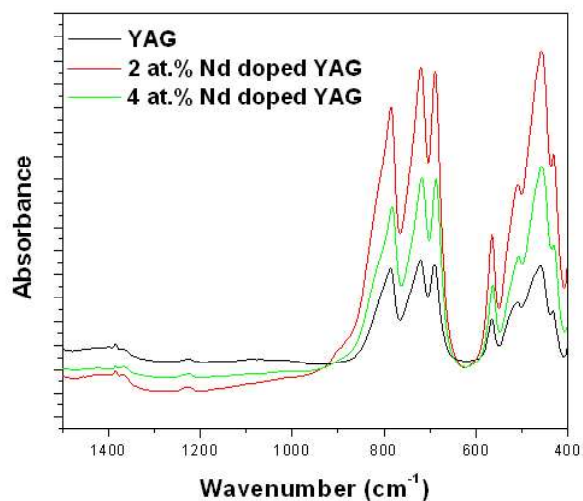


Figure 2. FTIR of 0 to 4 atomic per cent Nd-doped YAG calcined at 900 °C for 2 h.

lower wave number were observed for both 2 and 4 atomic per cent neodymium ion doping. No new peaks were observed on addition of dopant. This accounts for the fact that the dopant ion occupies the lattice positions in YAG without distorting the parent structure¹⁴.

XRD patterns of YAG (Fig.3) calcined at 800 °C for 4 h showed the characteristic peaks (JCPDS 33-40) but the background intensity was very high indicating incomplete crystallisation. However at 900 °C for 2 h complete crystallisation of the phase pure cubic YAG structure was

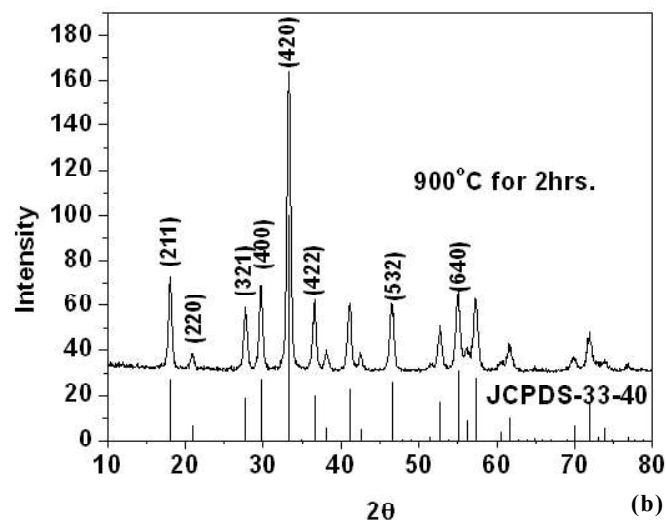
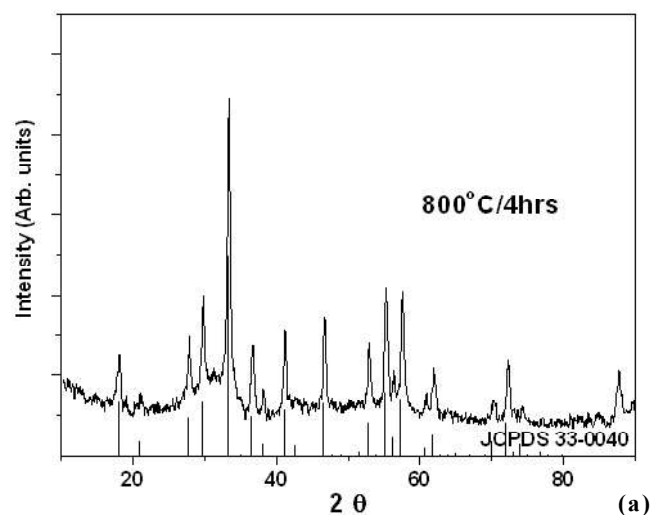


Figure 3 (a and b). XRD depicting complete crystallisation to phase pure YAG.

obtained. Crystallite size was calculated using Scherrer's equation¹⁵ as

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

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. The primary particle size of the samples was ~25 nm.

The cell parameters of undoped and doped YAG were calculated with the help of diffraction angles and interplanar spacing from the XRD data. The cell parameter, a of cubic YAG was 12.008 Å (JCPDS 33-40). With the increase in dopant concentration, the value of cell parameter also increased (Fig.4). This observation supported the fact that Nd substitutes the lattice site of Y in YAG cubic structure without disturbing the garnet structure. Further, the absence of any extra peak in the XRD graphs confirmed that the compounds were phase pure and Nd had been uniformly doped in the desired lattice structure. From EDX spectra (Fig.5) it was observed that there was an increase in the area under the peaks of Nd with the increase in dopant concentration. The elemental composition in Tables 1(a) and 1(b) indicate that the concentration of Nd is approximately doubled from 2 atomic per cent to 4 atomic

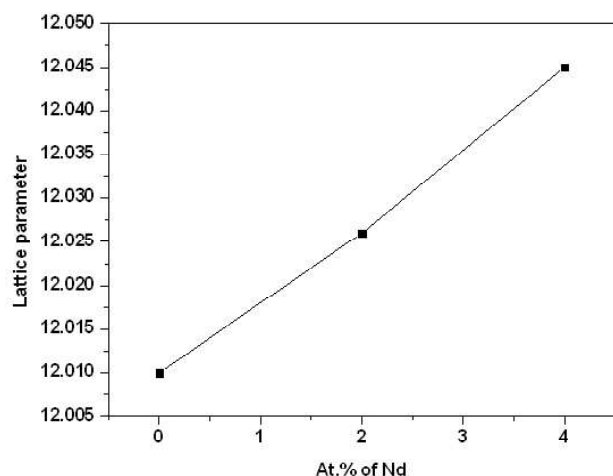


Figure 4. Lattice parameter variation with dopant concentration.

per cent. Elemental composition analysis by EDX becomes difficult when rare earth metal ions are involved. Maybe this is the reason, accurate quantitative analysis of Nd:YAG is never being discussed in the literature. Even in this

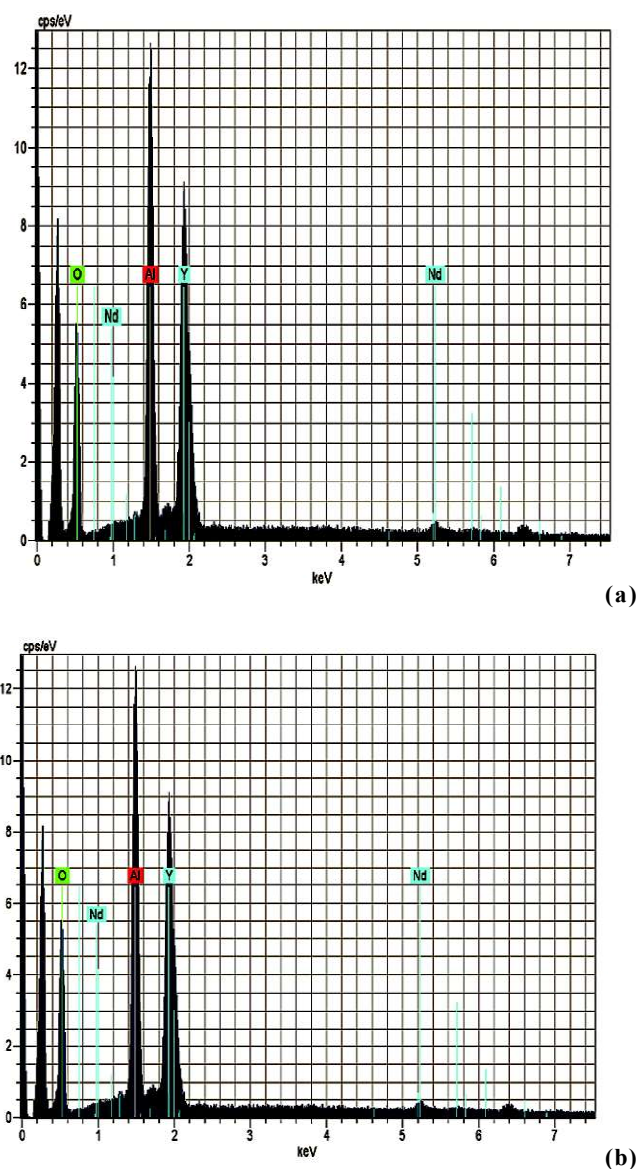


Figure 5. EDX spectra of (a) 2 atomic % and (b) 4 atomic % Nd³⁺.

Table 1 (a). 2 atomic per cent Nd doping

Element	Series wt. %	Unn. C wt. %	Norm. C at. %	Atom. C %	Error
Aluminium	K-series	9.76	20.18	24.34	0.5
Yttrium	L-series	24.41	50.46	18.47	1.0
Neodymium	L-series	0.67	1.38	0.31	0.0
Oxygen	K-series	13.53	27.97	56.88	1.7
Total:		48.38	100.00	100.00	

Table 1 (b). 4 atomic per cent Nd doping

Element	Series wt. %	Unn. C wt. %	Norm. C at. %	Atom. C %	Error
Aluminium	K-series	9.71	19.91	23.58	0.5
Yttrium	L-series	23.21	47.57	17.10	0.9
Neodymium	L-series	1.55	3.17	0.70	0.1
Oxygen	K-series	14.32	29.35	58.62	1.7
Total:		48.79	100.00	100.00	

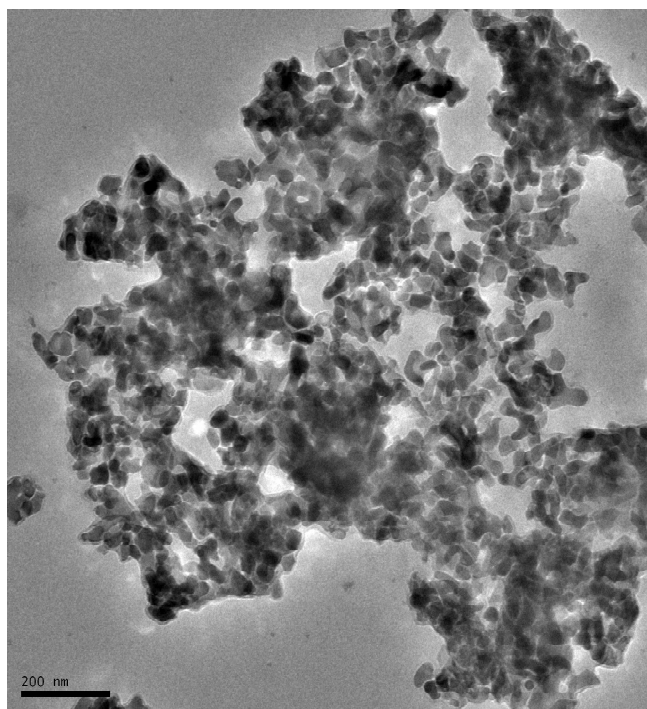


Figure 6. TEM of nanopowders.

extensive work on Nd doping⁷, elemental composition (of Nd) is discussed only by the increase in the peak of Nd in EDX graphs and increase in lattice parameter.

A typical TEM (Fig. 6) showed particles in the size range of 25-50 nm. The particle size and shape was uniform which can lead to versatile application of these Nd:YAG nanopowders.

4. CONCLUSIONS

Phase pure YAG and Nd³⁺-doped YAG were synthesised by sol-gel process using nitrate-citrate sol.

- Complete crystallisation of YAG took place at 900 °C for 2 h.
- On doping Nd³⁺, there was no change in the phase purity.
- Homogeneous doping with 2 and 4 atomic per cent neodymium ion took place as indicated by cell parameter increase and confirmed by EDX spectra.
- Particles were morphologically uniform and very small (in the range of 25-50 nm).

This method is simple and robust for obtaining highly neodymium doped phase pure Nd:YAG at low temperature and can be scaled-up to large batches efficiently.

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