착화합물로써 EDTA이 사용된 $Y_2O_3:Eu^{3+}$ 형광체의 발광 및 형태 특성

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Luminescence and morphology properties of $Y_2O_3:Eu^{3+}$ phosphors using EDTA as chelating agent

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Abstract

The preparation and luminescence characterization of yttrium oxide doped with trivalent europium phosphors by sol-gel method have been investigated. Aqueous metal nitrate solution was mixed with EDTA which was chosen by the most suitable material of sol-gel formation one of appled various 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 was then heated at 1200℃ for 3hrs in atmosphere, the luminescence characterization of resultant $Y_2O_3:Eu^{3+}$ phosphor was enhanced upto maximum 30% significantly than conventional method through increasing porous region and decreasing particle sizes.

Keyword: $Y_2O_3:Eu^{3+}$ phosphor; sol-gel method; luminescence; phosphor; chelating agent

1. Introduction

The light generating components of full color emission are called phosphor. Phosphors are composed of host lattice and optically excited activator, typically 3d or 4f metal. For phosphor application in the accomplishing full color and flat panel display, 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[1,2]. 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 yttrium oxide phosphor is a well-known as a red emitting phosphor used widely in cathode ray tube, plasma display panel and field emission display because of its high brightness, acceptable atmospheric stability and hazardous constituents. Traditionally, the $Y_2O_3:Eu^{3+}$ phosphors are prepared at 1400~1600℃ for several hours by solid state method[3]. The phosphor synthesized through conventional method happen inhomogeneous agglomeration and the particle size is very big. Therefore those must be ground to get small powder. The luminescence efficiency and morphology of phosphor greatly decrease in this process and crystalline is broken. Through sol-gel method, it is possible to synthesize phosphors having high surface area[4,5]. 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[6]. We now report that the luminescence properties of $Y_2O_3:Eu^{3+}$ phosphors are turned by simple sol-gel method. Especially, the EDTA when applied as chelating agent in $Y_2O_3:Eu^{3+}$ aqueous solution, produced powders having maximum 30% higher PL intensity than that of conventional products.

2. Experimental

High purity yttrium oxide(Y_2O_3), europium oxide(Eu_2O_3) were used as initial materials. Ethlylenediaminetetraacetic acid (EDTA) from Aldrich Chemicals were used as chelating

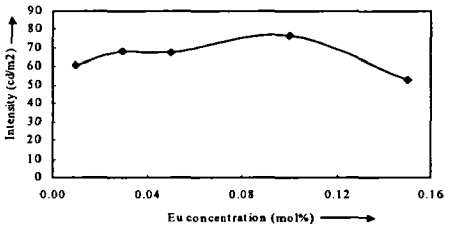
materials. In these experiments, Y_2O_3 and Eu_2O_3 were reacted with diluted HNO_3 to make aqueous solution and the amount of HNO_3 is adjusted just enough to dissolve Y_2O_3 and Eu_2O_3. Each chelating agents were added into solution at appropriate proportion and dried with stirring at temperature of 100℃ on hot plate. 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 [5].

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

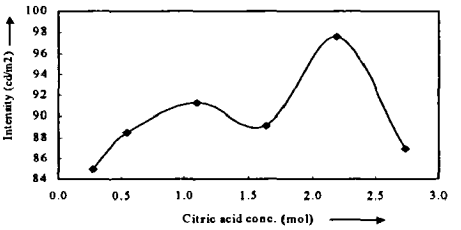
3. Results and discussion

Y_2O_3 and Eu_2O_3 were dissolved in diluted nitric acid and were mixed with various 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 yellow 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.

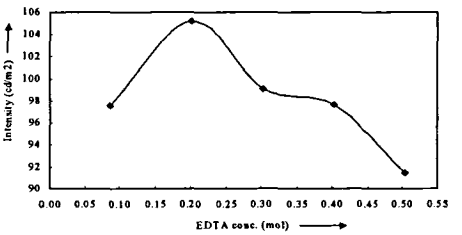
In present experiments, the sample which was used EDTA as chelating material has been observed to be compared with those of established reports from the viewpoint of luminescence and morphology. We report the effect of EDTA for Y_2O_3:Eu^{3+} phosphors. For comparison, Eu^{3+} doped yttrium oxide phosphors, with general formula $(Y_{1-x}Eu_x)O_3$, where $0.01 \leq x \leq 0.15$ were prepared by conventional method. H_3BO_3(2wt%) was added as flux in the mixture to decrease the temperature. The power was milled for 2hrs in water and the milled paste was dried and then fired at 1200℃ for 3hrs. And the Y_2O_3:Eu^{3+} phosphor also was prepared using citric acid with same procedure based on Ref.[5] by sol-gel method. Fig. 1 shows concentration quenching of chelating agents, which was made with optimal composition through conventional method. As shown Fig. 1, the sample which was chelated by EDTA, produced more stronger emission than existing reports. It considered that Eu_2O_3 enter the Y_2O_3 crystal lattice well with decreasing activator defects such as surface or boundary band between metallic ions because the EDTA combined more stronger with metal ion than the other chelating agents. Fig. 2 is SEM of the phosphor obtained by different method and material.



a) Concentration quenching of Eu^{3+} by solid state method



b) Concentration quenching of citric acid by sol-gel method

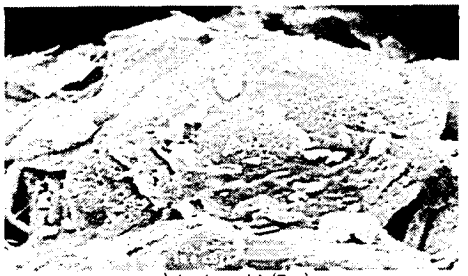


c) Concentration quenching of EDTA by sol-gel method

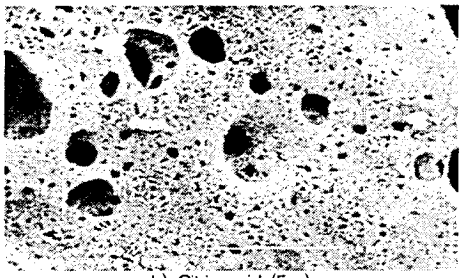
그림 1. Eu^{3+} 농도소광 및 킬레이트 첨가량에 대한 발광세기
Fig 1. Concentration quenching of applied chelating agent, which was made with optimal composition obtained by conventional method

We noticed that the phosphors used EDTA have homogeneous and small-sized particles. According to different synthesis such as solid state and sol-gel method, the transformation of shape appear a different morphology of powder and although the applied method is same, the size and uniformity of particle become each other diversely in obedience to used materials, that is, in the resultant powder was sintered at 1200℃ for 3hrs to obtain the phosphor, the Y_2O_3:Eu^{3+} phosphor that citric acid and boric acid were used are irregular and big particle with the range of above 5㎛

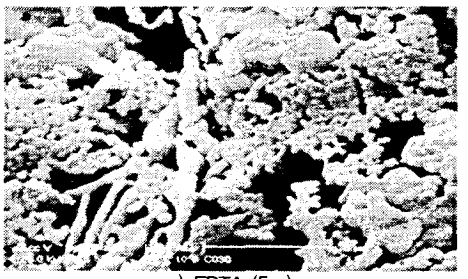
due to particle cohesion while the particle of phosphor in Fig.2c) is more regular and the grain is not only homogeneous but also small in the range between 1 and 3 μm.



a) boric acid (5μm)



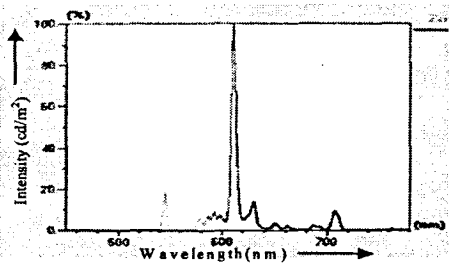
b) Citric acid (5μm)



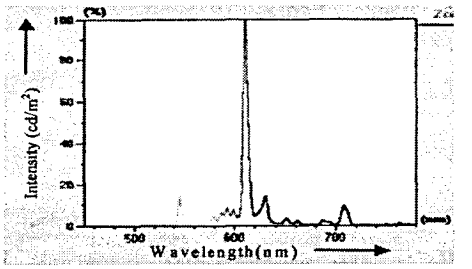
c) EDTA (5μm)

그림 2. 합성법과 킬레이트에 따른 형광체의 표면특성
Fig 2. SEM of the phosphor sintered at 1200℃ according to applied method and material.

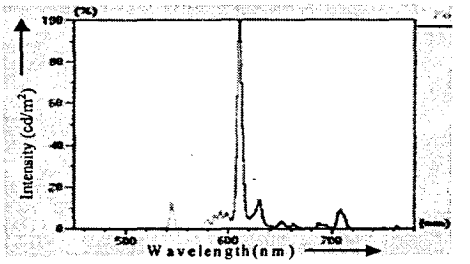
It is novel that only the sol-gel method of citric acid have been seen the evidence of very fine particle having porous or spongy-like structure to promote complete crystalline because of sintering at low temperature. However, we must pay attention to the fact that the EDTA sample acted as chelating agent emits in the same wavelength of 611nm without a certain change although luminescent properties due to complete crystallinity and higher surface region in the same conditions were enhanced, as shown Fig. 3 and Fig. 4.



a) boric acid



b) citric acid



c) Ethylenediaminetetraacetic acid (EDTA)

그림 3. EDTA에 의해 합성된 형광체의 발광스펙트럼
Fig 3. Emission spectra of phosphor sintered at 1200℃ for 3hrs by sol-gel method using EDTA

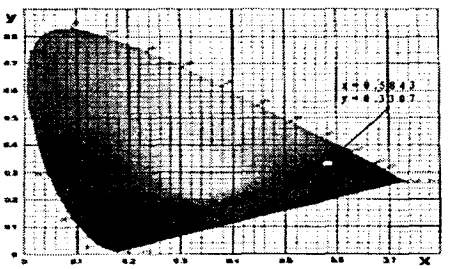
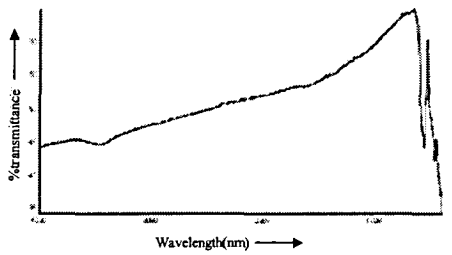


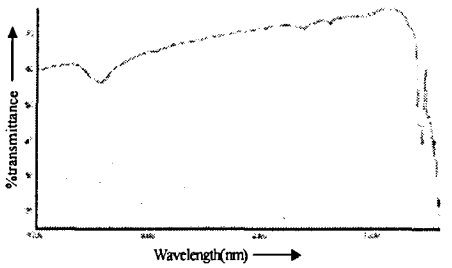
그림 4. EDTA에 의해 합성된 $Y_2O_3:Eu^{3+}$형광체의 색좌표
Fig 4. The color coordinates area of phosphors prepared by sol-gel method using EDTA

The emission spectrum for all samples consists of lines in the red spectral area with color coordinates of x=0.5843, y=0.3307. 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

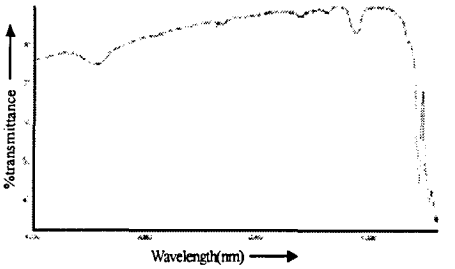
the Eu^{3+} ion. The most intense line at 611nm corresponds to the hypersensitive transition between the $^5D_0$ and $^7F_2$ level of the Eu^{3+} ion. The IR spectra for $Y_2O_3:Eu^{3+}$ phosphor prepared by EDTA are shown in Fig 5 compared with published paper synthesized by sol-gel method using citric acid and by solid state method, the IR peaks composed generally of similar three parts:the first part with a peak at 3455 cm^{-1}, which arise from the absorption of O-H vibration, the second part peaking at 1384 and 1620cm^{-1} which come from the group in citrate or ethylenediaminetetraacetate(EDTA) and the third part with a weak peak at 1136cm^{-1} due to the absorption of small amount of CO_3^{2-}. Also we found that the absorption peaks of three sharp band peaking at 560, 462 and 414cm^{-1} appear, which arise from the absorption of Y_2O_3 lattice, indicating the complete crystallization of Y_2O_3. The results for applied EDTA as chelating materials show almost same particle size, IR spectra and emission spectra compared with that of Y_2O_3:Eu used citric acid. We could know that the novel phenomenon was investigated only in case of $Y_2O_3:Eu^{3+}$ phosphor synthesized by EDTA.



a) Boric acid



b) Citric acid



c) Ethylenediaminetetraacetic acid (EDTA)

그림 5. EDTA에 의해 합성된 $Y_2O_3:Eu^{3+}$의 IR 스펙트럼
Fig 5. The IR spectra of $Y_2O_3:Eu^{3+}$ phosphor synthesized by conventional method and Ref.[8].

4. Conclusion

The present method synthesizes $Y_2O_3:Eu^{3+}$ phosphor having a homogeneous particles shape and high purity brightness of red colour at 611nm 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 Y_2O_3 crystal lattice well with decreasing activator defects such as surface residue or boundary band between metallic ions. The Y_2O_3:Eu phosphor used EDTA had almost same IR spectra, emission intensity, emission line and color coordinates in comparison to samples prepared by solid state method, while very high brightness was obtained because of 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 30% compared with published reports.

Reference

[1] R.N.Bhargava, D.Gallagher, X.Hong and A.Nurmikko, Phys.Rev.Lett., Vol. 72, pp. 416, 1994.

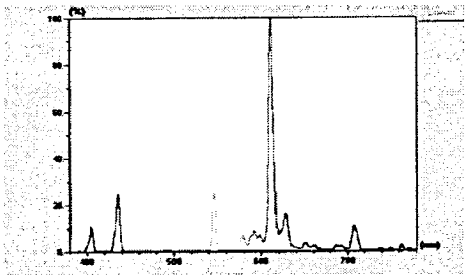
[2] P.Maestro and D.Huguenin, J.Alloys.Compd, Vol. 225, pp. 520, 1995.

[3] P.Maestro, D.Huguenin, A.Seigneurim, F.Deneuve, P.L.Lann and J.F.Berar, J.Electrochem.Soc., Vol. 139 No. 5, pp. 1479-1482, 1992.

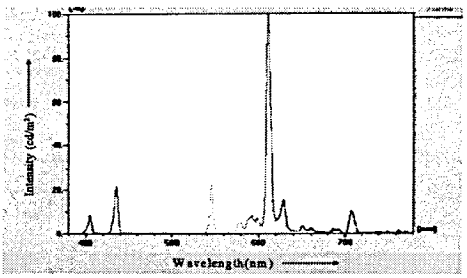
[4] R.P.Rao, J.Electrochem. Soc., 1996, Vol. 143, No. 1, pp. 189-197, 1996.

[5] J.Zhang, Z.Tang, Z.Zhang, W.Fu, J.Wang and Y.Lin, Mater.Sci.Engng, Vol. A334, pp. 246-249, 2002.

[6] J.A.Castellano, Handbook of Display Technology, Academic Press, INC., San Diego, 1992.



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.

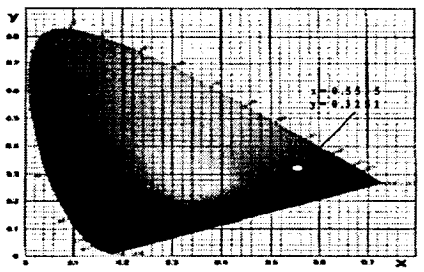


그림 5. EDTA에 의해 합성된 $Gd_2O_3:Eu^{3+}$의 색좌표

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

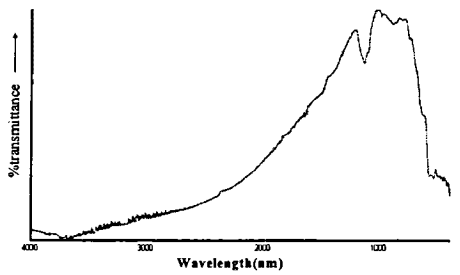


그림 6. EDTA를 사용하여 합성한 $Gd_2O_3:Eu^{3+}$의 IR 스펙트럼

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.

Reference

[1] R.N.Bhargava, D.Gallagher, X.Hong and A.Nurmikko, Phys.Rev.Lett., Vol. 72, pp. 416, 1994.

[2] S.H.Byeon, M.G.Ko, J.C.Park and D.K.Kim, Chem.Mater. Vol. 14, pp. 603, 2002.

[3] C.Sihai, I.Takashi and K.Keisaku, J.Phys. Chem. Vol. B 102, pp. 6169, 1998.

[4] J.Zhang, Z.Tang, Z.Zhang, W.Fu, J.Wang and Y.Lin, Mate.Sci.Eng, Vol. A334, pp. 246-249, 2002.

[5] J.P.Zheng and H.S.Kwok, J.Opt.Soc.Am. Vol. B 9, pp. 2047-2053, 1992.