

Doping effect of Mg on photoluminescence properties of YAG:Ce phosphor

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Abstract - We present the investigation of Mg codoped YAG:Ce phosphors synthesized by single step combustion synthesis method by mixed fuel at 500°C. The XRD results show that YAG phase can even form at low temperature without further sintering. This temperature is much lower than that required to synthesize YAG phase via the solid state reaction method. The doping effect of Mg on the luminescence intensity of YAG:Ce were studied. The results show that the luminescence intensity of YAG:Ce decreases significantly with the increase in concentration of Mg. The phenomenon of energy transfer was studied in detail. The CIE coordinates show slight red shift on expense of emission intensity.

Key Words: YAG:Ce, wLED, codoping, combustion synthesis

1. INTRODUCTION

Yttrium aluminum garnet ($Y_3Al_5O_{12}$, YAG) has been known as one of the most common phosphor host materials. Rare-earth-doped yttrium aluminum garnet materials have wide applications as solid state laser media and are promising phosphor candidates. Cerium (Ce) activated yttrium aluminum garnet (YAG:Ce) is a well known phosphor that can be used in many ways[1]. Presently commercial white LEDs available in market use coating of YAG:Ce phosphor on a blue LED chip. The yellow emission is intense enough to complement the residual blue light that escapes through the phosphor and produce white light. It is the most suitable phosphor that can be utilized suitably in white LED commercial market. Therefore, any improvement in the luminescence of YAG:Ce is **exceptionally valuable to raise the light efficiency** for different applications.

For the purpose of widening luminosity spectra, the emission of YAG:Ce phosphor may be tailored through the incorporation of an additional codoping element. The energy transfer from sensitizer to activator by rare earth ions has been investigated in many inorganic hosts. In contrast to single Ce doped YAG phosphor some co-doped YAG:Ce phosphors have been extensively

studied that increase the emission efficiency and broaden luminosity spectra[2]. The materials commonly used are rare earth elements, such as Pr^{3+} , Sm^{3+} , Eu^{3+} , Gd^{3+} or Tb^{3+} ions[3-5]. Conversely, few studies examine YAG:Ce phosphors co-doped with transition elements and alkali metals. In this work, we reported the effect of doping of magnesium in optimized YAG:Ce phosphors. Their structure, luminescence and energy transfer properties were investigated.

YAG phosphors are usually prepared via a solid-state reaction of yttria (Y_2O_3) and alumina (Al_2O_3). However, it produces powders of relatively large and widely varying grain sizes and contain stable intermediate phases such as yttrium aluminium perovskite (YAP; $YAlO_3$) and yttrium aluminium monoclinic (YAM; $Y_4Al_2O_9$). A high temperature of 1600 –1800°C and prolonged heating are required to obtain the pure phase, and this method also requires several hours of sintering and milling. In recent years, several wet chemical techniques such as coprecipitation method, sol-gel, combustion, hydrothermal synthesis and spray-pyrolysis synthesis were used to prepare the single phase phosphor [6]. However, they are time-consuming and involve complex procedures. Moreover, phase pure materials are not obtained in one step and prolonged annealing at temperatures around 1400°C is necessary. In contrast, the combustion method is quite simple, and the combustion reaction lasts only for a few seconds.

2. EXPERIMENTAL

In the present work, YAG:Ce have been synthesized by single step combustion synthesis (CS) with mixed fuels carried out at 500°C furnace temperature without taking recourse to any post thermal treatment. As reported in our previous paper YAG:Ce powders were synthesized and the optimal concentration of Ce in YAG have been chosen as 1mol% [7]. In optimized YAG:Ce, co-dopant Mg was introduced in various concentration at Al^{3+} site to study effect on luminescence intensity. For synthesis of YAG:Ce, the starting materials used for preparation of the phosphor were Y_2O_3 (99.90%), $Al(NO_3)_3 \cdot 9H_2O$ (99.99%), $Ce_2(CO_3)_3$ (99.99%), HNO_3 (69% GR), NH_2CONH_2 (99.99%) and $C_2H_5NO_2$ (99.99%). To study effect of codoping of Mg in the optimal concentration of Ce; $MgCl_2$ with $SiO_2 \cdot H_2O$, were added.

3. RESULTS AND DISCUSSION

The structure of the phosphor powder was characterized by X-ray diffraction patterns recorded on Philips PANalytical X'pert Pro diffractometer. PL characteristics were studied using a Hitachi F-4000 spectrofluorimeter at room temperature using 1.5 nm spectral slit widths in the range of 200–700 nm. All measurements were performed at room temperature.

Fig.1 shows the XRD pattern of the YAG:Ce (1 mol%) phosphor synthesized by CS at 500°C. An excellent match is obtained with JCPDS file 33-0040 corresponding to YAG. Pure phase formation of YAG confirms since lines corresponding to YAP, YAM or YAH were completely eliminated in this pattern.

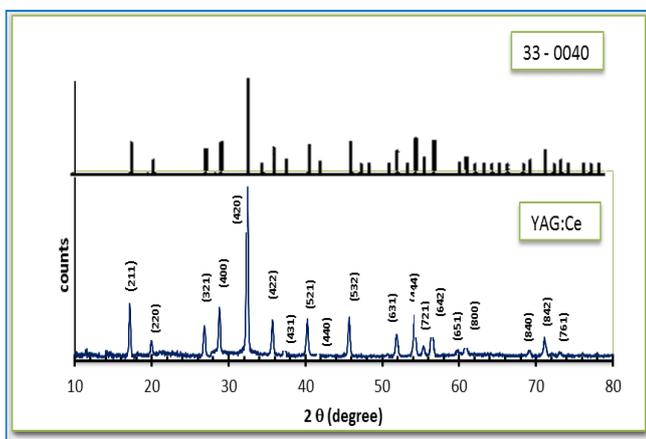
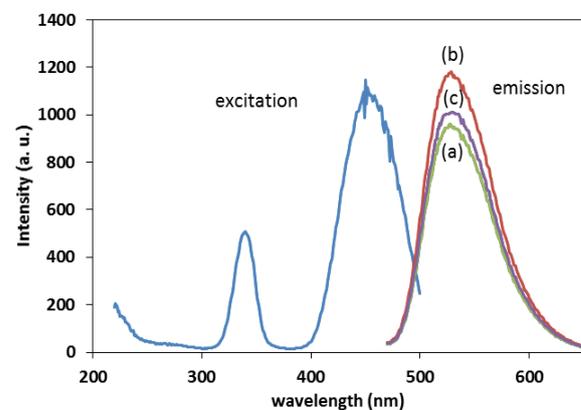


Fig. 1: XRD patterns of the YAG:Ce compared with JCPDS 33-0040.

Figure (2) shows the photoluminescence (PL) excitation and emission spectra for different Ce^{3+} concentration (0.5mol%,1mol%,1.5mol%) synthesized by combustion synthesis. The maximum intensity was achieved for about 1 mol% Ce^{3+} concentration. When Ce^{3+} amount was increased beyond this limit concentration quenching effect was observed due to the increase of intra ionic non-radiative relaxation between adjacent Ce^{3+} ions resulted in a decrease of the PL intensity. Thus the optimal concentration for Ce^{3+} has been chosen as 1 mol%. It is a well known fact that the PL excitation spectrum of YAG:Ce, sample consists of two excitation bands, one at 340 nm in the UV and the other at 460 nm in the blue region at RT. The broad band from 400 to 500 nm is most intense, which makes it possible for the phosphors to apply with blue LEDs. There is only one broad emission band located from 450 to 650 nm, which is an ideal yellow light that complements the blue light emitted by LED chip to generate white light. Ce^{3+} has a single electron in the 4f shell with $4f^1$ configuration and its excited state is $4f^05d^1$. In YAG host, Ce occurs in trivalent state by losing its two 6

s electrons and one of the 4f electrons. Due to shielding effect by outer shell electrons, the f-orbital remain non bonding where as the low lying d orbitals are sensitive to the host crystal coordinative environment. For Ce^{3+} , the lowest excited state is derived from the 5d configuration which forms a 2-D term, which splits into $^2D_{3/2}$ and $^2D_{5/2}$ state. As the crystal field splitting of the 2-D level of Ce^{3+} ion is large in the garnet structure, the emission from 4f-5d levels is broad in character with the observed transition energies varying with the nature of host lattice. The Ce^{3+} emission is involved with the ground $4f_1$ and the excited $4f_0^5d_1$ state, each of which is split into $^2F_{7/2}$, $^2F_{5/2}$ and $^2D_{3/2}$, $^2D_{5/2}$ states, respectively, due to the spin-orbit coupling. The Ce^{3+} emission results from the electron



transition from the lowest 5d band to $^2F_{7/2}$, $^2F_{5/2}$ states of the Ce^{3+} ion.

Fig. 2: PL spectra for $Y_{3-x}Al_5O_{12}:xCe$ with varying the amount of Ce, Emission spectrum ($\lambda_{ex} = 460$ nm)

(1) $x=0.5$ mol%,(b) $x=1$ mol%,(c) $x=1.5$ mol%; and Excitation spectrum ($\lambda_{em} = 528$ nm) for 1 mol% Ce.

In view of the improvement of luminescence properties of YAG singly doped phosphors, the way of double activation in the host lattice could be successfully used. The co-activators change the symmetry and vibrational modes around the luminescent centers and influences the Stark splitting of the 4f levels in the rare earth which results in change in crystal field around it [8]. The co-activators may act as a sensitizer for the energy transfer to the rare earth ion[9] or a charge compensator or as a preventer of nonradiative energy transfer via defects[10] or a luminescence killer. Usually, the luminescence spectrum modifies when there is double incorporation of different lanthanide ions into host crystalline lattice due to the formation of new emission centers. Many groups reported the effect of the substitution of Y and Al ions in the YAG structure with smaller or larger ions. The present study investigate codoping of Mg in the optimal concentration of Ce (i.e. 1mol%).

Figure (3) shows emission spectra for Mg codoped YAG:Ce (1mol%) powders excited at 460 nm. Since Mg²⁺ ions occupy Al³⁺ sites quadrivalence ion Si⁴⁺ is introduced to balance the charge difference between Mg²⁺ and Al³⁺ as studied in previous work by Katelnikovas et.al [11]. The concentration of Mg and Si varies as 1,5 and 8mol%.

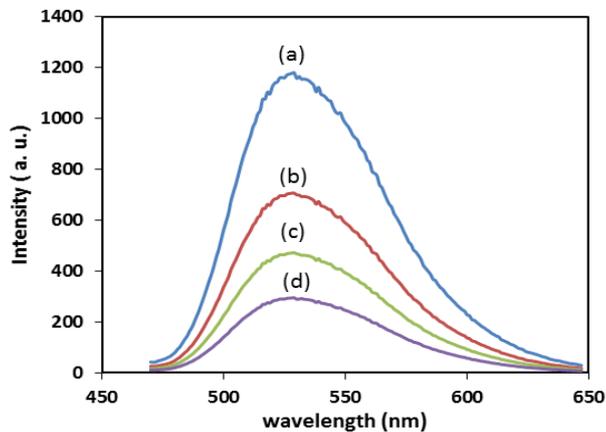


Fig. 3 : PL emission spectra ($\lambda_{exc} = 460 \text{ nm}$) of $Y_{3-x}Al_{5-y-z}Mg_ySi_2O_{12}:xCe,yMg,zSi$ ($x=1 \text{ mol\%}$) ;(a) $y,z = 0$ (b) $y,z = 1 \text{ mol\%}$ (c) $y,z = 5 \text{ mol\%}$ (d) $y,z = 8 \text{ mol\%}$

The spectra shows that emission intensity declines intensively with the increase of Mg²⁺-Si⁴⁺ content whereas emission wavelength progressively shifted from 528 nm to 534 nm. The emission intensity for phosphor showing the maximum shift of its emission wavelength for 8 mol% is about 25% relative to that of nonsubstituted YAG:Ce. The decrease in the emission intensity may be due to the energy transfer between Ce and Mg ions. In general, the energy transfer from a sensitizer to an activator in a phosphor may take place via exchange interaction and electric multipolar interaction[12,13].

On the basis of Dexter's energy transfer expressions of multipolar interaction and Reisfeld's approximation, the following relation can be given as:[14]

$$\frac{I_0}{I_s} \propto C_{Ce+Mg} \text{ or } \frac{I_0}{I_s} \propto C_{Ce+Mg}^{n/3}$$

where I₀ and I_s are the luminescence intensities of the sensitizer with and without activator present, and C is activator and sensitizer ion concentration. The plots of (I₀ / I_s) versus C correspond to the exchange interaction and C^{n/3} with n = 6, 8, 10 correspond to dipole-dipole, dipole-quadrupole, and quadrupole-quadrupole interactions respectively. Fig.4. illustrate the relationships between I₀ / I_s and C_{Ce+Mg} and C_{Ce+Mg}^{n/3} for various molar concentrations of Mg. The linear relationships were compared by the fitting factors of R values.

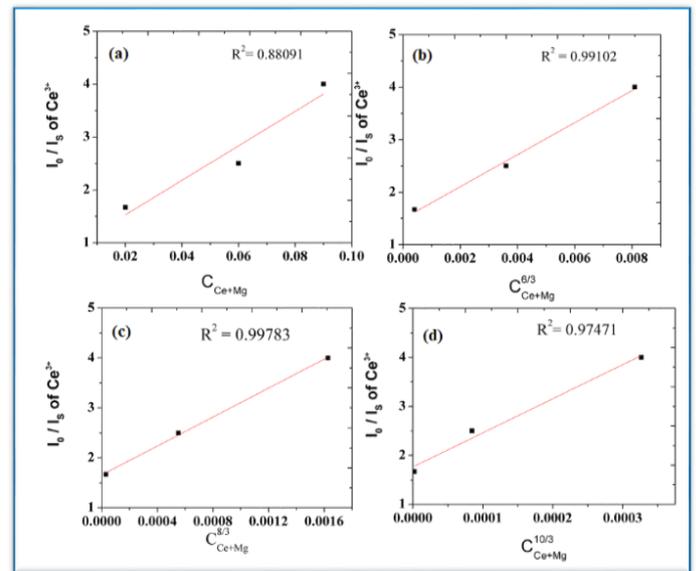


Fig. 4.: Dependence of I₀/I_s of Ce on (a) C_{Ce+Mg} (b) C_{Ce+Mg}^{6/3} (c) C_{Ce+Mg}^{8/3} (d) C_{Ce+Mg}^{10/3}

The fitting factor R reaches the optimal one for (I_s/I₀) \propto C_{Ce+Mg}^{8/3}; which implies that energy transfer from Ce to Mg occurs via dipole-quadrupole interaction.

The CIE chromaticity diagram of YAG:Ce, Mg upon 460 nm excitation is shown in Fig.5.

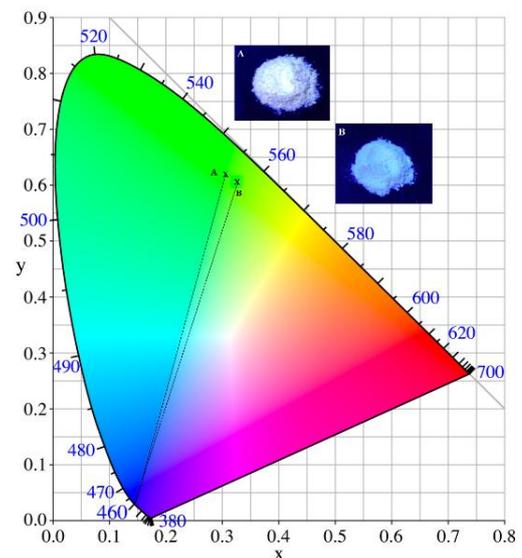


Fig.5: Representation of the CIE chromaticity coordinates for (A)YAG:Ce(1mol%) and (B) G:Ce(1mol%),Mg(8mol%)

The CIE coordinates shift towards red side of the diagram. The inset in fig.5 also shows digital photos of the selected YAG:Ce and YAG:Ce,Mg phosphors. It can be seen that a slight shift only has been detected with the expense of emission energy.

4. CONCLUSIONS

In summary, a simple methodology of synthesizing YAG:Ce codoped with Mg with mixed fuel is presented. XRD analysis verified the pure phase of YAG even at 5000C without further sintering. The doping of Mg in YAG:Ce is possible even at low temperature. The emission intensity of YAG:Ce (1 mol%) reduces with Mg-Si codoping but induces red shift of wavelength. The mechanism of energy transfer from a sensitizer Ce to an activator Mg in YAG:Ce phosphors was demonstrated to be an electric dipole quadrupole interaction. The CIE coordinates show shift on expense of emission intensity.

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