EFFECT OF Zn ADDITION ON LUMINESCENCE OF $\text{Y}_2\text{O}_3\text{:Eu}$ NANOPOWDERS USING SOLUTION COMBUSTION METHOD

ESMAEIL TOHIDLOU[†]

*Engineering Department, University of Sistan and Baluchestan, Zahedan, P.O.Box: 9816745563-161
Sistan-Baluchestan, Iran
etohidloo@yahoo.com*

YADOLAH GANJKHANLOU

*Materials and Energy Research Center, P.O. Box: 14155-4777
Tehran, Iran
yadolahl@gmail.com*

MAHMOOD KAZEMZAD

*Materials and Energy Research Center, P.O. Box: 14155-4777
Tehran, Iran
kazemzad@gmail.com*

MAHDI SHAFIEE AFARANI

*Engineering Department, University of Sistan and Baluchestan, Zahedan, P.O.Box: 9816745563-161
Sistan-Baluchestan, Iran
shafieeafarani@gmail.com*

In this study, the effect of Zn doping on photoluminescence, Chromaticity and structural properties of $\text{Y}_2\text{O}_3\text{:Eu}$ compound were studied. For this purpose, various $\text{Y}_2\text{O}_3\text{:Eu}$ samples containing different Zn^{2+} concentration and distribution were prepared by combustion method. The resultant samples were characterized by X-ray diffractometry (XRD), Photoluminescence spectroscopy (PL) and scanning electron microscopy (SEM). The XRD patterns of samples were also examined by Rietveld refinement method and results showed that the samples had nano-sized crystallites. It has been also shown that doping of Zn^{2+} ion in structure of $\text{Y}_2\text{O}_3\text{:Eu}$ compound can effectively enhance the PL intensity and chromaticity of $\text{Y}_2\text{O}_3\text{:Eu}$ compound, while doping of Zn at surface of $\text{Y}_2\text{O}_3\text{:Eu}$ powder reduces PL intensity, crystallinity and chromaticity of this compound.

Keywords: Photoluminescence; Zinc; Europium doped yttrium oxide; combustion.

[†] Lecturer and Member of Engineering Department, University of Sistan and Baluchestan

1. Introduction

Europium doped nanophosphors have wide applications in developing various displays (such as field emission displays, cathode ray tubes, back color of liquid crystal displays and plasma display panels), high density optical memories, biomedical tagging for genes and chromosomes, three color lamps and luminescent paints.^{1,2} Yttrium oxide is one of the most convenient hosts for Eu doped phosphors. The chemical and thermal stabilities of Y_2O_3 are higher than chalcogenide (sulfide and selenide) compounds such as $Y_2O_2SO_4$ and ZnS .³⁻⁵ It has also higher quantum efficiency and stability against high current densities, but unfavorable chromaticity and conductivity of $Y_2O_3:Eu$ compound decreases the cathodoluminescence intensity and results in limited application for this compound.⁴ These limitations can be overcome by addition of zinc to the $Y_2O_3:Eu$ phosphor. Solid state method has been usually applied for synthesis of this phosphor. It has been reported that the Zn^{2+} ion would be doped in dead layer (surface) of this phosphor, if conventional solid state method was applied for synthesis.³ By using defect chemistry, Shin et al.³ showed that cathodoluminescence (CL) intensity of $Y_2O_3:Eu$ phosphor was improved by addition of Zn in dead layer of this phosphor while doping of Zn into the structure of the phosphor decreases CL intensity. Although this conclusion is valid for CL results but the mechanism of excitation in PL and is not as same as the CL. Consequently, this result probably is not legitimate for PL. Therefore, in this study we try to study the effect of Zn doping in PL intensity and Chromaticity of $Y_2O_3:Eu$ compound.

Many researchers focused on developing simple and efficient synthetic methods for nanophosphors production.^{2,4,5,7,8} Herein we apply combustion method for synthesis which is both simple and economic technique applied for production of nanomaterials and it can be applied for production of phosphorescence compounds.²

2. Experimental

2.1. Samples preparation

Europium and yttrium nitrates were freshly prepared by reaction of europium and yttrium oxides (Eu_2O_3 , Y_2O_3) with nitric acid. The excess acid was eliminated by slow warming of solutions up to dryness. The Zinc carbonate [$Zn(CH_3COO)_2$] was used as Zn source. The stock solutions were prepared by dissolution of nitrate salts in deionized water in volumetric flask. Aqueous solutions of Europium, Zinc and yttrium salts with known stoichiometry were mixed together and urea was added as a fuel to the mixture (the molar ratio of urea to cations ion is 2.5 which is stoichiometric ratio in combustion reaction). The clear solution was heated in a muffle furnace until evaporation of excess water and suddenly combustion of the mixture. In order to doping of Zn at the surface of $Y_2O_3:Eu$ phosphor, $Y_2O_3:Eu$ phosphor prepared by the same route at first. Then, the resultant spongy product was grinded and impregnated in Zinc acetate solution following by heating until dryness of the solution. The

product finally was treated thermally at 600°C for an hour. Table 1 lists the compositions of prepared samples.

Table 1 composition of the prepared samples

sample	sample compositions	Zn ion distribution
A	Y ₂ O ₃ :Eu(3%)	-----
B	Y ₂ O ₃ :Eu(3%),Zn(2.5%)	at lattice
C	Y ₂ O ₃ :Eu(3%),Zn(2.5%)	at surface

2.2. Samples characterization

The resultant powder was characterized by XRD, SEM and PL analysis. The X-ray powder diffraction (Philips DW3710 using Cu K α radiation at 50 KV and 250mA in the range of 5-70) was used for crystal phase identification and estimation of the crystallite size. Photoluminescence spectra were recorded by PerkinElmer LS-6 spectrometer with 1nm step size and 60 nm/min speed in the range of 300-800 nm.

For determination of chromaticity color coordination (CIE), at first tri-stimulus values (X, Y, Z) for photoluminescence spectrum with intensities of $P(\lambda)$ are determined using the following formula:

$$X = K \int_{380}^{780} P(\lambda) \bar{x}(\lambda) d(\lambda), Y = KP(\lambda) \bar{y}(\lambda) d(\lambda), Z = K \int_{380}^{780} P(\lambda) \bar{z}(\lambda) d(\lambda) \quad (1)$$

Where $K = \frac{1}{P(\lambda)Y(\lambda)d(\lambda)}$ and $x(\lambda)$, $y(\lambda)$ and $z(\lambda)$ are the spectral stimulus values for the red, green and blue respectively at 2°. The spectral stimulus values are available in Ref. 6. Then, chromaticity color coordination can be calculated using the following formulas:

$$x = \frac{X}{X+Y+Z}, y = \frac{Y}{X+Y+Z}, z = \frac{Z}{X+Y+Z} \quad (2)$$

Rietveld refinements^{9,10} were carried out using Maud Software^{11,12} and using silicon standard sample (NBS640) for correction of instrument broadening, zero shift error and sample displacement error.

3. Results and discussion

Figs. 1 A, B and C show the XRD patterns of the samples. It can be seen that all sample have cubic phase with space group Ia-3 like Yttria structure. According to main peak intensity of sample, it can be concluded that by doping of Zn ion in surface, the crystallinity of sample was decreased whereas the crystallinity was not changed significantly by adding zinc in lattice.

Fig.1 XRD patterns and Rietveld patterns of all samples (the below bars show the cubic Y_2O_3 diffraction lines and the solid lines under each Figs. show the difference between predicted and recorded XRD pattern).

Table 2 lists the crystallite sizes, lattice parameters and micro-strains of samples that were computed by Rietveld refinement method. This Table showed that sample B had greatest lattice parameter and micro-strain. When Zn ion incorporated to the host lattice, it caused distortion of host lattice. As a result, the micro-strain and lattice parameter of the host was changed. Also, it can be seen that the crystallite size of sample B to the sample A was declined. Distortion and micro-strain of sample B decrease the crystallite size of this sample. Sample C had the smallest crystallite size indicating the low crystallinity of this sample. This lower crystallinity originated from grain growth inhibition caused by zinc oxide accumulated on the surface (grain growth can be prevented by lattice mismatch at surface). The agreement factor R of the refinement of samples XRD was also shown in Table 2. This factor was smaller than 10 for all samples and had the same level for all samples. Therefore, it can be concluded that good refinement was performed. For more validating of this conclusion, the difference between recorded XRD pattern and Rietveld predicted XRD Pattern is also shown at the bottom of figures 1 A, B and C. As it can be seen here, the difference values are almost zero at whole range of 2θ , indicating that good refinements were being performed.

Table 2 Results of Rietveld refinement of the samples.

sample	Lattice parameter (nm)	crystallite size (nm)	r.m.s micro-strain %	R
A	1.063	26.926	0.434	9.11
B	1.065	21.025	0.509	9.62
C	1.063	12.468	0.257	9.51

Fig. 2 represents the photoluminescence of samples. The peaks observed in 575-650 and 530-550 ranges were related to $^5D_0 \rightarrow \sum^7F_J$ ($J=0, 1, 2,$) and $^5D_1 \rightarrow ^7F_1$ transitions. The most important transitions are $^5D_0 \rightarrow ^7F_2$ and $^5D_0 \rightarrow ^7F_1$ transitions which are related to electric and magnetic dipole transitions, respectively. In this figure, it can be observed that the photoluminescence intensity enhances by doping of Zn ion in host lattice. For more evidence of this result, the peak ratio of electric dipole transition ($^5D_0 \rightarrow ^7F_2$) to magnetic dipole transition ($^5D_0 \rightarrow ^7F_1$) was calculated for all samples. This ratio is known as asymmetric ratio which is used as normalized intensity in some reports for comparison of various samples.¹³ Sample B has the highest value in comparison with samples A and B. Ekambaram et al.² assumed that doping of divalent ions in $Y_2O_3:Eu$ compound, makes interstitial oxygen decrease following by photoluminescence intensity improvement. This is due to absorption of some part of excitation radiation by interstitial oxygen without exhibiting of any emission.

Fig.2 photoluminescence spectra of all samples

Fig. 3 depicts CIE color coordinate of samples. From this figure it can be observed that sample B have the best chromaticity to the red color standard (which is shown with St in Fig. 4).

Fig.3 CIE color coordinate (chromaticity) of various samples

Fig. 4 depicts the SEM micrograph of sample B and C. It can be seen in both of samples B and C that the particles are partially agglomerated as a result of heat treatment. In addition, it can be seen that the sample B has to some extent ordered particles while the sample C has not. The latter contains more or less disordered particles and agglomerates indicating that the sample C has lower crystallinity than that of sample B.

Fig.4 SEM image of sample B and C.

4. Conclusion

In conclusion, the effect of Zn ion doping and its distribution on optical and crystallographic properties of $\text{Y}_2\text{O}_3\text{:Eu}$ compounds was studied. Results showed that incorporation of Zn ion in $\text{Y}_2\text{O}_3\text{:Eu}$ lattice, can effectively enhance the chromaticity and photoluminescence intensities without affecting the crystallinity. Nevertheless, doping of Eu in surface of $\text{Y}_2\text{O}_3\text{:Eu}$ compound decreases the crystallinity of sample which results in lower crystallinity and chromaticity of this sample.

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