

Ceramic Materials (Phosphors) for Display Applications

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Abstract

Phosphors the ceramic materials should able to work in tough environment surrounded and bombarded by high energy Vacuum Ultra Violet (VUV), UV or electron beam radiations in any discharge tube. The plasma display panel (PDP) is increasingly gaining attention over conventional cathode ray tube (CRT)-based TVs as a medium of large format (60⁺) television (TV), particularly high definition TVs (HDTVs). Improvements have been made not only in size but also in other areas such as resolution, luminescence efficiency, brightness, contrast ratio, power consumption, and cost reduction. The formation of a phosphor host and doping process by solid solution is critical and is highly dependent on the reaction temperature and conditions. Since the purity of starting chemicals is very important to the synthesis of phosphors, the starting chemicals are typically 99.9%, 99.999% in purity. Required amounts of starting ingredients are mixed in the presence of an appropriate flux (if necessary) and fired at high temperatures (1200°C) in air or in a controlled atmosphere (N₂, C, CO, or N₂ with 2-5% of H₂). The present paper reports the synthesis and luminescence characteristics of different ceramic materials (phosphors) for display applications

Introduction

The tough materials in the ceramic form are the inorganic silicate phosphors; zinc silicate doped with divalent manganese ions is well known for its high luminescence efficiency coupled with excellent color purity and application for lamps and cathode ray tubes as a green phosphor. Zn₂SiO₄ and Sr₂CeO₄: Eu has been identified as a very suitable host matrix for many rare earth dopant ions with excellent luminescent properties in the blue, green and red spectral zones including its chemical stability. However last past few years, greater attention has been paid to the study of luminescence properties of rare earth ions (Mn²⁺, Ce³⁺, Tb³⁺ and Eu³⁺ etc..) doped zinc silicate phosphors in powder and thin film forms with a view to examining their application for flat panel display devices for

example as a plasma display panels, field emission displays and thin film electroluminescence devices etc. Terbium and Ce ions are very good luminescent performance. Therefore Rare earth ions are better candidates for luminescence centers. Properties, relevant for PDP application, of Mn²⁺-activated Zn₂SiO₄ phosphors have been investigated. The luminescence properties of Mn doped zinc silicate nano-crystalline phosphors, already reported as well as known Zn₂SiO₄:Mn²⁺ shows a strong green emission, since we know that Zn²⁺ and Mn²⁺ ions have similar oxidation states, and ionic radius. The Sr₂CeO₄:Eu is a very good phosphor in emission region of 400-650 nm which is a visible region.

Experimental Details

ZnO, SiO₂ and MnCO₃ were mixed and ground thoroughly using ball mill prior to this all the materials are weighed as per the required quantities. Then this mixture was fired initially at 1000 °C

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for 2 hrs and fired again for 1200 °C for 4 hours in air. Analytical grade reagents with purity greater than 99% were used for the synthesis this material. To prepare Sr₂CeO₄ host phosphor, the starting chemicals, strontium nitrate and cerium nitrate of assay 99.9% were taken in appropriate stoichiometry of 2:1 were weighed, mixed and grounded using agate mortar and pestle for 1 hour to make fine powder. The samples were heated at 1200°C for 4 hours in air using muffle furnace with a heating rate of 4°C/min. The same procedure was followed to prepare La, Pr, Nd, Sm, Eu, Gd, Tb, Er, Dy (0.5%) doped Sr₂CeO₄ phosphor. The photoluminescence spectra were recorded at room temperature using Spectrofluorophotometer (SHIMADZU RF5301 PC), XRD using synchrotron beam line-12 and SEM (XL 30 CP Philips) studies are done on the prepared samples.

Results and Discussion

Zn_{2-x}Mn_xSiO₄ is a classical green emitting phosphor, and it has been used in many applications, such as CFL, CRT, PDP etc. In this paper, Zn₂SiO₄:Mn²⁺ green phosphor was synthesized using the solid-state reaction method. Photoluminescence and crystalline properties were examined as functions of the firing temperatures. Zn_{2-x}Mn_xSiO₄ was ground and fired at 1200 °C for 4 hours in air, but intensity of emission is weak. Therefore the conditions of firing were changed and Zn_{2-x}Mn_xSiO₄ was grinded and fired at 100°C for 2 hours in air and again grinded and fired at 1200 °C for 4 hour

in air respectively. When varies SiO₂ value from 0.9 to 1.8 however the ZnO is 1.92 as well as MnCO₃ is 0.08 are constant, The SiO₂ concentration (1.1) show good PL Spectra. The PL peak observed at 524 nm in these phosphors suggests their potential use as green emitting phosphors.

Sr₂CeO₄ doped with La, Pr, Nd, Sm, Eu, Gd, Tb, Er, Dy (concentration 0.5%). The prepared phosphors are characterized by doing XRD using synchrotron beam line on Indus-2, RRCAT, Indore and SEM using CP30 Philips. Figure-1 is the XRD of Sr₂CeO₄ doped with Eu&Er(0.5%) phosphor. The crystallite size was calculated using Scherer's formula $D = K\lambda / \beta \cos\theta$, where K the constant (0.94), λ wave length of the X-ray (0.895Å), β the full width at half maxima (FWHM) and θ the Bragg angle of the XRD big peak. The average crystallite size was calculated using Scherer's formula is 12 nm. The PL emissions are centered mainly on 470 nm followed by the characteristic emissions of the rare earth elements. The present phosphor can be used as White Light LEDs.

The excitation spectra of Zn₂SiO₄:Mn²⁺ under 254 nm is presented in Fig.2. The excitation 254 nm is the strongest excitation, which is attributed to the charge transfer transition of Mn²⁺. Fig.2 is the photoluminescence spectra of Zn₂SiO₄:Mn²⁺ (1.92:0.08), however SiO₂ concentration is 1.1 excited with 254 nm. This PL Spectra show highest intensity when SiO₂ concentration varies 0.9 to 1.6. Increase in SiO₂ concentration from 1.3 to 1.8% the PL intensity also decrease when temperature increase from 1300 to 1400. Using two fold firing system,

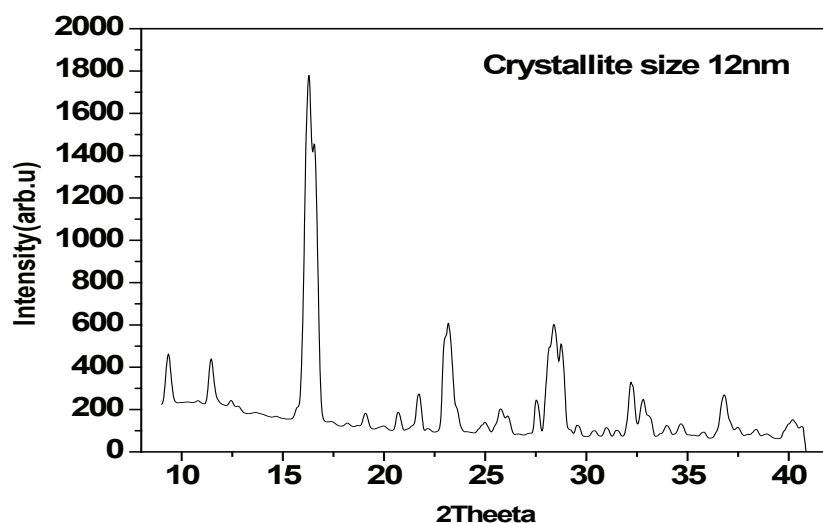


Fig. 1. XRD Pattern of Sr₂CeO₄:Eu(0.5%),Er(0.5%)

first step to fire at 1000 °C in air for 2 hour take out the sample cooled and grinded and again fire for 1200 °C for 4 hours in air medium. $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$ (1.92:0.08) of 1000/2h+1200/4h fired samples is show highest PL intensity with a PL peak position at 524 nm when compare to all PL emission spectra. It is noted that the PL intensity is increasing when SiO_2 concentration increase up to certain value such as 1.1. The mission at 524 nm is due to d-level spin-forbidden transition of Mn^{2+} (${}^4\text{T}_1 \rightarrow {}^6\text{A}_1$).

Finally the experimental data show that different SiO_2 concentrations and different firing temperatures in air medium lead to formation of good $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$. Therefore we concluded that SiO_2 concentrations having important role to achieve good PL intensity. $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$ phosphors have been very important phosphor as a green component in the PDP application. The efforts have been made for the performance of $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$ phosphors to the PDP application. However very complicated interactions between Mn ions, the decay behavior is too difficult to be interpreted.

The excitation and emission spectra of Sr_2CeO_4 prepared by solid state and combustion routes (with urea and citric acid as fuel) are presented in Fig.3. Excitation at 280 nm and 290 nm exhibited broadband emission peaking at 475 nm. This luminescence originates from the ligand (O^{2-}) to metal (Ce^{4+}) charge transfer transition. Due to completely allowed nature of transition, the luminescence is quite intense. The luminescence intensity of Sr_2CeO_4 was found to be varying depending on the method of preparation. Cerates prepared through combustion synthesis

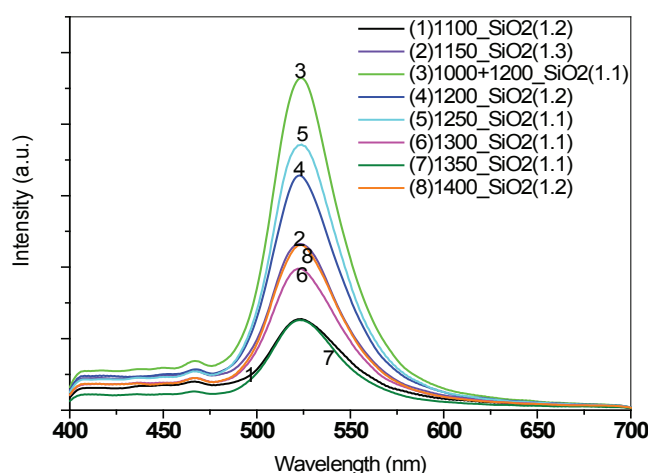


Fig.2. PL Emission Spectra of $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$ phosphors

exhibited maximum luminescence compared to cerates prepared by solid-state reaction urea and citric acid fuels, the samples prepared using citric acid exhibited better luminescence intensity. The improved emission intensity at 475 nm from combustion synthesized phosphor was probably due to excellent homogeneity of reactants at molecular level in case of combustion synthesis. This apart, during the combustion process a large amount of gas evolves which may help in the formation of sub micrometer sized particles increasing the packing density resulting in enhanced luminescence intensity

Excitation and emission profiles of rare earth doped and the blank Sr_2CeO_4 are shown in the Fig.3. The excitation peak of Eu^{3+} usually appears at 394 nm in several hosts was conspicuously absent in $\text{Sr}_2\text{CeO}_4:\text{Eu}^{3+}$ only 261 nm excitation peak was observed. Upon excitation at 280 nm both Ce^{4+} emission and Eu^{3+} emission were observed. The emission spectra of strontium cerate with Eu^{3+} and without Eu^{3+} were different. The blank cerate samples showed emission peak at 467 nm whereas Eu^{3+} doped samples exhibited several peaks at 466,490,511,538,557,587,616 nm, the Ce^{4+} emission band at 467 nm. All these peaks are from characteristic emission of Eu^{3+} ions. Similarly, the representative emission peaks of Dy^{3+} were observed at 482 nm and 572 nm respectively. However, Gd^{3+} does not luminescence in this host. The presence of rare earths (Eu^{3+} , Dy^{3+} , and Gd^{3+}) has substantially quenched the Ce^{4+} emission intensity as seen in the Fig.3.

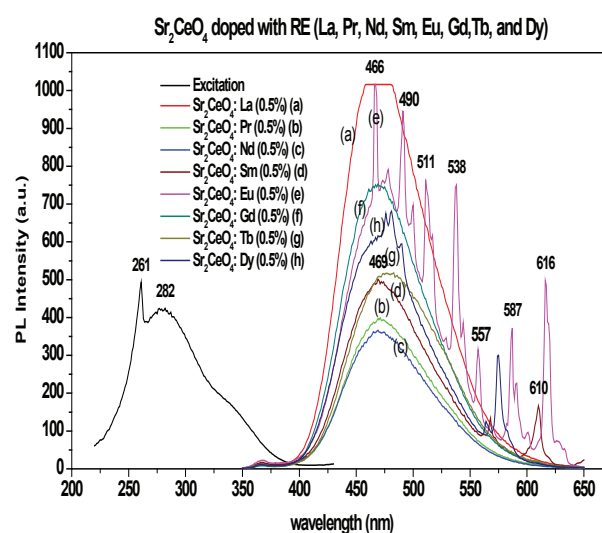


Fig.3. Excitation and emission of RE^{3+} (0.5%) doped Sr_2CeO_4 phosphor

Conclusion

Zinc silicate doped with Mn^{2+} phosphors were prepared via high temperature solid state reaction in air medium. Overall results show that the PL intensity monitored at 524 nm with 254 nm excitations displays a good green emission from $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$ phosphor system. The ${}^4\text{T}_1({}^4\text{G}) \rightarrow {}^6\text{A}_1({}^6\text{S})$ transition, is directly responsible for the green light emission. Sr_2CeO_4 prepared through combustion route exhibited better luminescence intensity than prepared through solid-state reaction. Doping of Eu^{3+} , Dy^{3+} and Gd^{3+} in this host quenched the cerium luminescence significantly. This quenching of cerium luminescence probably due to energy transfer from cerium to rare earths dopants prepared in inert atmosphere exhibited the higher luminescence intensity. Ce^{3+} was significantly present in the surface of the samples along with Ce^{4+} and the origin of luminescence is still a matter of investigation. However, the excellent luminescence intensity makes it a promising candidate for display and illumination in blue region and $\text{Sr}_2\text{CeO}_4:\text{Eu}$ looks a good candidate for white LED as a single host.

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