LUMINESCENCE MECHANISM OF HIGHLY EFFICIENT YAG AND TAG PHOSPHORS

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Abstract

The highly efficient yttrium aluminum garnet ($Y_3Al_5O_{12}$ or YAG) and terbium aluminum garnet ($Tb_3Al_5O_{12}$ or TAG) were prepared by solid state reaction (SSR). Particle distribution was very narrow and homogenous by using multilevel sieve after chemical route. Luminescence properties were improved and optimized by co-doping TAG with 2 activators: Ce^{3+} and Eu^{3+}. Introducing Eu^{3+} in the host lattice of TAG: Ce is more effective than in YAG:Ce. Luminescence mechanism and the role of Tb in the host lattice as a sensitizer are discussed.

Introduction

The idea of a white light emitting diode (LED) seems not to be inherently unusual or surprising. It was not until the recent successful creation of high frequency light LEDs in the blue/ultraviolet region when the white LED made its debut. With the perspective of a highly efficient, cold light source, the LED market will have an enormous growth and the white LED will be a likely candidate for the replacement of the light bulb once production costs fall as the technology advances. The first commercially available white LED based on phosphors was produced by Nichia Co., which was also first to manage to make the blue LED. Nichia used a blue light emitting Gallium Indium Nitride and coated the chip with yellow fluorescent phosphor $Y_3Al_5O_{12}$: Ce, well known now as (YAG: Ce). A little later another yellow phosphor $Tb_3Al_5O_{12}$: Ce (TAG: Ce) was also used by OSRAM Co with GaInN chip for white light production. YAG and TAG, activated with trivalent cerium, have been found to be efficient phosphors for converting the blue LED radiation into a very broad yellow emission band. The yellow emission from YAG: Ce and TAG: Ce are intense enough to complement the residual blue light which escapes through the phosphor in order to produce a white light. By far, YAG: Ce and TAG: Ce have been the most excellent phosphors satisfactorily applied in white phosphor-based LED commercial market. Therefore, any

improvement in the luminescence of YAG: Ce and TAG: Ce is extremely valuable to raise the light efficiency for different applications.

Usually these TAG: Ce and YAG:Ce phosphors are synthesized by solid state reaction (SSR) method and they have the similar properties. We also used this SSR method, because the phosphors with large-size particles from SSR show a more intense luminescence than those with small-size particles from other methods.

The aim of this study is to modify the sample preparation, to investigate the phosphors properties and luminescence mechanism of highly efficient YAG and TAG samples and to improve and optimize the luminescence parameters.

Experimental details

The samples TAG: Ce and YAG: Ce as well as (Y, Tb) AG: Ce phosphors were synthesized by SSR in Korea Advanced Institute of Technology (KAIST) [1]. In order to synthesize TAG: Ce and YAG:Ce phosphor, high purity yttrium oxide (Y_2O_3), aluminum oxide (Al_2O_3), terbium oxide (Tb_4O_7), and cerium oxide (CeO_2) were used as raw materials. They were mixed thoroughly by using ethanol as a solvent for mixing. Generally, sintering temperature and reaction time are two important factors that affect the crystallization and luminescence intensity. In our case raw materials were fired at 1500^o C for 5 hours. After these procedures, the phosphors were yellow in color, due to presence of the Ce^{3+} ion in the garnet structure.

X-ray diffraction measurement – The crystal structures of the prepared samples were determined by X-ray diffraction measurement using goniometer (Rigaku, D/max- C(3kw) with Cu- Kα (λ = 1.5418 Å) at 40 kV and 45 mA. The scan rate was 3 ^{o}/min and covered the range between 10^o and 80^o.

Photoluminescence (PL) measurement – In order to investigate the optical properties, PL was measured by using xenon lamp (500 W) and DARSA system. Measurement was done at λ_{exc} = 450 nm.

Morphology and size measurement – For observation of the particle size and morphology, SEM micrographs of phosphor powders were taken by using SEM (Philips, XLFSEG). In order to control the particles size of the phosphor the laser diffraction was carried out using HELOS particle size analysis system.

Results and discussion

Some fragments of SEM images of TAG: Ce, (Y,Tb)AG:Ce, and YAG:Ce phosphor powders are presented in fig.1. Qualitatively the particle sizes of TAG: Ce phosphor are larger

than those of the YAG:Ce phosphor prepared in the same conditions.

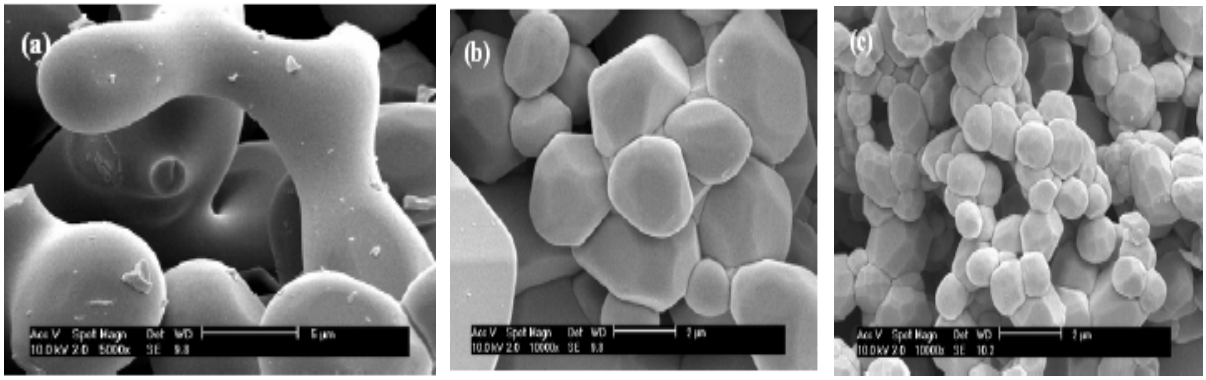

Fig.1. SEM images of (a) TAG: Ce, (b) (Y,Tb)AG:Ce and (c) YAG:Ce

For quantitative analysis of particle dimensions, the special method of the laser diffraction was carried out using HELOS particle size analysis system. The comparative results are shown in fig.2.

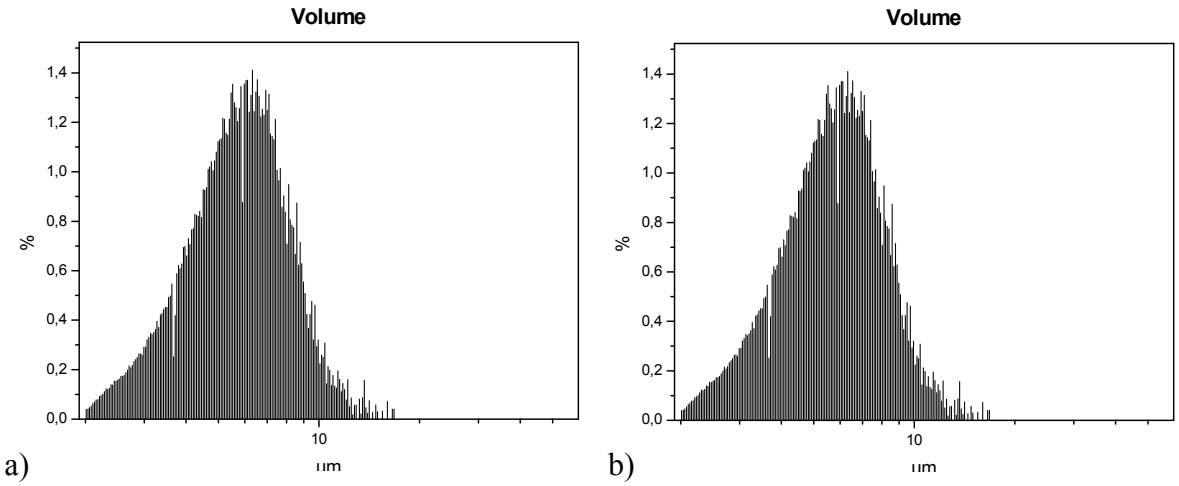

Fig.2. Real particle distribution in solid state reaction for YAG (a) and TAG (b) phosphors

For both YAG and TAG phosphors, the particle distribution is relatively large with maximum at 6 and 8 micrometers, respectively. Moreover, the PL emission intensity of TAG: Ce phosphor is stronger than that of YAG:Ce phosphor. These two results are consistent with the well known fact that as phosphor powder size becomes larger, PL emission property becomes better [2].

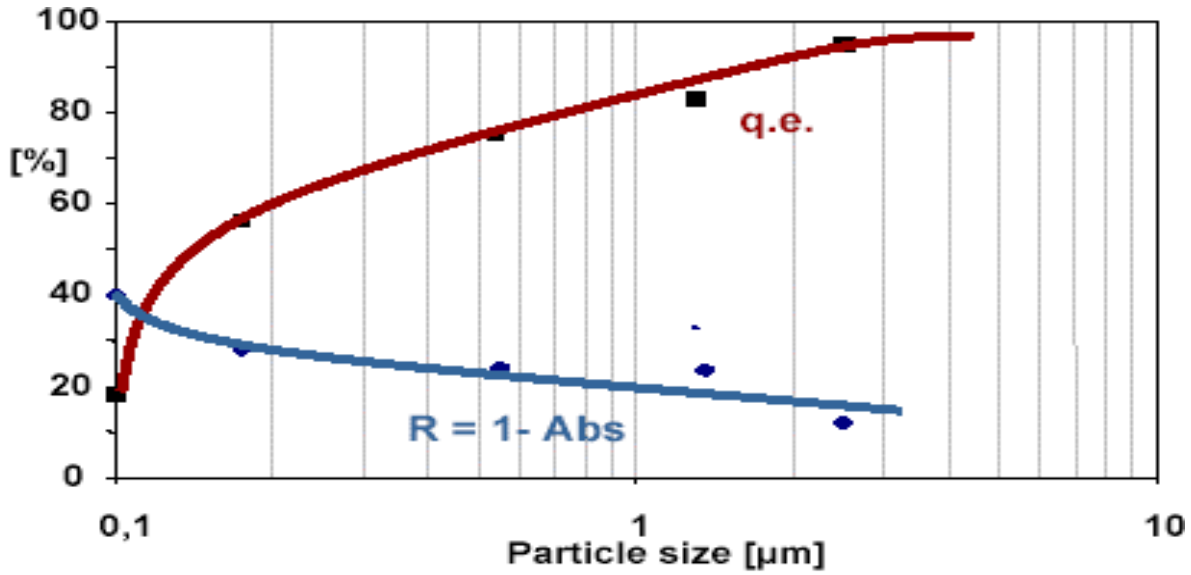

Fig.3. Influence of particle size on luminescence intensity

Unfortunately, the large and non-homogenous particle distribution has some disadvantages in the LED application. First of all, the particles with large size dispersion have different quantum efficiency and different luminescence. Secondly, different particles have non-homogenous distribution in LED packaging that makes worse the packaging process and decrease the device luminescence. It is demonstrated in the following model (fig.4)

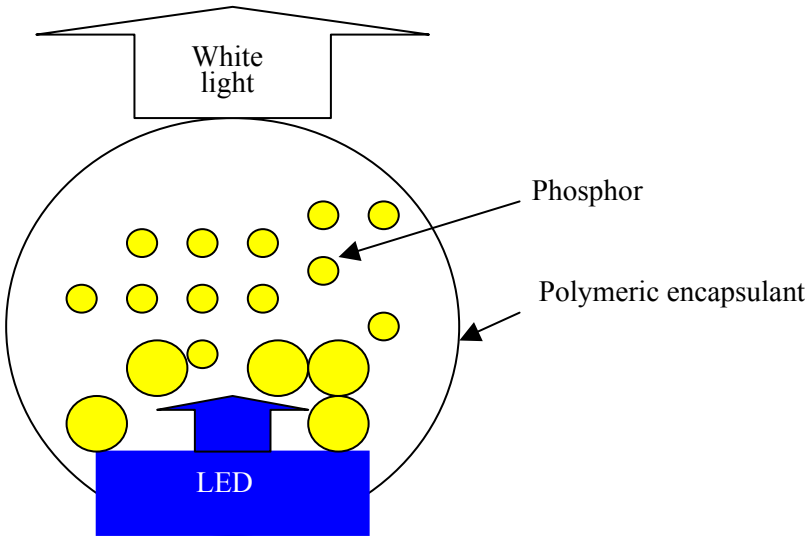

Fig.4. Schematic presentation the LED device with non-homogenous particle distribution.

For obtaining of the phosphors with homogenous narrow particle distribution we separated phosphors by particle sizes using the multilevel sieves after chemical route. The basic principle of this construction is presented in fig.5. The distinctive feature is that upper sieve has a 2 μm more grid than lower one.

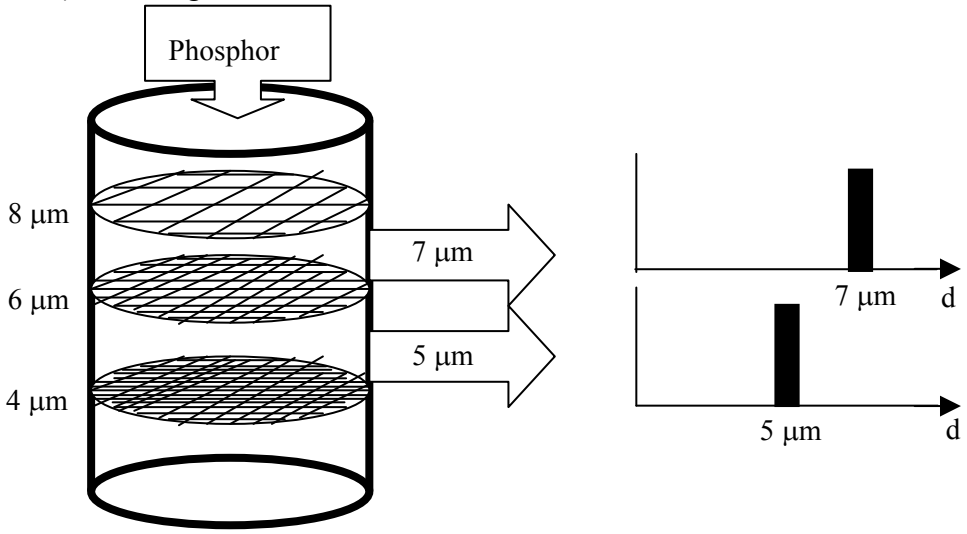

Fig.5 Separation of phosphors with multilevel sieves

Due to this process, the homogenous phosphors with optimized particle size introduce in LED, and the final device efficiency increases by about 15-20%.

Fig. 6 shows X-ray diffraction patterns of synthesized phosphors. These results indicate that other intermediate phases such as YAP and YAM were entirely transformed at 1500°C into YAG. YAG:Ce and TAG: Ce have the same crystal structure which is garnet with a different lattice parameter: lattice parameter of $Tb_3Al_5O_{12}$ is 12.074 Å and that of $Y_3Al_5O_{12}$ is 12.01 Å [3].

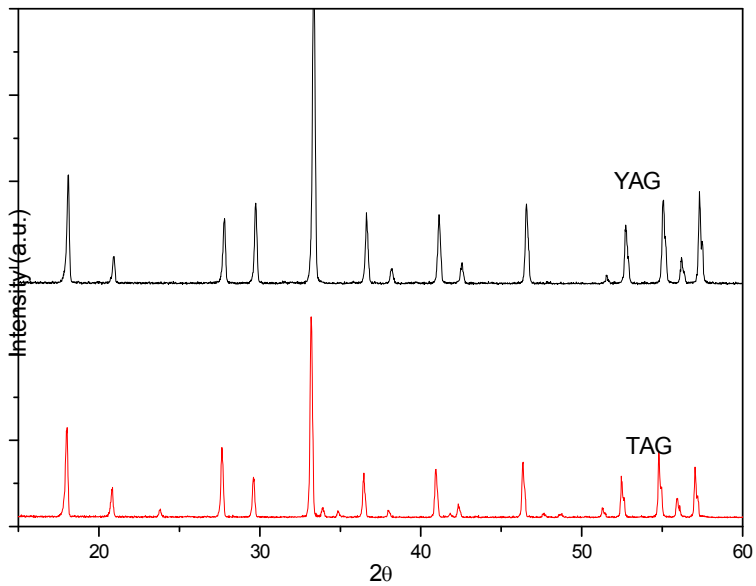

Fig.6. X-ray diffraction patterns of YAG:Ce and TAG: Ce phosphors

The unit cell of garnet structure is shown in fig.7.

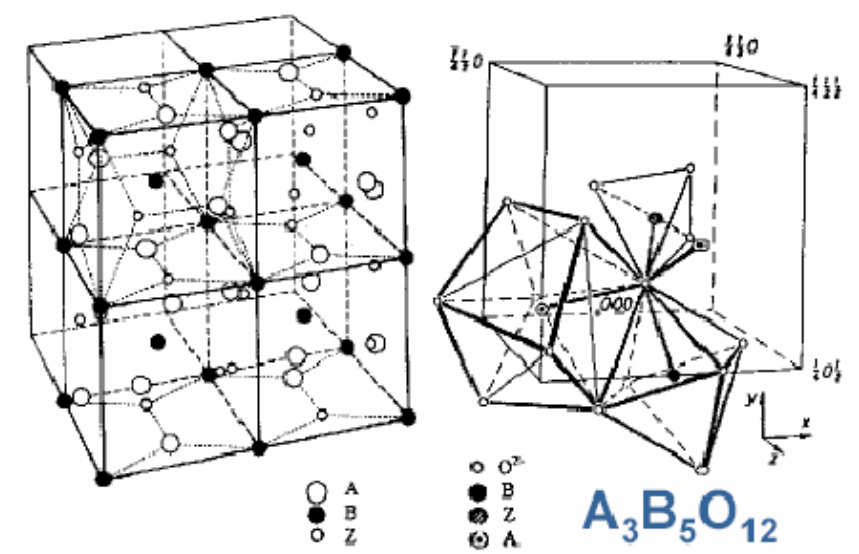

Fig.7. Garnet structure unit cell.

In garnet structure, there are 24 dodecahedral sites, 16 octahedral sites, and 24 tetrahedral sites. Tb^{3+} ions and Y^{3+} ions are located in dodecahedral sites [3]. W.W. Holloway et al. [4] reported that substitution by larger ions in the Y^{3+} sites shifted the emission peak to a longer wavelength while larger ions in the Al^{3+} sites shifted the emission peak to a shorter wavelength. Substitution by larger ion of Y sites increases the deviation of cubic component of the crystal field. Then excitation occurs at lower energy and emission band shifts to a longer wavelength region [5]. We can verify this emission band shifts in Fig. 8. Theoretically, compared with YAG:Ce, the spectrum of the TAG: Ce is slightly shifted to the red, because of reduced local symmetry. The ionic radius of Tb^{3+} (1.18 Å) is a little bigger than Y^{3+} (1.16 Å). However, this shift is not sufficient to compensate for lack of a red component.

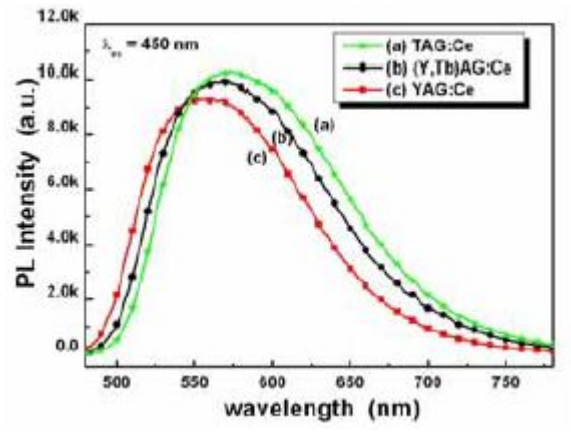

Fig.8. PL emission spectra of (a) TAG: Ce, (b) (Y,Tb)AG:Ce and (c) YAG:Ce phosphors

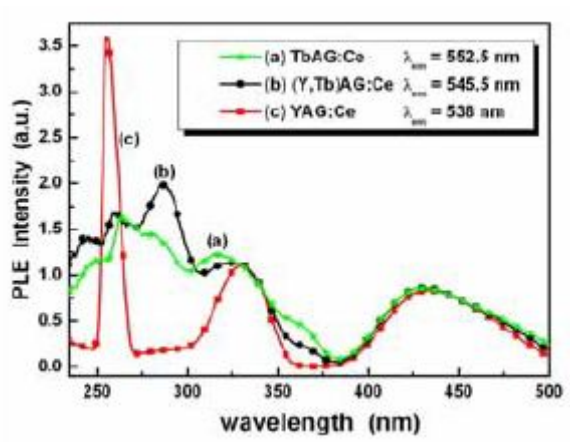

Fig. 9. PL excitation spectra of (a) TAG: Ce, (b), (Y, Tb)AG:Ce and (c) YAG:Ce phosphors

Figures 8 and 9 show the PL emission and excitation spectra of TAG: Ce, (Y,Tb)AG:Ce, and YAG:Ce phosphor. Emission spectra are under 450 nm excitation. The maximum emission peaks of TAG: Ce, (Y,Tb)AG:Ce, and YAG:Ce phosphor are at 552.5 nm, 545.5 nm, and 538nm, respectively. A broad yellow emission of YAG:Ce phosphor is due to 5d→4f transition of Ce^{3+} ion. Usually the emission consists of a broad band with two peaks in the long-wavelength region of ultraviolet. Since the ground state of the Ce^{3+} ion is a doublet ($^2F_{5/2}$ and $^2F_{7/2}$, fig. 10) with a separation of about 2000 cm^{-1}, Ce^{3+} emission band is expected to show two peaks. This doublet character of the emission band depends on temperature and Ce^{3+} concentration and is not always observed [5]. In this fig. 8, we can verify only one emission band in visible range.

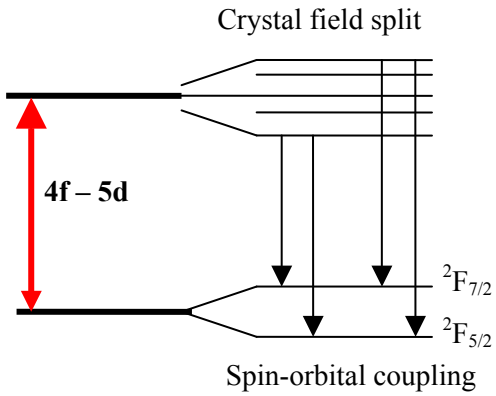

Fig.10. A simplified energy level scheme of the Ce^{3+} ion ($4f^1$) [5]

Fig.10 shows a simplified 5d energy level scheme of Ce^{3+} ion in the garnet structure. Since excitation band of Ce^{3+} ion in YAG host material is at around 450 nm, we used 450 nm blue light excitation source, and then we measured PL spectra in 480 nm ~ 780 nm region. In garnet structure crystal field splitting of ^2D level of Ce^{3+} ion is large [5]. 4f →5d band difference corresponds to the blue light. From fig.8 TAG: Ce as well as YAG:Ce shows a broad band emission. In this case, the emission is also due to the 5d→4f transition of Ce^{3+} ion. This Ce^{3+} emission in the two yellow phosphors is in the green and red region due to the crystal field effect [6].

Fig. 9 shows the difference between PL excitation spectrum of TAG: Ce and that of YAG:Ce phosphor. The difference is remarkable in the ultraviolet region. Fortunately, in blue spectral region, two phosphors have the same excitation spectra, so that we can apply both these two phosphors to the white emitting light source using blue emitting LEDs. However, any improvement in the luminescence of these phosphors is extremely valuable to raise the light efficiency for different applications. In order to obtain white LED with high color rendering index (CRI), a separated red light source with secondary phosphor emitting at red region will work. Therefore, it is like to achieve the objective by co-doping Ce^{3+} and other

rare earth ions into YAG and TAG phosphors. Red emission is found from a number of rare earth ion activators, such as trivalent Eu (at 590 and 610 nm), Sm (at 616 nm), or Pr (at 611 nm). All of them originate from f–f transitions. Search is underway in finding suitable ions for co-doping with Ce to increase the red component to improve the CRI of white light. Using double Eu-Ce or Sm-Ce activation in YAG phosphor does not seem very fruitful, because it only diminishes the Ce luminescence, but using them in TAG could increase essentially the luminescence and improve CRI. In combination Eu-Tb-Ce terbium plays the role of sensitizer, it absorbs the exciting radiation from the LED and subsequently transfers this energy to Eu and Ce. Moreover, one additional way of transfer energy is possible: the radiation transitions in Tb may excite directly the neighboring Eu and Ce atoms. In such case, Tb^{3+} in TAG does not serve as a doping element but becomes a part of the host structure. After migration in the Tb sublattice the activation energy is transferred from Tb^{3+} ($^5D_4 \rightarrow {}^7F_J$) to a Eu^{3+} activator ($^7F_J \rightarrow {}^5D_J$). This part of the process was demonstrated for the single-doped case of TAG:Eu in [7]. The luminescence mechanism could be understood from energy level diagram (Fig.11) and quantitatively is confirmed by 3-level model for energy transfer [8,9]

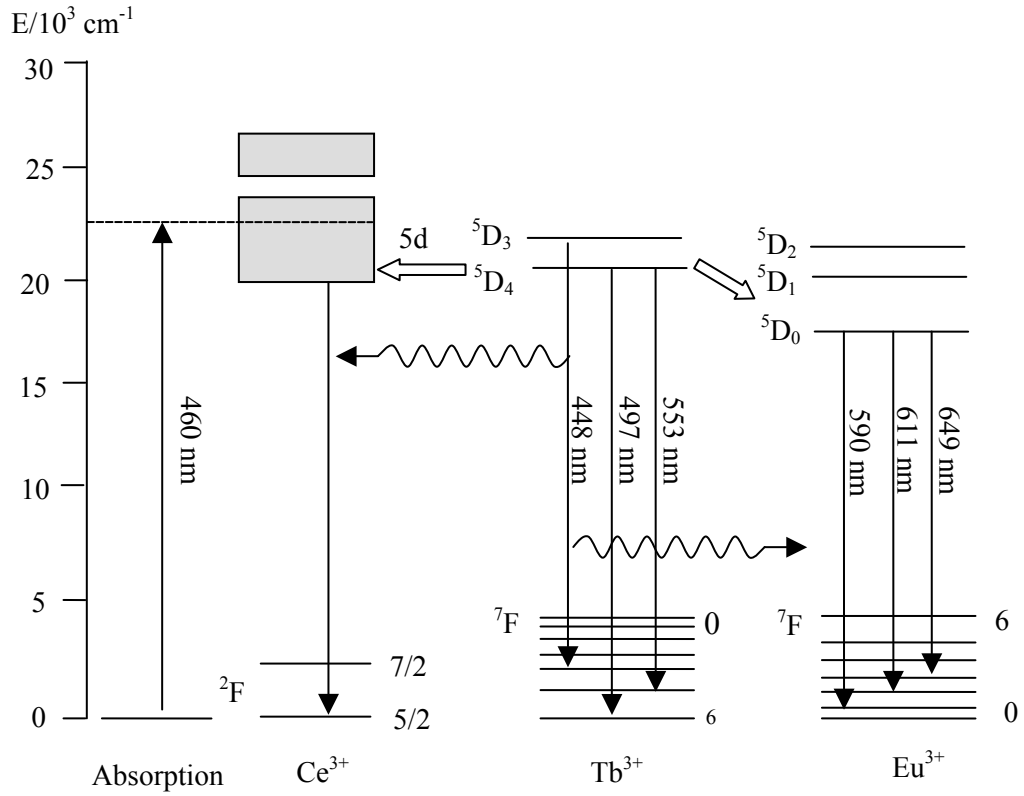

Fig.11. Luminescence mechanism in TAG:Eu,Ce

The common way to improve the emission spectra of lighting devices is co-activation of the conversion phosphors, for example with Eu^{3+}, which shows an intense line emission in the

red. A codoping with Sm^{3+}, Pr^{3+} or Eu^{3+} looks very fruitful for improvement of luminescence properties of YAG:Ce and TAG: Ce. The luminescence is more intense when the gap between the excited state and the more energetic component of the ground state multiplet, is larger. This explains the prominent role played by Eu^{3+} as co-activator. Introducing Eu^{3+} in the host lattice of TAG: Ce is more effective than in YAG:Ce. When Eu^{3+} is introduced in YAG, the part of exciting LED energy will excite the Eu^{3+} ions and reduce the Ce^{3+} excitation, that decrease the luminescence intensity. In the case of TAG, Tb^3 transfers its energy to Ce^{3+} and Eu^{3+} and can be used as a sensitizer. In addition, one new luminescent mechanism can exist when Tb luminescence excites direct Ce^{3+} and Eu^{3+}. The total luminescence increases and red shift appears, that improves CRI and CIE. It is very important to optimize the concentrations of activators and co-activator to improve the properties. TAG seems to be more perspective than YAG in the white light devices

Conclusions

In this study, we have investigated the PL properties and luminescent mechanism of TAG: Ce and YAG: Ce phosphors. They have similar structure, and the properties are expected to be similar and determined by Ce doping. In TAG: Ce and YAG:Ce phosphors, there are excitation bands in blue spectral region and it means that the yellow TAG: Ce and YAG:Ce phosphors can be good candidate materials for the application of white emitting light source using blue emitting LEDs.

Since Tb^{3+} ion is larger than Y^{3+} ion, crystal field splitting of 5d energy level of Ce^{3+} ion is larger in TAG: Ce phosphor. Therefore emission band shifts to a longer wavelength, so white emitting light source using blue emitting LEDs and TAG: Ce phosphor can overcome weak red emission intensity of that using blue emitting LEDs and YAG:Ce phosphor. In the case of using TAG: Ce phosphor to fabricate white emitting light source, we can expect better white emitting light source for illumination.

However, this shift in red region is not sufficient to compensate the lack of a red component. A codoping with Sm^{3+}, Pr^{3+} or Eu^{3+} looks very fruitful. The luminescence is more intense when the gap between the excited state and the more energetic component of the ground state multiplet, is larger. This explains the prominent role played by Eu^{3+} as co-activator.

Introducing Eu^{3+} in the host lattice of TAG: Ce is more effective than in YAG:Ce. When Eu^{3+} is introduced in YAG, the part of exciting LED energy will excite the Eu^{3+} ions and reduce the Ce^{3+} excitation, that decrease the luminescence intensity. In the case of TAG, Tb^3 transfers its energy to Ce^{3+} and Eu^{3+} and can be used as a sensitizer. In addition, one new luminescent mechanism can exist when Tb luminescence excites direct Ce^{3+} and Eu^{3+}. The

total luminescence increases and red shift appears, that improves CRI and CIE. It is very important to optimize the concentrations of activators and co-activator to improve the properties.

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Acknowledgement

This research was supported by the International Cooperation Research Program of the Ministry of Science and Technology, Republic of Korea.

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