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RESEARCH ARTICLE

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YAG:Ag nanophosphors – synthesis and characterization

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ABSTRACT

Yttrium Aluminium Garnet ($Y_3Al_5O_{12}$)-YAG and Silver (Ag) of four different mol% in YAG (0.5, 1.0, 1.5 and 2.0 mol % of Ag) – YAG:Ag were synthesized by Pechini method. The synthesized pure YAG was white in colour but the incorporation of Ag in the YAG matrix forms colour centre and turns to pink. The intensity of pink Ag doped YAG is increasing with the increase in mol% of Ag. In the present work the synthesis and the preliminary characteristics about the structure, morphology, elemental composition and optical properties were studied using X-ray diffraction (XRD), Fourier Transform Infrared (FTIR), Scanning Electron Microscopy-Energy Dispersive Spectroscopy (SEM – EDAX), Ultraviolet–visible spectroscopy (UV-Vis) and Photoluminescence spectroscopy (PL). The sharp peak in the XRD reveals the good crystalline nature of the samples. The bending and stretching vibrations of the oxygen groups associated with YAG was observed in FTIR spectra. Tube like morphology was noticed in the SEM and increase in crystallite size is also perceived in YAG:Ag. The elemental mapping by EDAX confirmed the purity of synthesised samples. UV spectra shows the absorption peaks due to Ag incorporated in the YAG matrix. The PL spectra reveals the blue and green light emitting properties of the synthesized YAG nanophosphors.

1. INTRODUCTION

Research and development of nanophosphors is a part of rapidly growing nanoscience and nanotechnology. YAG–based nanophosphors have drawn significant interest due to their excellent luminescence property, high physical stability and low synthesis cost. Doping of the rare earth metals into the host matrix demonstrate an approach to develop highly efficient and stable nanophosphors for light and display devices. Especially these phosphors have applicability in the field of colour television display, flat panel display, plasma display panels, device indicators, automobile, headlights, etc. and hence they are emerging as an important class of the optical materials [1].

Recently, *S.A. Hassanzadeh-Tabrizi et al* [2] reported cerium-doped yttrium aluminium garnet (YAG:Ce) powder that were synthesized by Pechini method. They observed pure YAG phase only after 800 ºC and the average size of the particles was about 70 nm. The photoluminescence spectrum of the crystalline YAG:Ce phosphors showed the green-yellow emission with 5d→ 4f transition as the most prominent group. Similarly green phosphor $Y_3Ga_5O_{12}$: Tb (YGG) was synthesized by *Nanfei Zhua et al* [3]. The excitation spectrum is dominated by the 4f→5d transition of Tb^{3+} at 263 nm. The strong emission peaks for the heavily doped phosphors are observed at 489 and 543 nm. *V. Tucureanu et al* [4] reported that cerium doped yttrium aluminium garnet (YAG:Ce) phosphors prepared by solid-state reaction method, particularly the sol gel and (co) precipitation methods. In addition to that the effect of co−doping with rare earth elements and the corresponding red/blue shift in the spectrum was explained in detail. It was seen that the transition from the amorphous phase to the crystalline phase appears at 800 ºC. Similarly *Manisha Upasani et al* [5] synthesized Magnesium (Mg) co-doped YAG:Ce

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phosphors by single step combustion method by mixed fuel at 500 ºC. The doping effect of Mg on the luminescence intensity of YAG:Ce was studied and the results showed that the luminescence intensity decreases significantly with the increase of Mg concentration. Three polycrystalline powders of Y–Al–O compounds, $Y_3Al_5O_{12}$ (YAG), $YAlO_3$ (YAP), $Y_4Al_2O_9$ (YAM) were reported by *Masaaki Harada et al* [6]. It was noted that all the compounds were obtained in a single phase. Thermal analysis showed that the crystallization temperatures were 900 ºC for YAG and YAM, and 1100 ºC for YAP, which was 300 ºC lower than that of sol–gel process and also reported the phase change of each compound with temperature. *Case Collins Reza T et al* [7] studied the excellent luminescence performance of yttrium aluminium garnet ($Y_3Al_5O_{12}$) phosphors as a function of Chromium (Cr^{3+}) concentration.

Yttrium aluminium garnet can be a useful matrix to dope certain rare earth elements to enhance the luminescent property of YAG. This paper reports the preparation of pure Yttrium Aluminium Garnet ($Y_3Al_5O_{12}$)-YAG and YAG:Ag by Pechini method. This may lead to differences in their optical and luminescent properties. The synthesized pure YAG was white in colour but the incorporation of Ag in the YAG matrix forms colour centre and turns to pink. The intensity of the pink is increasing with the increasing mol% of Ag. In the present work the synthesis and the preliminary characteristics about the structure, morphology, elemental composition and optical properties were studied using X-ray diffraction (XRD), Fourier Transform Infrared (FTIR), Scanning Electron Microscopy-Energy Dispersive Spectroscopy (SEM – EDAX), Ultraviolet–visible spectroscopy (UV-Vis) and Photoluminescence spectroscopy (PL).

2. EXPERIMENTAL DETAILS

Yttrium nitrate $Y(NO_3)_3.6H_2O$, aluminium nitrate $Al(NO_3)_3.9H_2O$) silver nitrate ($AgNO_3$) citric acid ($C_6H_8O_7$), ethylene glycol ($C_2H_6O_2$) and distilled water (H_2O) of high purity (99.99%) from sigma aldritch were used for the synthesis. Yttrium Aluminium Garnet ($Y_3Al_5O_{12}$) was synthesized by Pechini method which involves stirring, drying and calcination. Pure $Al(NO_3)_3.9H_2O$, $Y(NO_3)_3.6H_2O$ were used as cation source. These nitrate salts that behaves as anion were dissolved in 80 ml of distilled water and citric acid at the ratio of 1:2. These metal salts were dissolved at molar ratio, Y: Al of 3:5 respectively. This mixture was stirred until a clear solution was obtained. Ethylene glycol which acts as a polymerization agent was added into the solution. The solution was continuously stirred at 80 ºC until the gel was formed. After the

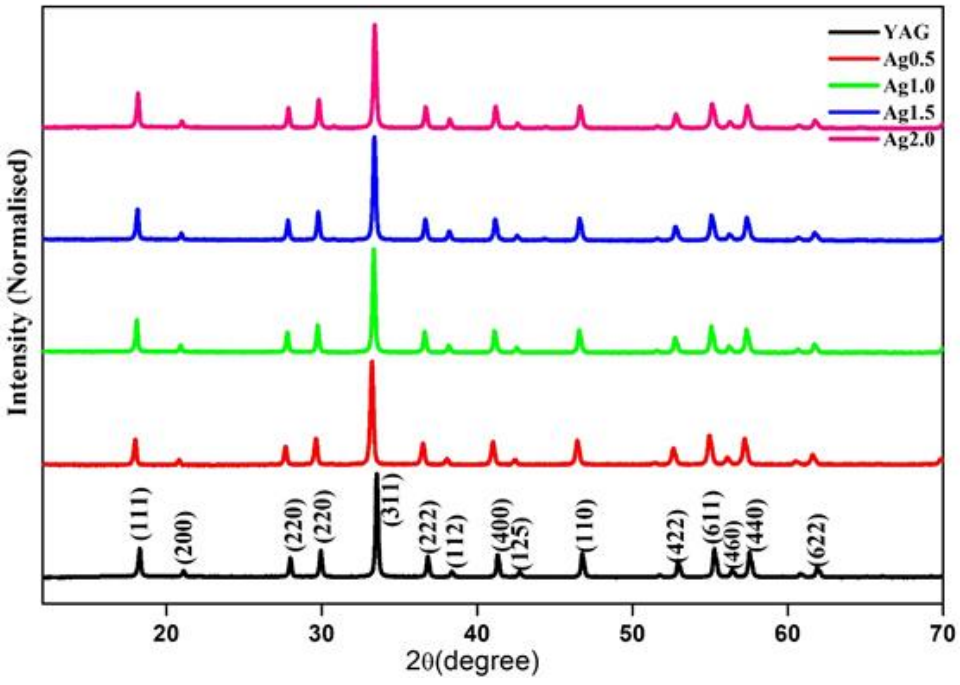

Figure 1. XRD pattern of YAG and doped YAG.

gelation, the gel was dried in oven at 100 ºC for 18 h. Then preheated for 4 h at 600 ºC. This powder was crushed and fired at 1200 ºC for 4 h and pure yttrium aluminium garnet nano powder was obtained. In the case of Ag doped-$Y_3Al_5O_{12}$, silver was added in 0.5, 1.0, 1.5 and 2.0 mol % with the cation source and stirred in 80 ml of distilled water. Similar procedure of YAG was followed to synthesis Ag doped YAG. In this work, Ag0.5, Ag1.0, Ag1.5 and Ag2.0 represents the 0.5, 1.0, 1.5 and 2.0 mol % of Ag in YAG matrix respectively. X-ray diffractometer (Model Panalytical) was employed using Cu-K_α radiation source operating at 45 kV and 40 mA. Radial scans were recorded) from 10° to 70°. FTIR spectra of YAG and Ag doped YAG nano particles was observed by FTIR spectrometer (Model: Nicolet 6700) having scan range from 400 to 4000 cm^{-1}. The spectra were observed in total reflectance mode at scanning rate of 8 cm^{-1}. Field emission gun scanning electron microscope (FEG-SEM) sigma-3 was used to investigate morphology of nanoparticles while energy dispersive spectroscopic analysis was performed by Oxford EDS detector coupled with FESEM (MIRA Tescan 3) at 20 keV energy for elemental analysis. The UV-visible absorption spectra of pure YAG and Ag doped YAG were recorded using V-670 spectrophotometer (double beam instrument) from 400 to 800 nm. Spectrofluorophotometer - Shimadzu RF-5301PC series is used to investigate the photoluminescence property of synthesised nano particles.

3. RESULTS AND DISCUSSION

3.1. Structural Properties

3.1.1. X-ray Diffraction (XRD)

X-ray diffraction (XRD) was performed to identify the crystalline phases in the synthesized nano phosphor powder. The XRD pattern is shown in figure 1. The sharp and well-defined peaks indicate the perfect crystalline nature of the YAG and Ag doped samples. The recorded pattern is well matched with the reported results of YAG phase (JCPDS: 33-0040). There is no sign of any impurity phase formation like yttrium aluminium perovskite and yttrium aluminium monoclinic. This result indicates that 1200 ˚C is the exact temperature to synthesis YAG materials. The addition of Ag in YAG does not show major changes in the XRD peaks except a slight shift towards a lower angle side. This suggests that there is expansion of YAG matrix after the addition of Ag.

Scherer's equation was used to calculate the crystallite mean size (D), [8]

$$D = \frac{k\lambda}{\beta cos\theta} \quad (1)$$

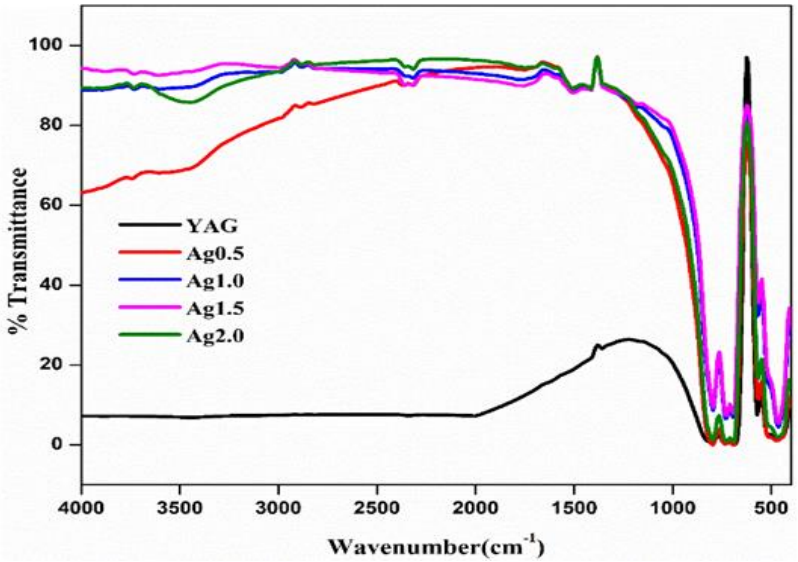

Figure 2. FTIR spectra of YAG and Ag doped YAG.

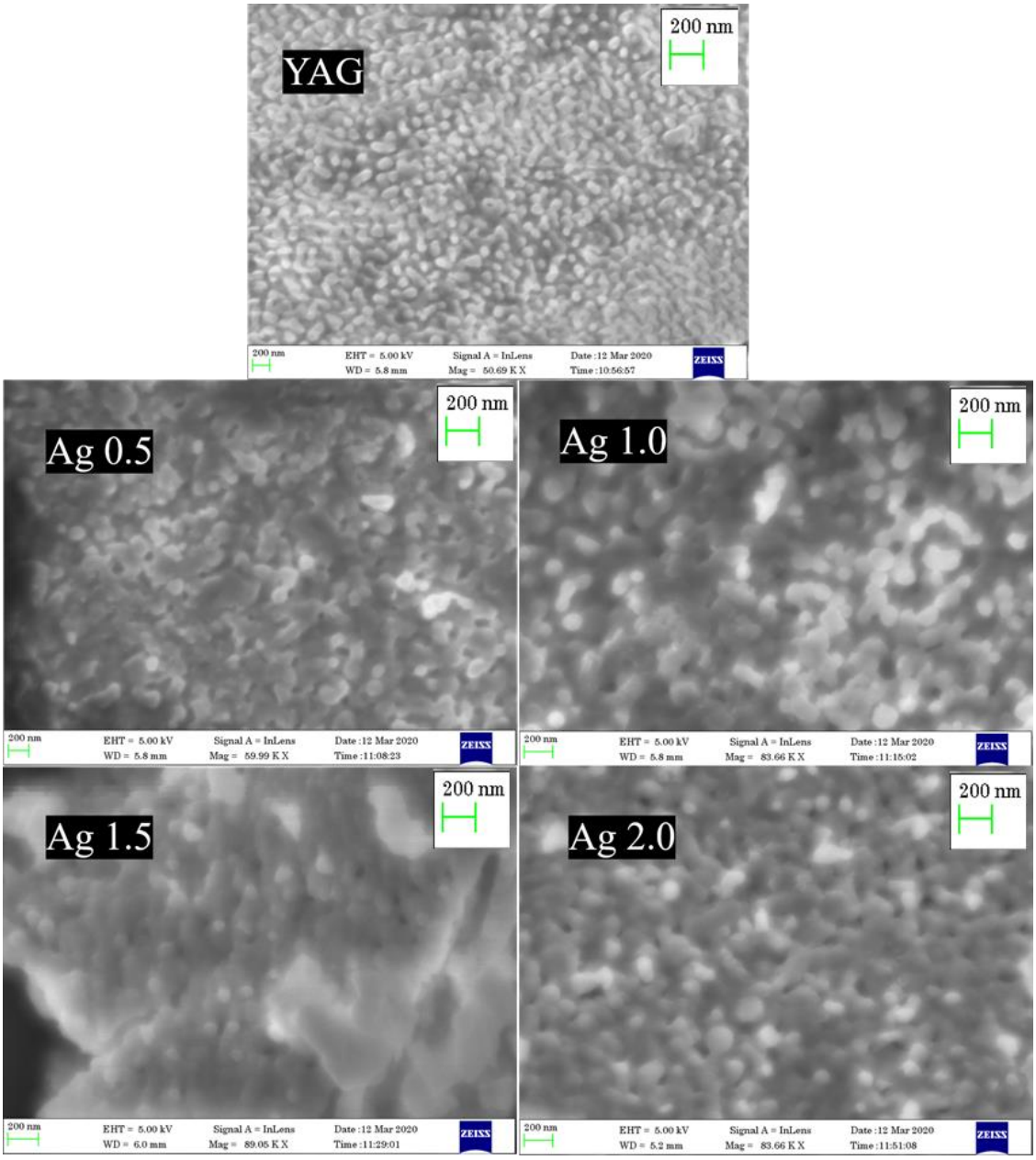

Figure 3. SEM micrograph of YAG and Ag doped YAG.

where k is dimensionless shape factor, λ (1.5418 Å) is x-ray wavelength and β is the line broadening at full width at half maximum of diffraction peak intensity. The crystallite mean size was calculated for all the samples using major intense diffraction peaks, resulting to 81nm for YAG. Whereas mean values of crystallite size calculated for the Ag doped YAG samples were 83 nm, 96 nm, 106 nm

Table 1. Elemental mapping results.

Element	Weight%	Atomic%	Element	Weight%	Atomic%
YAG			**Ag 1.5**		
O K	35.50	63.71	**C K**	36.44	56.29
Al K	20.88	22.21	**O K**	26.07	30.23
Y L	43.62	14.08	**Al K**	11.83	8.13
			Y L	25.17	5.26
			Ag L	0.50	0.09
Total	**100.00**	**100.00**	**Total**	**100.00**	**100.00**

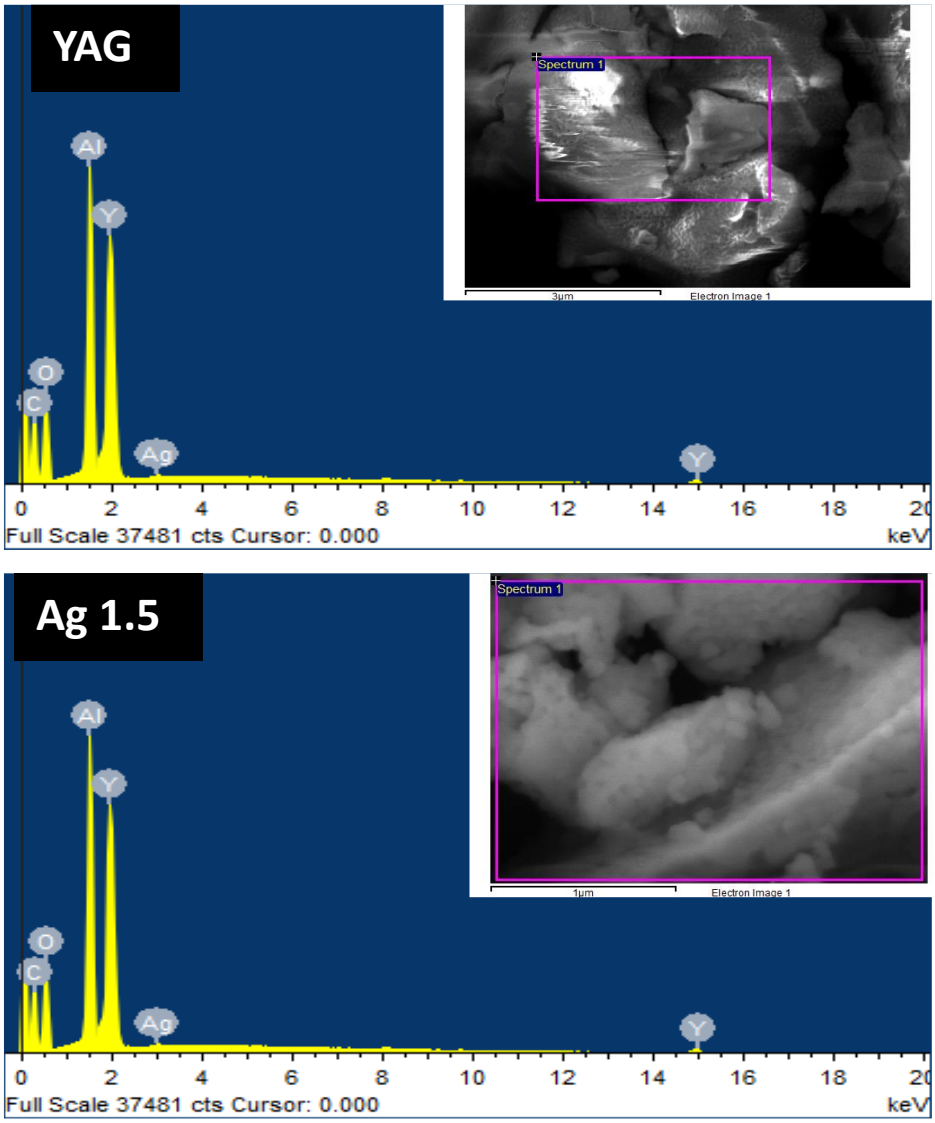

Figure 4. Elemental mapping of YAG and Ag1.5.

and 122 nm for Ag0.5, Ag1.0, Ag1.5 and Ag 2.0 respectively. The increase in particle size coexist with the lattice expansion.

3.1.2. Fourier transform Infrared Spectra (FT-IR)

FTIR spectra of YAG and doped samples are shown in figure 2. The peaks 3718-3433 cm^{-1} represents the vibrations of absorbed water H_2O which has O-H stretching vibrations [9]. The peaks from 2954 cm^{-1} to 2846 cm^{-1} represents the C-H (CH_2+CH_3) symmetrical and asymmetric stretching vibration [10]. The peaks at 1789 and 1435 cm^{-1} represents the COOH vibrations. The peaks at 800-400 cm^{-1} represents the metal oxygen [M-O] vibrations. Peaks at 763 cm^{-1}, 725 cm^{-1}, 692 cm^{-1} are metal oxygen vibrations corresponds to Al-O,Y-O,Y-O-Al stretching [11].

3.2. Morphology and elemental composition

3.2.1. Scanning Electron Microscope (SEM)

The surface micrographs are shown in figure 3 for all the prepared samples. It is obvious that all the samples are showing tube like morphology [12]. The minimum crystallite size was observed in pristine YAG and the crystallite size is increasing with Ag doping. In addition to that the melting of edges is also seen in the Ag doped samples. This may be due to higher sintering temperature [13, 14]. The bright spots in the Ag doped samples are

owing to the presence of Ag. Elemental mapping was done in YAG and Ag1.5-YAG sample and the results are shown in figure 4 and Table 1. It shows that the atomic composition is in par with the calculates values of YAG and Ag1.5 obtained from elemental analysis.

3.3. Optical properties

3.3.1. Ultraviolet - Visible spectroscopy (UV-Vis)

Ultraviolet–visible spectroscopy refers to absorption spectroscopy or reflectance spectroscopy in part of the ultraviolet and visible regions of the electromagnetic spectrum. The absorption or reflectance in the visible range directly affects the apparent color of the chemicals involved. The electronic transition of atoms and molecules occur in this region of the spectrum.

The optical absorption spectra of the pure YAG and Ag doped YAG are shown in figure 5. The absorption peak in the visible range at 420 nm is

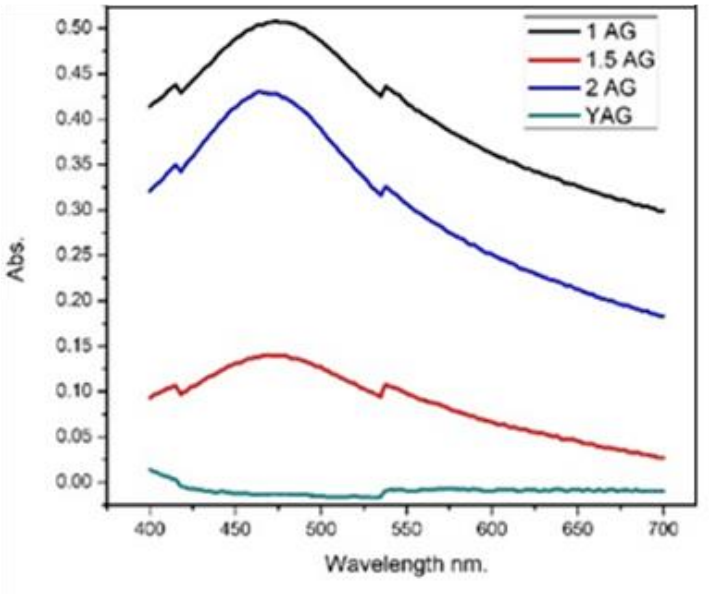

Figure 5. UV-Visible spectra of YAG and Ag doped YAG.

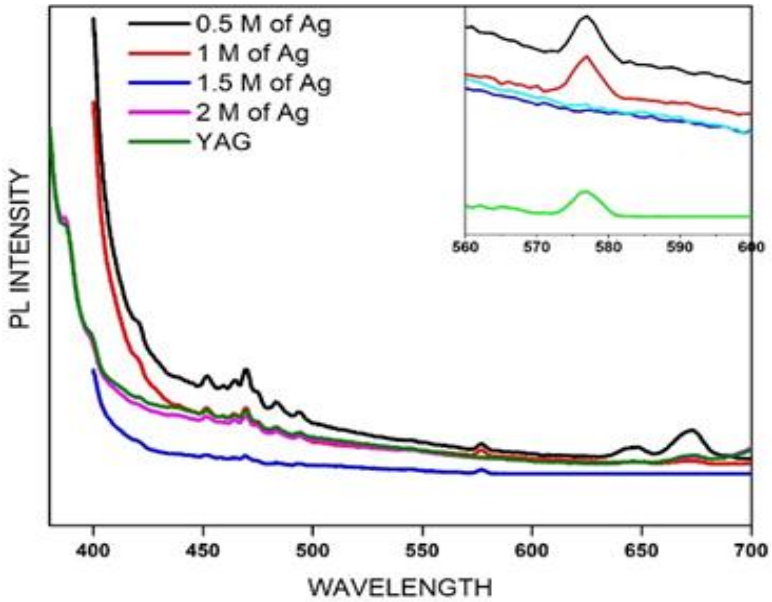

Figure 6. PL spectra of YAG and Ag doped YAG.

due to the incorporation of Ag in YAG matrix. The narrow gap between the valence and conduction band gives rise to surface plasmon resonance. The area under the absorption peaks increase as concentration of Ag in YAG increases. It can be seen that this peak exhibit blue shift [14]. On the other hand, the broad band absorption in the UV region of spectra can be attributed to the inter-band transition of electrons in silver nanoparticles [15].

3.3.2. Photoluminescence spectra (PL)

Photoluminescence spectroscopy is analytical technique that can determine quantities such as emission and excitation spectra and luminescence lifetimes. By this technique, a sample is excited by photons and the excess energy released by the sample through the emission of light can be detected and recorded for different modes, i.e., excitation, emission and luminescence decay lifetime. A spectrofluorometer is an instrument capable of recording the emission spectrum or both the excitation and emission spectra.

The PL spectra of YAG and Ag doped YAG nanophosphors are shown in figure 6. The luminescence properties of the pure and Ag-doped YAG samples were investigated and the excitation peak at 475 nm matches well with the blue light emitting properties [11]. Thus, it reveals that YAG sample can efficiently absorb the blue light. It is noted that the PL spectra were composed of one strong visible emission band positioned at about 578 nm in all the prepared YAG and Ag doped YAG nanophosphors. The strong peak observed at 578 nm in pure YAG and Ag0.5 and Ag1.0-YAG corresponds to green emission [16].

4. CONCLUSIONS

$Y_3Al_5O_{12}$ yttrium aluminium garnet nanophosphors and Ag doped YAG was prepared by Pechini method. The pure phase of YAG and cubic structure was confirmed from the XRD pattern. The peaks were indexed as per the JCPDS data. The sharp peak in the XRD reveals the good crystalline nature of the samples. Lattice expansion is indicated by the shift towards lower diffraction angle after the addition of Ag is also visible in the XRD pattern. The bending and stretching vibrations of the oxygen groups associated with YAG was observed in FTIR spectra. Tube like morphology was noticed in the SEM and increase in crystallite size is also perceived after Ag was doped in YAG matrix. The melting of grain suggested that the sintering temperature is high. The elemental mapping confirmed the purity of synthesised samples and it in accordance with the calculated values. The absorption spectra at the range of 420 nm are obtained due to incorporation of Ag in YAG matrix. The PL spectra reveals the excitation peak at 475 nm which denotes the blue light emitting properties and the strong peaks at 578 nm in pure YAG and Ag0.5-YAG and Ag1.0-YAG that corresponds to green light emission hence proving its luminescence property.

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