착화합물로써 EDTA이 사용된 $Gd_2O_3:Eu^{3+}$ 형광체의 합성 및 발광 특성

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Synthesis and luminescent properties of $Gd_2O_3:Eu^{3+}$ red phosphors used EDTA

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Abstract

The synthesis and luminescent properties of trivalent europium activated gadolinium oxide red phosphors by sol-gel process have been investigated. Aqueous metal nitrate solution was mixed with EDTA which was chosen by the most suitable material of sol-gel formation as chelating agents. We noticed that the samples when are heated with EDTA at a temperature of 100℃ for 1hrs, produced brownish and crisp powders due to condensation reaction on decomposition, dehydration and formation of sol-gel. Hence, when the powder pre-heated at about 100℃ was then heated at 1200℃ for 3hrs in atmosphere, the luminescence properties of resultant $Gd_2O_3:Eu^{3+}$ phosphor was measured by SEM, FT-IT and brightness intensity was shown 20% higher than those prepared by conventional method and by other chelating agent.

Keyword: $Gd_2O_3:Eu^{3+}$ phosphor; sol-gel method; luminescence; phosphor; chelating agent

1. Introduction

$Gd_2O_3:Eu^{3+}$ is an efficient red emission phosphor and has been used widely in fluorescent lights(FL) and cathode ray tube(CRT). Phosphors are composed of host lattice and optically excited activator, typically 3d or 4f metal. For phosphor studies in the accomplishing full color and flat panel display (FPD), it is desirable to have small particle size, high luminescence, thermal stability, radiation resistance for high resolution and chemical purity for optimum chromaticity and brightness[1]. Thereby, researchers have studied the newer materials and the reformed technique to improve the performance of phosphors. Oxide phosphors were found to be optimal for low voltage displays. Especially, Eu^{3+} doped gadolinium oxide phosphor is a well-known as a red emitting phosphor used widely with $Y_2O_3:Eu^{3+}$ for plasma display panel (PDP) and field emission display (FED) because of its high brightness, acceptable atmospheric stability and hazardous constituents. Traditionally, the $Gd_2O_3:Eu^{3+}$ phosphors are prepared mainly at 1400~1600℃ for several hours by solid state method[2]. The phosphor synthesized by conventional method happen inhomogeneous agglomeration and the particle size is very big. Therefore those must be ground or milled to get small powder. The luminescence efficiency and morphology of phosphor greatly decrease in this process and crystalline is broken frequently.

In our present work, a simple sol-gel method, in which ethylenediaminetetraacetic acid(EDTA) is used as the chelating agent, is possible to synthesize phosphors having high surface area[3-5]. The advantages of this method are that mixed powders are atomically obtained in the as-synthesized condition and the defects associated with incomplete reactions are removed. Also, it is easy to control the composition and the porous structure of uniformity is available. The active precursors are sintered in low temperatures

with minimizing the potential for contamination compared with conventional method. We now report that the EDTA when applied as chelating agent in $Gd_2O_3:Eu^{3+}$ aqueous solution by sol-gel method, the luminescence properties of $Gd_2O_3:Eu^{3+}$ phosphors are enhanced. The red phosphor produced powders having maximum 20% higher PL intensity than that of conventional products.

2. Experimental

High purity gadolinium oxide (Gd_2O_3), europium oxide (Eu_2O_3) were used as starting materials. Ethlylenediaminetetraacetic acid (EDTA) from aldrich chemicals were used as chelating materials for the sol-gel process. The procedure used to prepare $Gd_2O_3:Eu^{3+}$ in present experiments is as follows. At first, Gd_2O_3 and Eu_2O_3 were reacted with diluted HNO_3(65%, A.R.) to make aqueous solution and the amount of HNO_3 is adjusted just enough to dissolve Gd_2O_3 and Eu_2O_3. According to the nominal composition of $(Gd_{0.95}Eu_{0.05})_2O_3$, the stoichiometric amount of $Gd(NO_3)_3$ and $Eu(NO_3)_3$ solutions was mixed with strong stirring to ensure the homogeneous mixture. EDTA as chelating agent was added into the solution at appropriate proportion and dried with stirring at temperature of 100℃ on the hot plate. The solution became a transparent gel with a high viscosity and the gel was streamed, boiled, frothed, fumed. The crisp powders obtained were sintered at 1200℃ for 3hrs to get phosphor powder. The synthesis procedure by sol-gel method is similar to Ref [4].

The photoluminescence (PL) and color coordinates (CIE) were measured using spectroradiometer CS-1000 of Minolta Company. The morphology and size of particles were obtained as confirmed by SEM techniques using Philips XL30. The IR spectra of phosphors sintered were measured using FT-IR Thermo Nicolet model.

3. Results and discussion

Gd_2O_3 and Eu_2O_3 were dissolved in diluted nitric acid and were mixed with EDTA as chelating materials to get a clear aqueous solution. The solution when was heated with stirring at 100℃ on the hot plate, was slowly evaporated and the solution turned to dark brown because the nitrate functional groups decompose around that temperature. With temperature maintaining. transparent sol was formed and the condensation reaction happened between -COOH functional groups the moment the water is formed. Water as being removed in aqueous solution, the sol turned into a transparent gel and viscous paste was acquired. The continuous heating at about 100℃ lead to the combustion of gel and a fluffy brownish black powders were ultimately obtained. For comparison, $Gd_2O_3:Eu^{3+}$ with general formula $(Gd_{1-x}Eu_x)O_3$, where $0.005 \leq x \leq 0.18$ were also prepared by traditional solid state method and sol-gel method, which the concentration of Eu^{3+} and the calcining temperature are the same. The Eu^{3+} concentration quenching of red phosphor synthesized by different method and chelating material are shown in Fig. 1 and Fig. 2 shows the luminescent intensity according to amounts of EDTA, which was made with optimal composition through sol-gel method. As shown Fig. 1, the sample which was chelated by EDTA in the $Gd_2O_3:Eu^{3+}$ phosphor, produced more stronger emission than existing reports. It considered that Eu_2O_3 enter the Gd_2O_3 crystal lattice well with decreasing activator defects such as surface residue or boundary band between metallic ions because the EDTA combined more stronger with metal ion than the other chelating materials.

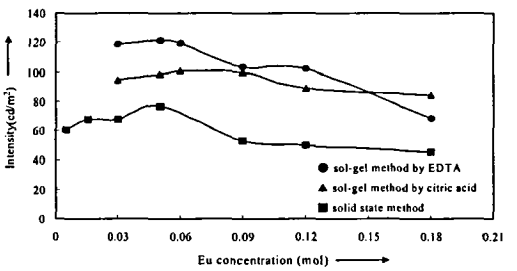


그림 1. Eu^{3+} 첨가량에 따른 형광체의 농도소광
Fig 1. Brightness of $(Gd_{1-x}Eu_x)O_3$ phosphor prepared as a function of Eu^{3+} concentration

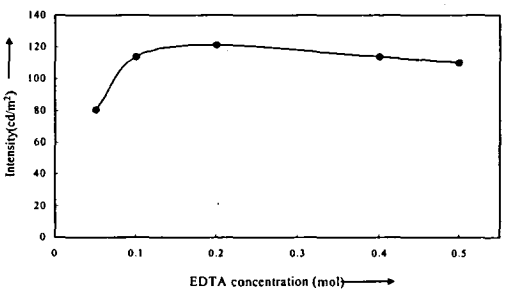
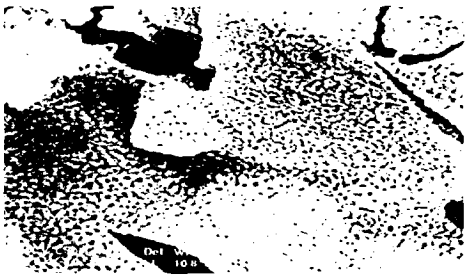


그림 2. EDTA 첨가량에 대한 $Gd_2O_3:Eu^{3+}$ 형광체의 발광세기
Fig 2. Emission intensity according to the concentration of EDTA chelating agent.

Fig. 3 is the SEM micrograph of the phosphor obtained by different method and material. We noticed that the phosphors used EDTA have porous and small-sized particles. According to different synthesis such as solid state and sol-gel method, the transformation of shape appear a very different morphology of powder and although the applied method is same, the size and uniformity of particle become variously each other for materials used, that is, in the resultant powder was sintered at 1200℃ for 3hrs to obtain the phosphor, the $Gd_2O_3:Eu^{3+}$ phosphor that citric acid and boric acid were used are irregular and big particle with the range of above 5㎛ due to particle cohesion while the particle of phosphor in Fig. 3c) is more regular and the grain is not only homogeneous but also small in the range between 1 and 3㎛. It is novel that only the sol-gel method of EDTA have been seen the evidence of very fine particle having porous or spongy-like structure to promote complete crystalline because of more stronger chelating ability at low temperature. However, we must pay attention to the fact that the EDTA sample acted as chelating agent emits in the same wavelength of 612nm without a certain change although luminescent properties due to complete crystallinity and higher surface region in the same conditions were enhanced, as shown Fig. 4 and Fig. 5. The emission spectrum for all samples consists of lines in the red spectral area with color coordinates of x=0.5515, y=0.3251. These correspond to transition from the excited $^5D_0$ level to ^7F_J(J=0,1,2,3,4) level of the $^4F_6$ configuration of the Eu^{3+} ion.

a) boric acid (5㎛)

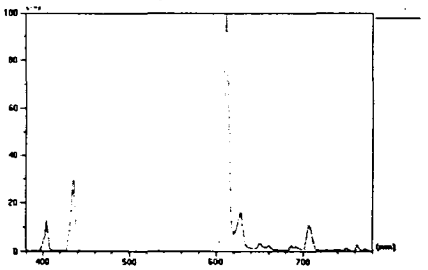
b) Citric acid (5㎛)



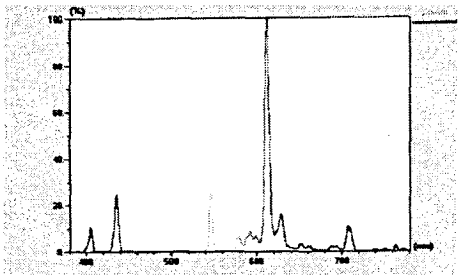
c) Ethylenediaminetetraacetic acid (EDTA) (5㎛)

그림 3. 합성 방법과 킬레이트에 대한 $Gd_2O_3:Eu^{3+}$의 표면
Fig 3. The SEM of the phosphor sintered at 1200℃ for 3hrs according to applied method and materials.

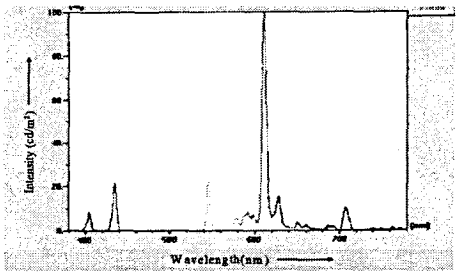
The most intense line at 612nm corresponds to the hypersensitive transition between the $^5D_0$ and $^7F_2$ level of the Eu^{3+} ion. The IR spectra for $Gd_2O_3:Eu^{3+}$ phosphor prepared by EDTA are shown in Fig 6. The IR peaks composed generally of similar two parts : the first part with a peak at 1139.59cm^{-1}, which arise from the absorption of CO_3^{2-} vibration, the second part peaking at 536.60cm^{-1} which come from the lattice in Gd_2O_3. The results for EDTA as chelating materials were enhanced slightly in view to particle size, IR spectra and emission spectra compared with that of $Gd_2O_3:Eu$ used citric acid. In future, further research will be studied to achieve the improvement of luminescence and morphology for $Gd_2O_3:Eu^{3+}$ phosphor by various method.



a) boric acid



b) citric acid



c) Ethylenediaminetetraacetic acid (EDTA)

그림 4. EDTA에 의해 합성된 $Gd_2O_3:Eu^{3+}$ 의 발광스펙트럼

Fig 4. The emission spectra of the phosphor sintered at 1200℃ for 3hrs according to applied method and material.

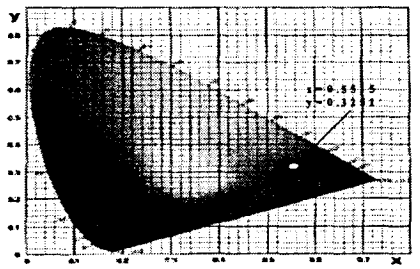


그림 5. EDTA에 의해 합성된 $Gd_2O_3:Eu^{3+}$의 색좌표

Fig 5. The color coordinates area of phosphors prepared in present experiments

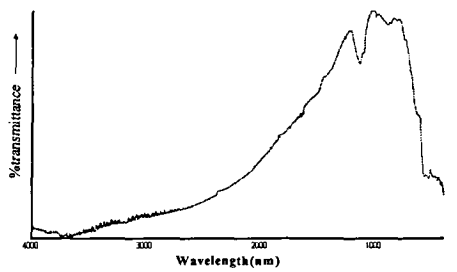


그림 6. EDTA를 사용하여 합성한 $Gd_2O_3:Eu^{3+}$의 IR 스펙트럼

Fig 6. IR spectra of $Gd_2O_3:Eu^{3+}$ synthesized by EDTA.

4. Conclusion

The present method synthesizes $Gd_2O_3:Eu^{3+}$ phosphor having a homogeneous particles shape and high purity brightness of red colour at 612nm wavelength, which can not be obtained by conventional methods. Because the EDTA combine more stronger with metal ion than the other chelating materials, Eu_2O_3 enter the Gd_2O_3 crystal lattice well with decreasing activator defects such as surface residue or boundary band between metalic ions. The Gd_2O_3:Eu phosphor which was used EDTA had almost same IR spectra, emission intensity, emission line and color coordinates in comparison to samples prepared by conventional method and sol-gel process used citric acid, while $Gd_2O_3:Eu^{3+}$ phosphor synthesized by EDTA was obtained very high brightness because of porous surface area by strong complex ability of EDTA.

Particularly, advantage of the present method is to have the average particle size under 3㎛ and to improve emission intensity about 20% compared with published reports.

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