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Phase pure synthesis of undoped and Nd doped nano-crystalline yttrium aluminum garnet

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ABSTRACT

We report a sol-gel process using citric acid as the complexing agent for the synthesis of undoped and 2 at.% Neodymium (Nd^{3+}) doped Yttrium Aluminum Garnet (YAG). The phase purity of the garnet structure was studied in details by using Fourier Transform Infra-Red Spectroscopy (FTIR) and X-Ray Diffraction (XRD) techniques. The average primary particle size calculated by using XRD data was ~25nm. Transmission Electron Microscopy (TEM) showed particles in the range of ~25 to 50nm confirming the result obtained by XRD.

KEYWORDS

Phase-pure YAG;
Sol-gel process;
Nd doping;
Cell parameter.

INTRODUCTION

$Y_3Al_5O_{12,}$ Yttrium Aluminum Garnet (YAG) is the most widely used host material for lasers. And Neodymium is a very important four level lasing material due to its certain properties. Synthesis of Nd:YAG by solid-state reaction involves high temperature treatment (1400^0-1600^0C) and does not yield phase pure product. Some intermediate metastable phases such as $Y_4Al_2O_9$ (YAM), hexagonal $YAlO_3$ and orthorhombic $YAlO_3$ are always associated with the cubic garnet structure of YAG[1]. So for the synthesis of phase pure YAG wet chemical routes are more in practice such as sol-gel process[2, 3] and co-precipitation[4]. Sol-gel process is a relatively simple process and easier to maintain the homogeneity of the contents throughout the process.

Synthesis of phase pure YAG and Nd:YAG is reported by a sol-gel process using nitrate precursors and citric acid as the complexing agent. Citric acid was chosen for its ability to complex all the metal cations to form a homogeneous matrix that will finally lead to phase purity of the final product.

EXPERIMENTAL

$Y(NO_3)_3.6H_2O$ (99.9% purity Alfa Aesar), $Nd(NO_3)_3.6H_2O$ (99.9% purity Alfa Aesar), $Al(NO_3)_3.9H_2O$ (99.9% purity Alfa Aesar) were the metal precursors and Citric acid anhydrous (99.5+% purity Alfa Aesar) the complexing agent. The metal precursors were taken in the stoitiometry of Y_3Al_5 and $Y_{2.94}Nd_{0.06}Al_5$ for 0 and 2 at.% Nd^{3+} respectively. The total cation to citric acid was taken in the ratio of 1:1, sufficient to complex all the metal ions. The nitrate-citrate sol was ultrasonically stirred to dissolve all the solid contents. The sol turned into gel at 80^0C in 16hrs. This gel was treated at 110^0C till complete drying. The porous brown precursor powders were obtained which on calcination at different temperatures up to 900^0C led to phase formation of YAG and Nd:YAG.

Thermo-Gravimetric Analysis (TGA) of the precursor was carried out in air at a heating rate of 10^{0}C/min from room temperature to 1300^{0}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 with the help of Philips X-Ray Diffractometer, PW 3020. Transmission Electron Microscopy (TEM) was done on FEI Philips Morgagni 268 by preparing samples on copper grids.

RESULTS AND DISCUSSION

TGA of the precursor is shown in Figure 1. The strong exotherm at 421.46^{0}C along with weight loss depicted by TGA corresponds to decomposition of the citrate network. Maximum weight loss of ~60% took place up to ~600^{0}C and beyond 900^{0}C the weight loss was negligible.

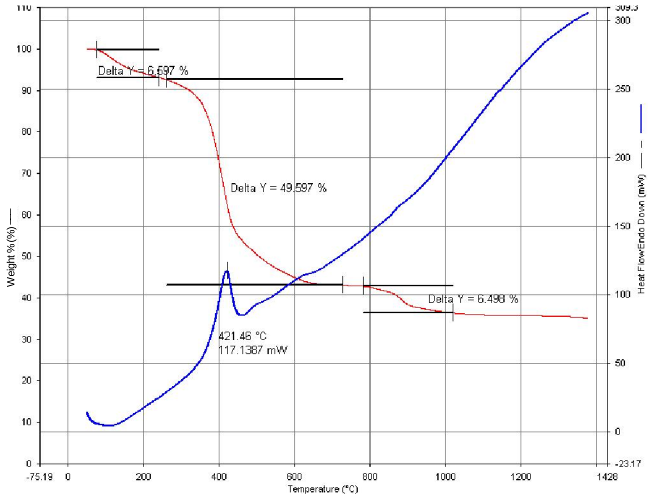

Figure 1 : TGA of YAG precursor

FTIR spectra of YAG precursor treated from 150^{0}C to 900^{0}C is shown in Figure 2. In the spectrum of the precursor at 150^{0}C there was no peaks in the M-O region, the bands at ~ 1562cm^{-1} and ~ 1384cm^{-1} can be assigned to the ionized carboxylates and carbonates resulting from the rupture of citrate network[5] and intensities of these peaks reduced significantly at 500^{0}C along with a broad band in the M-O region. The decrease in intensity of these bands with increase in calcination temperature confirms the decomposition of citrate network consistent with the sharp weight loss observed from TGA. At 700^{0}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^{0}C, the broad band in the region of 800-400cm^{-1} is replaced by several peaks at 784, 719, 688, 566, 511, 455 and 428 cm^{-1} which may be attributed to the M-O vibrations in YAG[6]. FTIR of Nd:YAG precursor treated at 900^{0}C for 2hrs showed slight shifts towards lower wavenumber. This implies that the dopant occupies the lattice positions in the cubic structure[7].

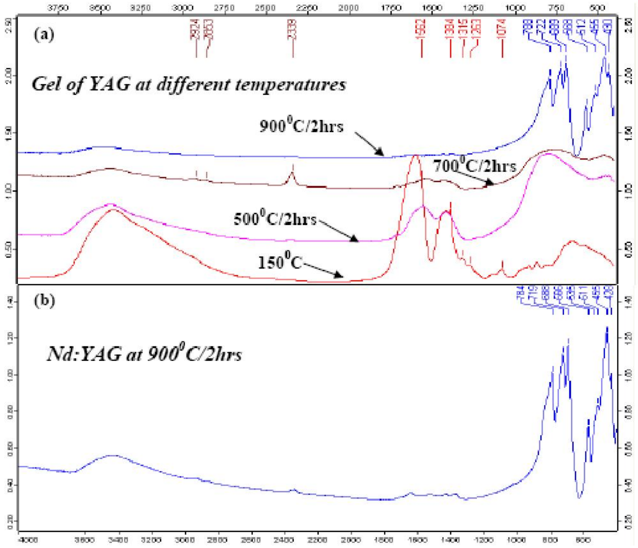

Figure 2 : FTIR of (a) YAG precursor at different temperatures (b) Nd:YAG precursor at 900^{0}C for 2hrs

Powder XRD of YAG and Nd:YAG calcined at 900^{0}C for 2hrs is shown in Figure 3. Both the powders showed the characteristic peaks of YAG as given in JCPDS 33-40. As shown in the figure there is no extra peak on doping Nd^{3+} in YAG. The only difference is in the cell parameter *a*, values of these powders. The cell parameters of YAG and Nd:YAG were calculated with the help of diffraction angles and interplanar spacing from the XRD data. For YAG it was 12.010 Å (value given in JCPDS 33-40 is 12.008 Å) and for Nd:YAG it was 12.025 Å. This is because Nd^{3+} is larger than Y^{3+}, when it replaces the latter from its lattice sites cell parameter also increases. Further high phase purity can be evidenced by the absence of any extra peak in the XRD graphs.

Particle size was calculated using Scherrer's equation[8]

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

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 primary particle size of the samples was ~ 25nm. TEM pictures of YAG and Nd:YAG nanopowders are shown in Figure 4. The particles seem to be weakly agglomerated as shown in the pictures, but they are uniform in size and shape in the size range of 25-50nm.

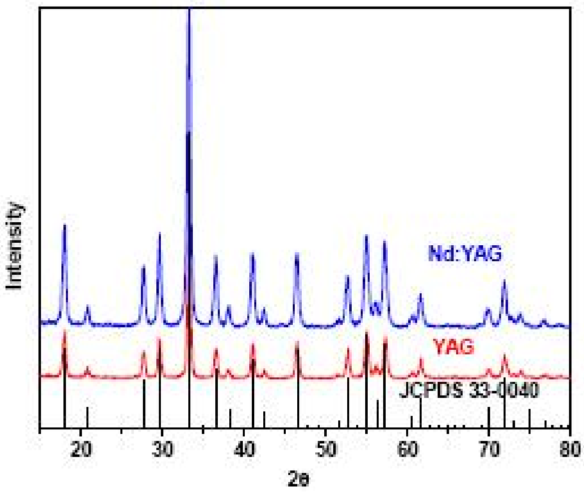

Figure 3 : XRD of phase pure YAG and Nd:YAG

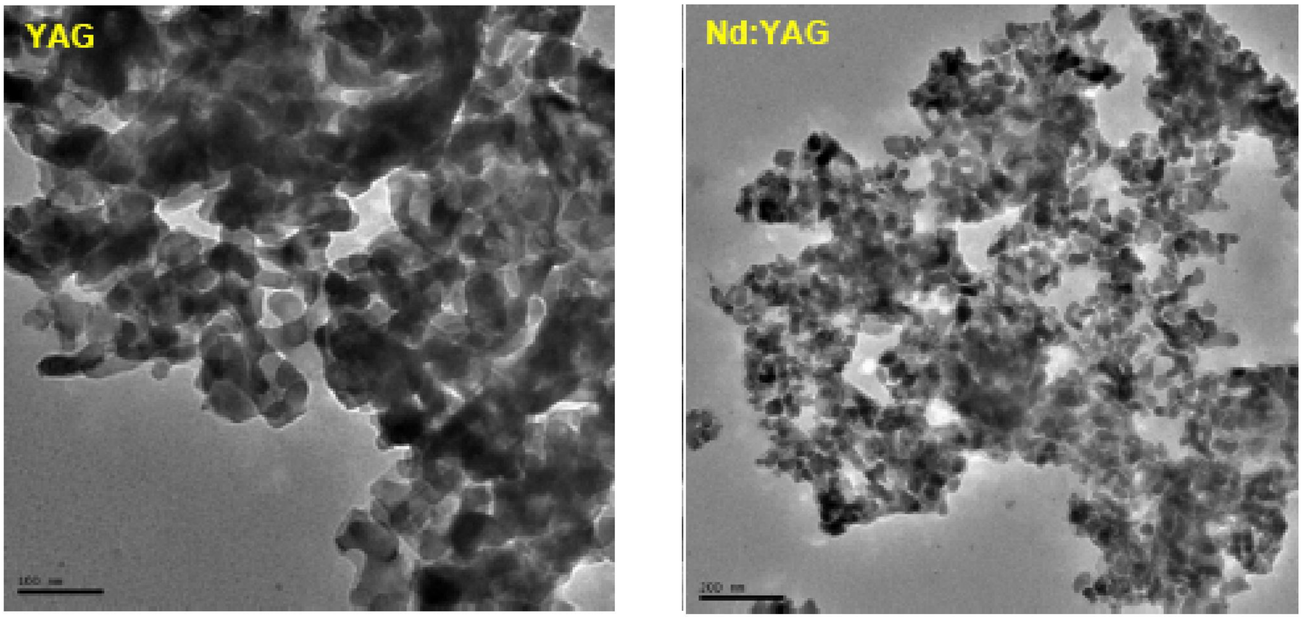

Figure 4 : TEM of 0 at% and 2 at% doped YAG nanopowders

CONCLUSION

Phase pure YAG and Nd:YAG were synthesized by nitrate-citrate sol-gel process. Phase purity was not affected on doping Nd^{3+} in YAG. This fact was confirmed by FTIR and XRD techniques. Citric acid is a very good complexing agent for the synthesis of phase pure Nd:YAG nanopowder. This sol-gel is simple and processing temperatures involved are relatively lower than other synthesis processes.

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