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Improved optical properties in nanocrystalline Ce:YGG garnets via normal and reverse strike co-precipitation method

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ABSTRACT

There is a difference in the growth of nanoparticles based on the environment in which nucleation occurs as is observed by changing the order of reactant being added to the precipitant present in excess called the normal strike and reverse strike method. The effect of particle size on optical properties of Ce:YGG (Ce doped yttrium gallium garnet) obtained via normal and reverse strike synthesis has been investigated. The normal strike route led to smaller particle size, good chemical homogeneity as well as significant improvement in photoluminescence properties compared to the reverse strike route. A comparative study of Ce:YGG nanoparticles, synthesized via the two different methods and their optical properties are discussed. There is an enhancement in the photoluminescence efficiency in nanoparticles obtained by the normal strike method mainly due to homogeneous distribution of active ions in the host which is essential to avoid quenching.

1. Introduction

Rare earth based oxides crystallizing in the garnet structure have been of interest as phosphors [1]. The size reduction of these phosphors is an effective tool to improve the efficiency of the optical properties of the garnets. Yttrium Aluminum Garnet (YAG) having formula $Y_3Al_5O_{12}$, possesses good optical properties as well as chemical stability. Apte et al. [2] have attempted the synthesis of YAG powder by normal and reverse strike precipitation. However, they were successful in synthesizing YAG only via the reverse strike (RS) route while normal strike (NS) route led to secondary phases. While Chiang et al. [3] have synthesized Ce:YAG via both RS and NS by choosing appropriate and different sources for aluminum. Yttrium gallium garnet (YGG) is also an interesting garnet with appropriate thermal and spectral properties [4]. It is a phosphor host and is normally synthesized via solid state reaction at high temperature (> 1350 °C). The process needs extensive ball milling and lengthy high temperature treatment with flux which generally introduces additional impurities and defects. YGG particles have also been produced by other techniques [5–7]. In this work, we have optimized a co-precipitation route for the synthesis of homogenously dispersed Ce-doped yttrium gallium garnet (YGG:Ce) which is an important luminescent material [8]. This is the first report of a comparative study of Ce:YGG using the normal strike method and by the reverse strike method. The effect of particle size on photoluminescence of the YGG:Ce phases has been discussed.

2. Material and methods

Sample preparation: Yttrium oxide (99.99%), gallium oxide (99.99%) and cerium oxide (99.99%) were dissolved in 2 M HNO_3 and stirred for 2 h at 80–90 °C. A solution of ammonium hydrogen carbonate (AHC, 2 M) was used as the precipitant. In **normal strike (NS)** the precipitant solution was added slowly into a mixed solution of cations to obtain the precipitate, and in **reverse strike (RS)** co-precipitation process, mixed cation solution was added slowly into the precipitant solution. After aging for 1 h, the suspension was filtered, and was washed several times with distilled water and absolute alcohol (to remove NO_3^- and NH_4^+ ions) and dried in oven. The precursor powder was then calcined at 1000 °C for 2 h to get phase pure Ce:YGG.

Characterization: X-ray studies were carried out on a Bruker D-8 Advance X-ray diffractometer using Ni filtered CuKα radiation collected in the 2Θ range of 20–70°. A step size of 0.02° and a step time of 2 s/ step were used. The Rietveld refinement was carried out using the TOPAZ software. The crystallite size was obtained by Scherrer's method. IR spectra were recorded on a Bruker Vector-22 spectrometer. SEM–EDAX studies were carried out on a Zeiss EVO40 scanning electron microscope. Diffuse reflectance spectra were obtained using a Perkin Elmer LAMBDA

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1050 spectrometer. A Fluoromax 4 Horiba spectrometer was used to obtain the photoluminescence data.

3. Results and discussion

In the co-precipitation method solubility product plays a major role, which directly depends on pH and needs to be controlled to maintain stoichiometry and particle size. In normal strike route, initially the pH is highly acidic which becomes basic by the addition of precipitant. Ga hydroxide precipitates at pH 4 while Y precipitates at higher pH. In the normal strike route initial pH is low which favors precipitation of Ga, resulting in primary nuclei and remain small as the rise in pH stops further precipitation of Ga. Y starts precipitating over the Ga nuclei till stable stoichiometry is reached. This indirectly leads to control the overall particle size of YGG.

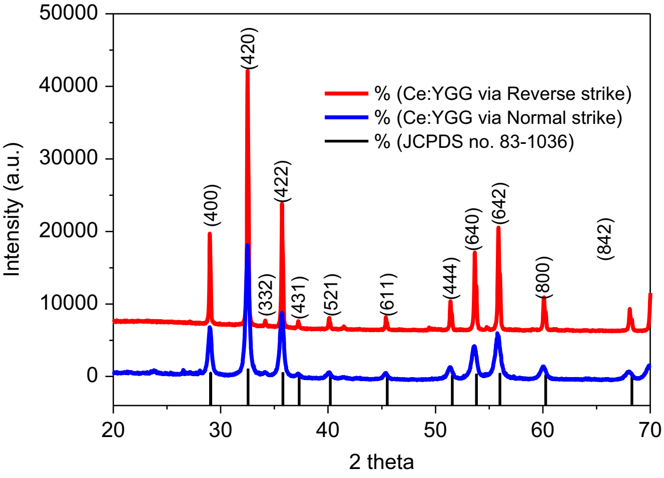

Fig. 1. (a) XRD of Ce:YGG synthesized via RS and NS, Rietveld refinement of (b) RS (c) NS.

X-ray diffraction studies: Fig. 1 shows the XRD patterns of YGG nanopowders synthesized by normal strike (900 °C for 2 h) and reverse strike (1000 °C). Comparing the XRD result of samples obtained by NS and RS routes, the NS route leads to pure garnet phase at 900 °C; however, the RS precursor was converted to YGG phase by calcining at 1000 °C for 2 h. All the reflections were in agreement with those of the reported YGG crystal structure (JCPDS no. 83-1036) corresponding to the cubic Ia3d space group. We observed that line broadening of reflections are comparatively more pronounced in the oxide obtained by the normal than the reverse strike route. This indicates smaller crystallite size which may be ascribed to reasons as mentioned above.

Rietveld refinement (Fig. S1) of the powder X-ray diffraction data of $Y_{2.94}Ce_{0.06}Ga_5O_{12}$ shows close match of observed and calculated patterns. Lattice parameters obtained via both routes are $a = 12.3461(8)$ Å (normal Strike) and 12.3096(6) Å (reverse Strike). We observed a slight shift in the lattice parameter which is due to the variation of crystallite size, as had already been discussed earlier [9]. With decrease in particle size there is also a shift of absorption bands in the Fourier Transform Infrared Spectroscopy (FTIR) spectra (toward lower wavenumber) (Fig. S2) along with decrease in intensity, which has been observed earlier by Lukowiak et al. [10].

Scanning Electron Microscopy (SEM) and High Resolution Transmission Electron Microscopy (HRTEM) studies: Fig. 2(a) and (b) shows SEM images of the samples synthesized by NS as well as for RS route. Micrographs show aggregation of particles with spherical morphology and relatively uniform particle size distribution.

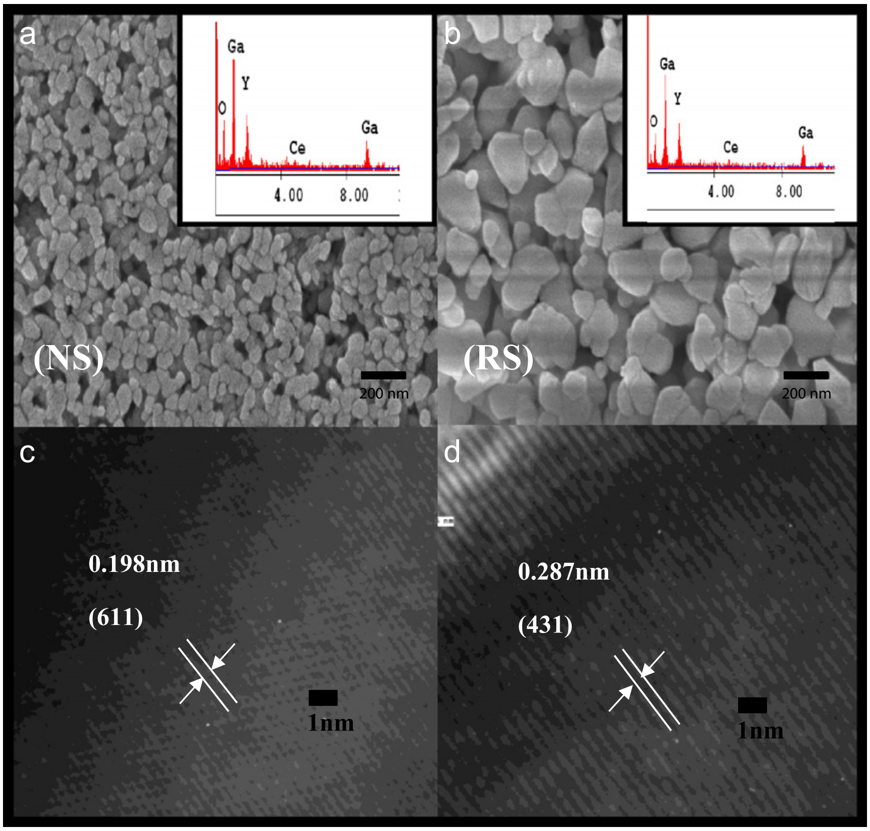

Fig. 2. (a) SEM images of Ce:YGG prepared by (a) RS and (b) NS strike co-precipitation route with EDAX in their insets and HRTEM micrographs (c) NS (d) RS.