

Low Temperature Synthesis and Photoluminescence Properties of Tb Doped YAlO₃ Nanoparticles

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Abstract— We have synthesized Tb doped YAlO₃ nanoparticles through combustion synthesis utilizing mixture of equimolar citric-ammonium nitrate as the fuel at temperatures as low as 400 °C. Phase purity of the synthesized materials is confirmed through powder x-ray diffraction. Interestingly, Tb doped samples crystallize in the orthogon system at as low as 400 °C, the lattice parameter increases owing to the increase in the ionic radii of the doped Tb atoms as compared to the parent Y atoms. The optical band gap of the doped sample reduces from 4.31 eV for undoped to 4.10 eV in case of 5% Tb doped bulk sample. Further we observe significantly lowering in bandgap to 3.75 eV in case of the same nanoparticles. We demonstrate that 2.5% and 5% Tb doped samples exhibit excellent photoluminescence properties and can be tuned to emit white light under appropriate excitation.

Keywords— Perovskites, Garnet, YAP, photoluminescence, combustion synthesis.

I. INTRODUCTION

Yttrium aluminium perovskite YAlO₃ (YAP) offers suitable host lattices for activation by rare earths. Tb plays an important role and YAP: Tb being luminescent find applications as phosphors in display applications such as display panels with low-energy excitation sources, solar energy converters, optical amplifiers and thermos luminescent dosimeters [1-5]. YAP is mainly synthesized by solid-state reaction methods starting with mechanical mixtures of oxides or oxide precursors (usually carbonates and oxalates) at temperatures above 1500 °C, up to 1800 °C [7]. Also in YAP synthesis, lot of other low energy consuming chemical routes [8] are emerging co-precipitation [9], sol-gel [10], hydrothermal [11], combustion synthesis [12, 13] or modified polymeric precursors [14]. The main aim of the present work is to establish lower temperature synthesis of rare earth doped YAP and to evaluate the synthesized samples for the photoluminescence applications.

II. EXPERIMENTAL SECTION

Different Tb concentration doped YAP samples were prepared by combustion method using the fuels Citric Acid and ammonium nitrate.

For synthesis of YAP: Tb, the starting materials were yttrium nitrate $Y(NO_3)_3 \cdot 6H_2O$ (Sigma-Aldrich, 99.9%), terbium nitrate $(Tb(NO_3)_3 \cdot 6H_2O, 99.5\%)$, aluminium nitrate $Al(NO_3)_3 \cdot 9H_2O$ (Alfa Aesar.), Citric Acid $C_6H_8O_7$ (Merck, p.a) and ammonium nitrate NH_4NO_3 (Merck, p.a). The precursors are weighed in stoichiometric proportions and dissolved in 20 ml of distilled water. The aqueous solution was stirred & heated on a hot plate at 80 °C for 5 hours to obtain transparent gel. The resulting gel in the porcelain dish is kept inside a muffle furnace at 400 °C. The mixture gets ignited and leaves out a foamy product. This was hand milled and taken for characterization. Three samples of Tb:YAP of varying doping concentrations - 1%, 2.5%, and 5% were prepared. The structure of all the samples were characterized by a powder X-ray diffractometer collected on the PANalytical X'pert diffractometer. Diffuse reflectance data was collected on LabIndia UV 3092 dual beam UV-Vis spectrophotometer equipped with integrated sphere to collect diffuse reflectance data on powdered sample between 200 to 900nm. SEM images and EDAX are recorded on JEOL JCM 6000Plus electron microscope. Horiba Fluoromax was used to collect the photoluminescence spectra on powdered samples. FTIR spectra was collected on Perkin Elmer Frontier Spectrometer by dispersing sample in KBr.

III. RESULTS AND DISCUSSION

A. X-ray Diffraction

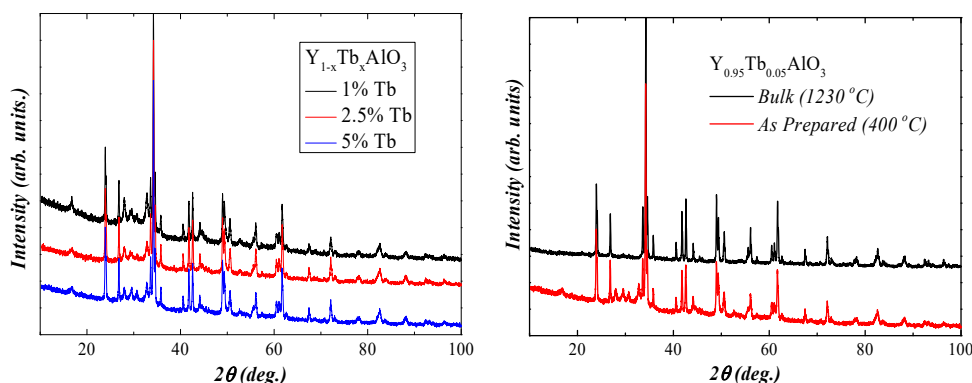


Figure 1: X-ray diffraction pattern for the Tb doped YAP nanoparticles

Hexagonal phase of YAP crystallizes in $P6_3/mmc$ space group with lattice parameter of $a=b=3.679$, $c=10.496$, cell volume around 123. The orthogonal YAP on other hand crystallize in $Pbmn$ space group with cell parameters $a= 5.180$, $b= 5.329$, $c = 7.371$ and volume around 203.51. With optimized fuel to metal nitrate ratio, we could initially obtain orthogonal phase dominant YAP at low temperatures of 400 °C. The x-ray diffraction pattern for the Tb doped $YAlO_3$ nanoparticles through combustion synthesis utilizing mixture of equimolar citric-ammonium nitrate are shown in **Error! Reference source not found.** (a). 1%Tb had secondary hexagonal phase and upon doping with higher Tb the secondary phase decreased, and the 5% doped sample showed around 98% of orthogonal phase. One of these samples, i.e., 5% Tb doped YAP ($Y_{0.95}Tb_{0.05}AlO_3$) is heat treated at higher temperature of 1230 °C to compare the performance with that of the as prepared sample (**Error! Reference source not found.** (b)).

Owing to the low crystallinity the crystallite size was calculated for the as prepared samples using Scherrer formula, $d = \frac{K\lambda}{\beta \cos \theta}$. Where d is the average crystallite size, K the dimensionless shape factor, β the full width half maxima of the peak and θ the peak position. The shape constant is considered as 0.94 by assuming the spherical shape of the nanoparticles. Accordingly, the 5% doped showed average crystallite size of 35nm, 2.5% doped samples had 45nm and 1% doped are having 42nm.

B. FTIR

To understand the chemical bonds, functionalized groups on the surface of the synthesised materials we probe the FTIR spectra in the wavelength range of 4000 to 400 cm^{-1} . As prepared samples show similar peak shapes and hence for clarity FTIR spectra of only as prepared and bulk 5% Tb doped samples is displayed in **Error! Reference source not found.** The broad peak centred around 3432 cm^{-1} signify the O-H stretching modes which may be due to the absorbed hydroxyl ions, it is notable that these are predominant in as prepared samples

indicating higher surface activity for hydroxyl groups. The peaks observed in the range 2970 cm^{-1} and 2930 cm^{-1} are from alkane C-H stretching modes. Weak 2345 cm^{-1} peaks are representation of the O=C=O modes of residual carbon. Peaks corresponding to the C=C alkene or conjugated alkene stretching appear at 1634 and 679 cm^{-1} . Peaks corresponding to carbon bonding are very weak and signify lower carbon residual in both the samples, meaning most of the carbon from the fuel being eliminated effectively during combustion. 679 cm^{-1} peaks can be assigned to C-Cl vibrational modes. Apart from these peaks the as prepared sample has peaks around 1527 cm^{-1} corresponding to N-O stretching, broader peak around 900 cm^{-1} corresponding to C-H vibrations, sharper peaks below 650 cm^{-1} are due to C-Cl or C-Br alkyl halides stretching. These indicate that there may be small amount of residual nitrogen, carboxyl group that may be remaining in case of as prepared samples as compared with bulk samples.

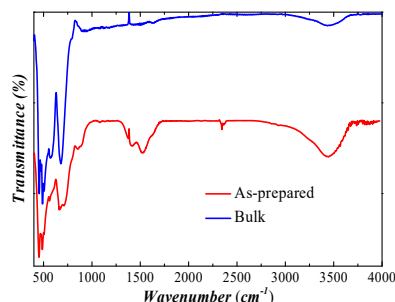


Figure 2: FTIR spectroscopy of the 5% Tb doped YAP samples (a) as prepared and (b) bulk

C. SEM

Morphology of the synthesised samples are probed using scanning electron microscopy, the same are tabulated in Figure 3. Most of the sample looks to be agglomerate owing to high surface to volume ratio and high reactivity of the surface. The 5% Tb doped bulk samples exhibits large grain sizes that can be assigned to higher crystalline state of these samples, due to treatment at elevated temperatures.

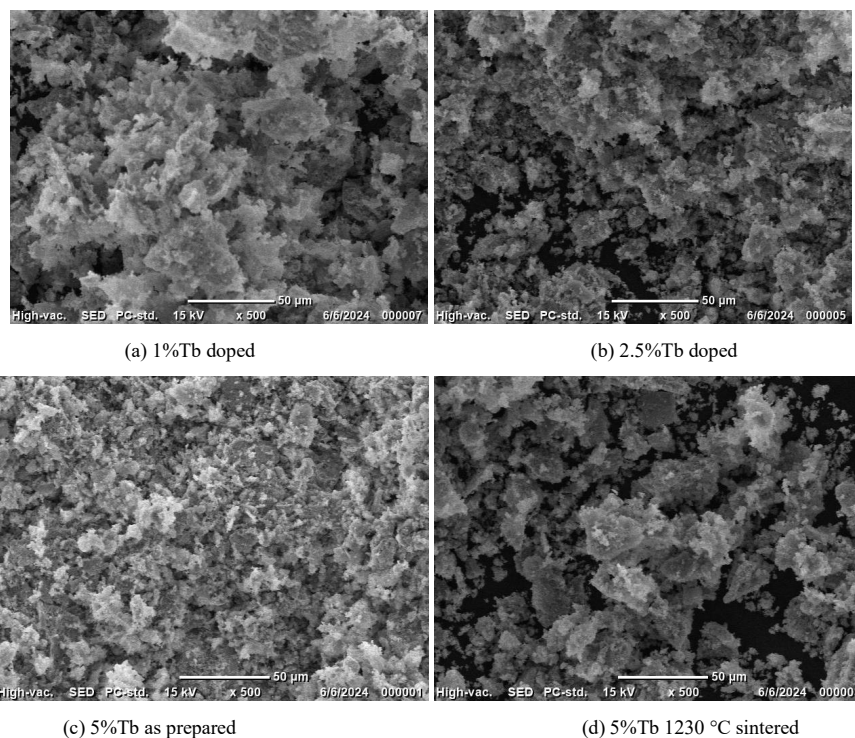


Figure 3: SEM of as prepared samples with different doping percentage of Tb.

D. UV Vis Spectrometer

The reflectance spectra under the UV-Visible radiation is shown in **Error! Reference source not found.** (a). We derive Kubelka-Munk plot from the diffuse reflectance data (**Error! Reference source not found.** (b)) using the function: $F(R_{\infty}) = \frac{K}{S} = \frac{(1-R_{\infty})^2}{R_{\infty}}$. The band gap obtained from these plots are 3.65eV, 3.85eV, 3.76eV for as prepared samples with 1%, 2.5% and 5% Tb doping respectively. The band gap for 5% doped bulk sample is found to be around 4.10 eV as compared to the expected value of 4.31 eV for $YAlO_3$. From these results we can conclude that nanoparticles result in significant decrease in the band gap so is the doping of Tb in to the Y lattice.

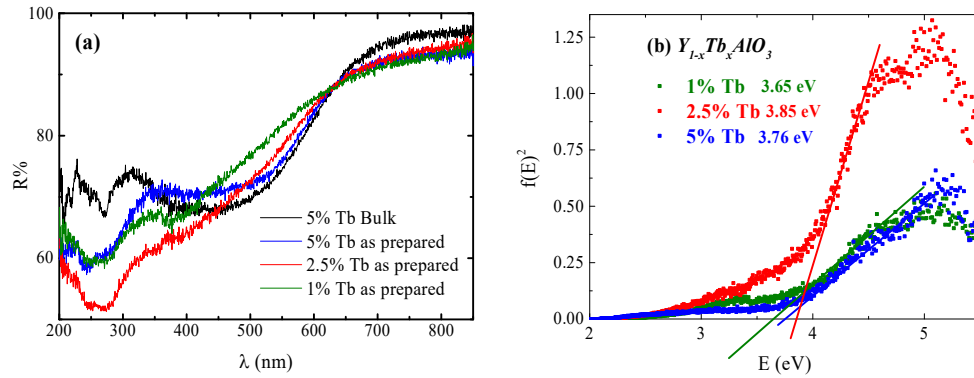


Figure 4: UV-Vis Reflectance spectra data and the Kubelka-Munk plot.

E. Photoluminescence

The photoluminescence spectra for the 5% Tb doped samples is displayed in Figure 5, we observe stronger PL peaks around 530 nm under excitation wavelength of 385 nm, under excitation of 270 nm we observe peaks around three region with equal intensity, CIE curve is probed for this curve and it shows potential emission of white light under 270 nm excitation and green light emission with 385 nm excitation. Hence, we confirm that this material can emit green or white light based on the energy of excitation.

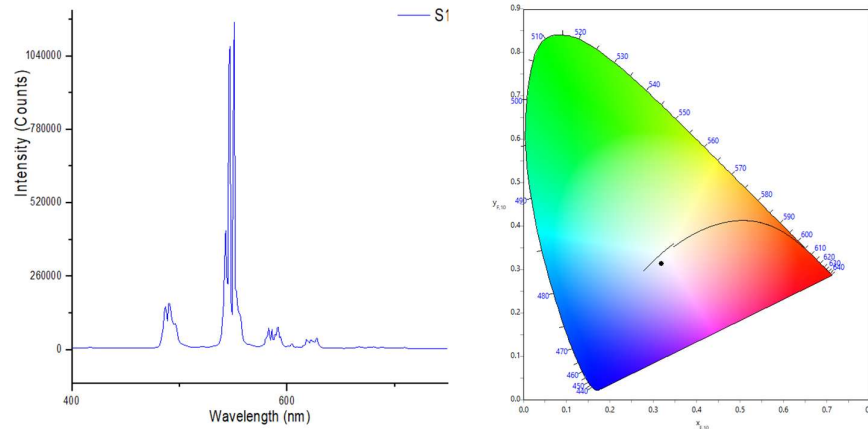


Figure 5: Photoluminescence spectra for 5%Tb doped sample

IV. CONCLUSION

Yttrium aluminium perovskites doped with Tb were synthesized at a very low temperature of 400 °C. The sample with 1%, 2.5 % and 5% Tb doped YAP crystallized in orthogonal system. The crystallite size for these samples was deduced to be 42 nm, 45 nm and 35 nm respectively. The optical band gap of the doped sample reduces from 4.31 eV (for pure $YAlO_3$) to 4.10 eV in case of 5% Tb doped bulk and significantly lowered in

case of nanoparticles with band gap of 3.76 eV. We demonstrate that 5% Tb doped samples exhibit excellent photoluminescence properties and can be tuned to emit white light.

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