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Preparation and Characterization of Y_2O_3, Sio2 Doped By Eu_2O_3 as Luminescent Ink

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Abstract

This article includes the preparation of luminescence materials from rare earth (Eu) ion doping Yttrium Oxide (Y_2O_3) 70% and SiO_2 25% and study the characteristics of phosphors for ultraviolet to visible conversion. The phosphor materials have been synthesized by two steps: Preparing the powder by solid state method using Y_2O_3, SiO_2 and Eu_2O_3 with doping materials concentration (70%, 25% and 5%) respectively and different calcination temperature (1000, 1200 and 1400 ^oC).

The second step is to prepare the colloid solution by dispersing the produced powder in a polyvinyl alcohol solution (4%) .

Powder preparation is achieved by mixing the powder according to weight percentage, milling by a ball mill using yttrium stabilized zirconia with the aid of propanol for homogenization then calcination the mixture at the above temperatures. The produced powder was characterized by X-Ray diffraction.

Colloid preparation is achieved by dissolving the PVA in water (4%) then dispersing the powder into the solution by using the hot plate magnetic stirrer and ultrasonic bath. The produced powder was characterized by using Fourier transform infrared (FTIR) and Photoluminescence spectra (PL).

The results of photoluminescence spectra show that samples were emitting red color with wave length of 612nm. The intensity of emission was increased with increasing calcination temperature.

Key Words: Luminescence, B. Solid State Reaction, C. X-Ray Diffraction.

Introduction

Luminescence is a collective term for the different ways in which substance emits visible light under the influence of certain radiation with the exception of pure heat. Also it was defined as the phenomenon of emission of light from various phosphor materials. Luminescence involves the excitation and subsequent relaxation of the valence electrons from there excited state. Luminescence is general terms of both phosphorescence and fluorescence [1]. Phosphorescence is a slow process in which emission continues for a few seconds, minutes or even hours after removing the excitation, whereas fluorescence is fast process in which emission stops abruptly after turning off the excitation [2].

In recent years, considerable research has been done on the synthesis and characterization of large band gap oxide materials (Wide-bandgap" refers to higher voltage electronic bandgaps significantly larger than one electronvolt eV. The exact threshold of "wideness" often depends on the context, but for common usage, "wide" bandgap typically refers to material with a band gaps of at least three eV)[3] such as Y_2O_3 and SiO_2 doped with rare-earth elements using different chemical methods such as sol-gel precipitation and combustion[4].

There are many advantages of luminescent materials, precise material deposition on substrate at well-defined positions, Small material consumption, Less material losses and it has excellent chemical stability [1]. Zhou Kai et al (2011), had presented a study on the effect of heat treatment on structure and up conversion emission of Er^{+3} doped GaF_3 / InF_3 based fluoride glasses. GaF_3 / InF_3 based oxyfluoried glasses were obtained by melt quenching method. They found that The intensity of green luminescence significantly increased in transparent glass-ceramic until the content of Er^{+3} reaches 2 mol.% compared to that in as –prepared, but without increasing linearly with the increasing time[5] . Wang Chaonan et al, had presented a study on the influence of synthetic condition(pH value of the precursor solution) on properties of Y_2O_3 : Eu^{+3} Nano phosphors by auto combustion method ,they indicate that samples prepared under high pH value have stronger luminescence intensity revealed by emission, samples with decreased pH value show a red shift and the decay curve show shorter lifetime with the increase of crystalline size [6].

There are many applications of luminescent materials which can be used in many fields, security ink, widely used in Cathode ray tube displays [7], plasma display panel[8], high radiation energy detection (such as to make films for X-ray detection) applications[9] and white light emitting diode (LED)[10] The aim of this work is to prepare luminescent ink from rare earth materials by solid state method which is the most widely used method for the preparation of polycrystalline solids from a mixture of solid starting materials. Solids do not react together at room temperature over normal time scales and it is necessary to heat them to much higher temperatures, often from 1000 to 1500°C in order for the reaction to occur at an appreciable rate. The factors on which the feasibility and rate of a solid state reaction include, reaction conditions, structural properties of the reactants, surface area of the solids, their reactivity and the thermodynamic free energy change associated with the reaction[11].

Experimental

The experimental part is performed by two steps the first is the preparation of the powder of Y_2O_3, SiO_2: Eu_2O_3 and the second step is preparation of the PVA colloid.

Materials used in the present work with their properties and sources are listed in table (1) below.

Table 1, Raw Materials and the properties

Item	Purity	Source	characterization
Y_2O_3	99.9%	Sigma Aldrich	Nano powder <50nm
SiO_2	99.5%	Sigma Aldrich	Nano powder <50nm
PVA	99%	Sigma Aldrich	n=89000-98000
Eu_2O_3	99.5%	Sigma Aldrich	Nano powder <150nm

Y_2O_3, SiO_2: Eu_2O_3 Powder Preparation

The powder is prepared by using solid state reaction. The starting materials and weights are listed in Table (2):

Table 2, The percentages of starting materials

Batch No.	Item	Weight Percentage %	Weight (g)
1	Y_2O_3 SiO_2 Eu_2O_3	70 25 5	4.142 0.393 0.461

Raw materials were weighed according to the above table in an electronic balance (five digits) inside a Nano-filtration system which shown in figure (1).

Fig. 1, Nano-filtration system (which conducted in laboratories of Sheffield Hallam University).

The powders were fed in a poly vinyl chloride bottles with balls made from yttrium stabilized zirconia (YSZ) as milling media, then the mixture was milled by using a ball mill for 24 hrs with 64.5 rpm, this process was performed with the addition of propanol to achieve homogenization.

After 24hr the mixture was poured inside stainless steel pan then dried in a Carbolite dryer for 4hr in 80 °C to evaporate propanol. The dried sample was calcined in an Naberthem furnace (which conducted in laboratories of Sheffield Hallam University) using an alumina crucible as a boat at a temperatures of 1000, 1200 and 1400 °C for 9 hrs.

The powder after calcination was milled again in the same previous way for 24 hrs with 64.5 rpm in order to prevent agglomeration.

X- Ray diffraction was used to characterize the powder after preparation by solid state method.

Colloid Preparation

To prepare the security ink, the powder was produced as colloid, this can be achieved by dispersing the powder in a poly vinyl alcohol $[CH_2CHOH]_n$, (n=89000-98000) inside a Nano-filtration system. First a solution of polyvinyl alcohol in water (4%) was prepared with the aid of Revotherm magnetic stirrer, homogenizer and heater which shown in Fig. (2).

Fig. 2, Magnetic stirrer, homogenizer and heater.

0.2 g of the powder was added to 20 ml of PVA solution. The suspension was also mixed and heated in a Revotherm magnetic stirrer and homogenizer with heating up to 50°C for 1 hr .Then mixing without heating for 2 hrs with the addition of 10 ml ethanol , a KERRY Ultrasonic bath(which conducted in laboratories of Sheffield Hallam University) was used for the third stage mixing and homogenization ,then the fourth stage of mixing and homogenization was achieved by magnetic stirrer and homogenizer for 2 hrs, The final product was a white solution which then tested by photoluminescence spectra and Fourier transform infrared.

Characterization

The characterization of powder was achieved by X-Ray diffraction.

The X-ray powder diffraction patterns presented in this work were measured in laboratories of Sheffield Hallam University using a theta to theta diffractometer (Philips), equipped with a Cu Kα source (generator: 40 kV and 40 mA) with wave length of 1.5418A, a scintillation detector with pulse-height analysis, and a variable knife-edge collimator for high resolution X-ray diffractometry. The best achievable instrumental resolution was 0.001° in 2θ.

Colloid Characterization

The prepared colloid characterization was achieved by measuring its photoluminescence spectra, in order to predict its capability to emit color (luminescence).

Photoluminescence spectra

Photoluminescence spectra is measured by using Fluoro Max-4 spectrofluorometer in laboratories of Sheffield Hallam University. The excitation wave length for all samples were 254 nm (at the ultraviolet region) produced by Xenon flash lamp then the emitted wave was detected by signal detector (photomultiplier tube and housing).

Fourier Transform Infrared

Fourier transform infrared is measured by NEXUS FTIR in laboratories of Sheffield Hallam University.

The variables of the instrument was
Number of scan: 64
Resolution: 4
Data spacing: 1.928cm^{-1}

Results and Discussion

X-Ray Diffraction

The analyses of X-ray diffractions for all synthesized samples were shown below according to their concentration and calcination temperature:

Figures (1), (2) and (3) shows the powder XRD patterns of the YSi:Eu powder with calcination temperature at 1000,1200 and 1400 ^{o}C indicate that a cubic structure of Y_2O_3:Eu was produced corresponding to the planes and 2θ. As shown in table (3):

Table 3

Planes(h k l)	2θ (degree)
(211)	20.53
(222)	29.18
(400)	33.81
(411)	35.92
(420)	37.91
(431)	43.49
(440)	48.54
(611)	53.21
(622)	57.59

When compared with International center for Diffraction Data (ICDD) card No. 25-1011 of cubic $(Y_{0.95}Eu_{0.05})_2O_3$[12]. There is peaks comes from SiO_2.

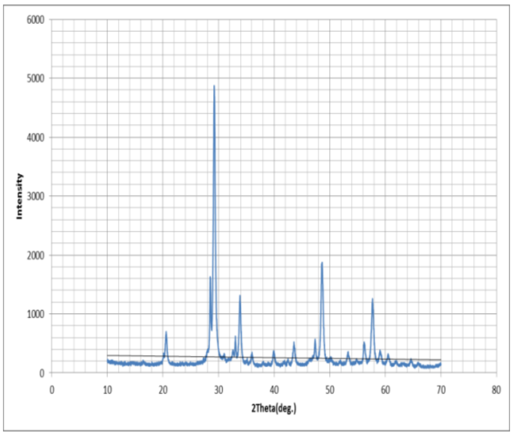

Fig. 3, XRD patterns for system Y Si Eu Calcined at1000˚C

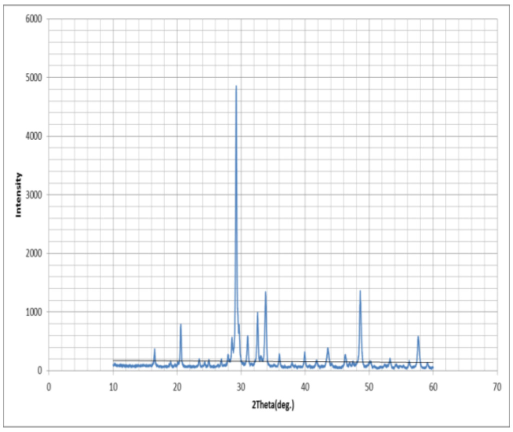

Fig. 4, XRD patterns for system Y Si Eu Calcined 1200˚C

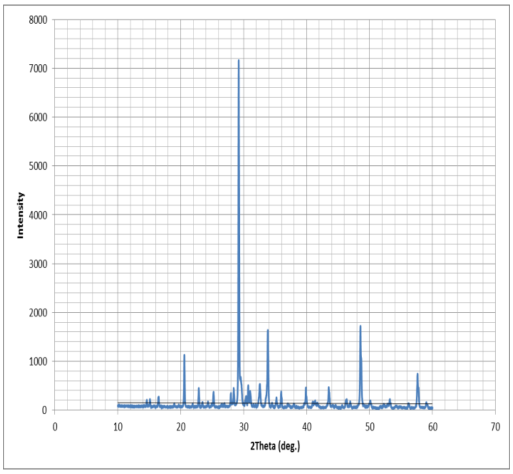

Fig. 5, XRD patterns Y: Si Eu Calcined 1400˚C

Fourier Transform Infrared

The analysis of Fourier transform infrared for all synthesized colloid is shown in figures (6) , (7) and (8) can be discussed by comparing it with the data of infrared absorption of pure materials according to the wave number. The broad peak at around 3340 cm^{-1} is originated from O-H stretching in hydroxyl groups. Both PVA and alcohol contain hydroxyl group. C-H stretching was observed at around 2980 cm^{-1} . Peak at around 2300-2400cm^{-1} is formed from C≡C group.

The peak at around 1600-1800 cm^{-1} was from C=O group. Absorption peak at around 1213-1420 cm^{-1} might originated from C-H bend and C-C stretching. C-O stretching was observed at around 1020-1100 cm^{-1}.

The absorption peak at around 890-1000cm^{-1} was originated from interaction between PVA chain of the solution and the surface of Y_2O_3, SiO_2 :Eu_2O_3 powder. Figures for all samples are shown below according to the concentration and calcination temperature.

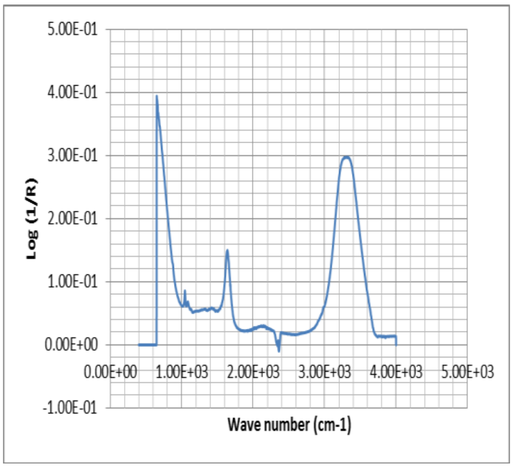

Fig. 6, The FTIR system of Y Si Eu calcined at 1000˚C.

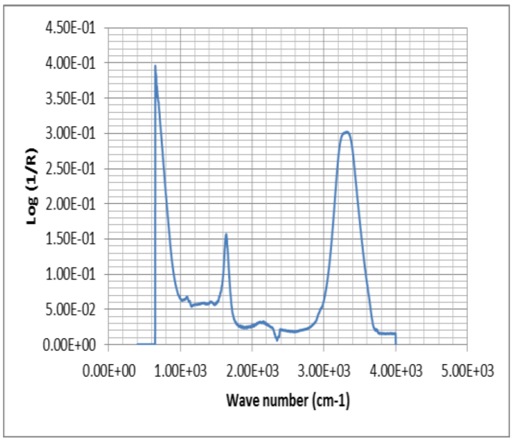

Fig. 7, The FTIR of system Y Si Eu calcined at 1200˚C.

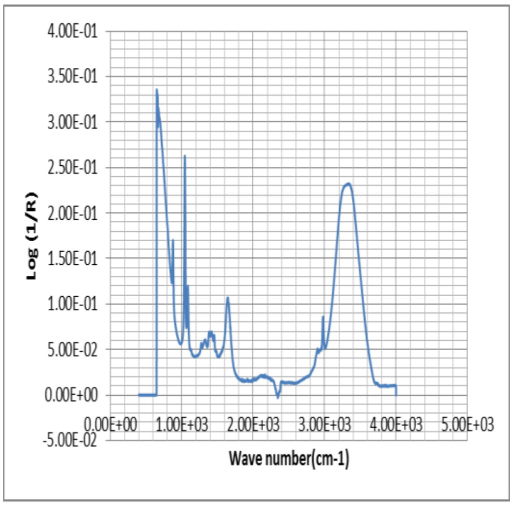

Fig. 8, The FTIR of system Y Si Eu calcined at 1400˚C.

Photoluminescence Spectroscopy

The analysis of Photoluminescence spectroscopy for all synthesized colloid are shown below according to the concentration and calcination temperature as shown in figures (9, 10 and 11).

From figure (9) below there are three peaks, the first one at wave length 508 nm it comes from 2λ(where the applied λ was 254 nm. The second tiny peak at wave length 612 nm from electron transition in Eu^{+3} ion from $^5D_0 \rightarrow ^7F_2$ (D,F represent energy level) and this peak represent the luminescent of sample which calcined at 1000˚C but it has low intensity when compared with the other two samples.The third peak at wave length 760 nm from 3λ (where λ is the applied wave length) .

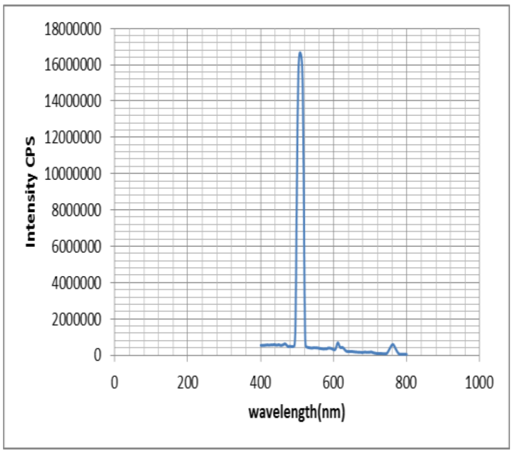

Fig. 9, Photoluminescence spectra of Y Si Eu calcined at 1000˚C.

From figure (10) below there are five peaks, The first peak at wave length 508 it comes from 2λ where the applied λ was 254 nm , The second peak at wave length 585 nm comes from electron transition in Eu^{+3} ion from $^5D_0 \rightarrow ^7F_1$. The third peak at wave length 612 nm comes from electron transition in Eu^{+3} ion from $^5D_0 \rightarrow ^7F_2$.

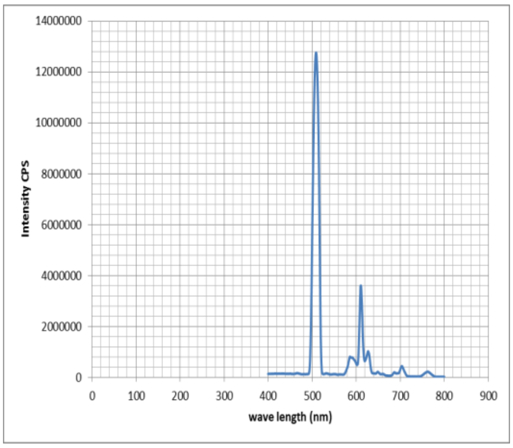

Fig. 10, Photoluminescence spectra of Y Si Eu 5% calcined at 1200˚C.

The fourth peak at wave length 700 nm comes from electron transition in Eu^{+3} ion from $^5D_0 \rightarrow ^7F_3$ (D,F represent energy level) . The fifth peak at wave length 760 nm it comes from 3λ (where λ is the applied wave length).The thired peak is represent the emission (luminescence) of this sample which calcined at 1200 ˚C and it is higher in intensity than sample calcined at 1000˚C

From figure (11) below there are four peaks, the first one at wave length 585 nm comes from electron transition in Eu^{+3} ions from $^5D_0 \rightarrow {}^7F_1$.

The second peak at wave length 612 nm comes from electron transition in Eu^{+3} ion from $^5D_0 \rightarrow {}^7F_2$ and this peak is represent the luminescence of sample calcined at 1400˚C ,it has higher intensity when compared with the other two samples. Photo luminescence intensity increased with increasing calcination temperature. The third peak at wave length 700 nm comes from electron transition in Eu^{+3} ion from $^5D_0 \rightarrow {}^7F_3$. The fourth peak at wave length 760 nm it comes from 3λ.

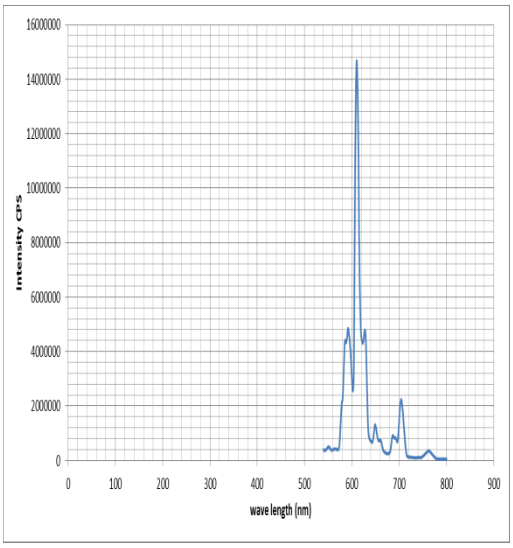

Fig. 11, Photoluminescence spectra of Y Si Eu 5% calcined at 1400˚C.

Conclusion

Stable luminescent colloid was produced from Y_2O_3,SiO_2:Eu powder dispersed in poly vinyl alcohol solution. Y_2O_3,SiO_2:Eu played a major role as luminescent centers in the colloid which emitted red luminescence. This colloid can meet several applications in optoelectronics such as for production of light emitting devices, light sensor, and luminescent displays in a very definitive sizes and shapes. In this work the colloid used as luminescent ink to print the valuable document and saving it from fake by writing it on a white paper, this cannot be read until applying ultraviolet light, then the wrote document will appear in red color. Increasing calcination temperature of the powder lead to increase luminescent intensity of the emission.

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