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Original Article

Luminescence studies on the europium doped strontium metasilicate phosphor prepared by solid state reaction method

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ABSTRACT

Europium doped strontium meta-silicate (namely $SrSiO_3:Eu^{3+}$) phosphor was prepared by traditional high temperature solid state reaction method. Crystal structure of sintered $SrSiO_3:Eu^{3+}$ phosphor was investigated which confirms the monoclinic structure. Energy dispersive X-ray spectrum (EDS) confirms the presence of elements in discussing phosphor. Thermoluminescence (TL) kinetic parameters such as activation energy (E), order of kinetics (b) and frequency factor (s) were calculated by peak shape method. The orange-red emission was originated from the $^5D_0-^7F_J$ (J = 0, 1, 2, 3, 4) transitions of Eu^{3+} ions; could be clearly observed after sample was excited at 396 nm. It is shown that the phosphor with almost pure orange-red color purity (99.62%) and with a quantum efficiency of 10.2% (excited by 396 nm) can be obtained, which is higher than the commercial red phosphors $Y_2O_3:Eu^{3+}$, $Y_2O_2S:Eu^{3+}$ with quantum efficiencies of 9.6% (excited by 394 nm) and 4.2% (excited by 395 nm), respectively. Mechanoluminescence (ML) intensity of discussing $SrSiO_3:Eu^{3+}$ phosphor was increased linearly with increasing the impact velocity of the moving piston; which suggest that, the discussed phosphor can be used as stress sensor. Thus, the present investigation indicates the piezo-electricity was responsible to produce ML in prepared phosphor.

1. Introduction

The phosphors are widely used in emissive displays. However, all currently used phosphors still need considerable improvement, such as lower current saturation, higher efficiency, and better chromaticity [1]. Oxide based phosphors (including silicate phosphors) are more chemically and physically stable than sulfide and aluminates phosphors under high Coulomb loading. Metal silicates have been widely reported as promising host materials for rare earth and transition metal ions with excellent luminescence properties in blue, green and red spectral regions [2]. Strontium silicate phosphor would be ideal from the manufacturing point of view, because both strontium and silica are abundant and are relatively inexpensive. These materials are widely used in the illumination, displays, storage devices, medical instruments and many more [3,4].

Rare earth oxides (RE_2O_3) are the most stable rare earth compounds, in which the rare earth ions hold typically a trivalent state [5]. Rare earth oxides have been widely used in the field of luminescent devices, optical transmission, bio-chemical probes, medical diagnosis and so for, because of their optical, electronic and chemical properties resulting from their 4f electrons [6,7]. Inorganic compounds doped with trivalent europium cations (Eu^{3+}) are used for many different applications. Luminescence properties of Eu^{3+} ions involve intra $4f^6$ (4f–4f) transitions mechanisms between the excited state to ground state [8,9]. The emission wavelength of the 4f–4f transition of Eu^{3+} is relatively insensitive to the host and temperature because the 4f shell is shielded by the outer filled 5s and 5p shells. Eu^{3+} ions were employed in luminescent devices such as fluorescent lamps and cathode ray tubes [10]. Currently transitions of Eu^{3+} ions have attracted considerable interest owing to the attempt to develop novel phosphors that can improve the color temperatures and the color rendering index of White Light Emitting Diode (WLED) [11].

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Recently, White Light Emitting Diodes (WLEDs) are expected to replace conventional incandescent and fluorescent lamps in the near future because of their benefits in terms of high brightness, reliability, long life time, low environmental impact and energy-saving. At present, the common way for manufacturing WLEDs is to combine a blue LED with $Y_3Al_5O_{12}:Ce^{3+}$ phosphor [12]. Although this type of WLEDs has a high luminous efficiency, it still reveals a low color rendering index because of deficiency in red light component [13,14]. Thus, it is needed to develop more efficient red or orange- red emitting phosphors suitable for the fabrication of WLEDs. So, we synthesized $SrSiO_3:Eu^{3+}$ phosphor and studied the luminescent properties. To the best of our knowledge, neither, both the photoluminescence (PL) and mechanoluminescence (ML) properties of Eu^{3+} doped $SrSiO_3$ phosphor nor the work of $SrSiO_3$ compound prepared by the solid state reaction method has been reported in the literature. Therefore, in the present work, we report the phosphor synthesis, structural characterization and luminescence properties of $SrSiO_3:Eu^{3+}$ phosphor by the solid state reaction method. Investigation on the crystal structure, surface morphology, elemental analysis, different stretching bands of sintered phosphor was determined by the X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), energy dispersive X-ray spectroscopy (EDS) and Fourier transform infrared (FTIR) spectroscopy techniques. Luminescence properties were also investigated on the basis of Thermoluminescence (TL), TL spectra, PL, CIE color coordinates, color purity, quantum efficiency, decay, ML and ML spectra studies.

2. Experimental

2.1. Phosphor synthesis

Europium doped strontium meta-silicate phosphor was prepared by the conventional high temperature solid state reaction method. The starting materials were strontium carbonate [$SrCO_3$ (99.90%)], silicon di-oxide [SiO_2 (99.99%)] and europium oxide [Eu_2O_3 (99.99%)], all of analytical grade (A.R.); were employed in this experiment. The contributions of europium oxide in the $SrSiO_3:Eu^{3+}$ phosphor was 2.0 mol%. Boric acid [H_3BO_3 (99.99%)] was added as flux. The chemical reaction used for stoichiometry calculation is:

$$SrCO_3 + SiO_2 + \xrightarrow{1250\ ^\circ C} SrSiO_3 + CO_2\uparrow$$
$$2SrCO_3 + 2SiO_2 + 2Eu_2O_3 \xrightarrow{1250\ ^\circ C} 2SrSiO_3 : Eu^{3+} + 2CO_2 + 3O_2\uparrow \quad (1)$$

Initially, raw materials were weighed according to the nominal compositions of $SrSiO_3:Eu^{3+}$ phosphor. Then the powders were mixed and milled thoroughly for 2 h using mortar and pestle. The ground sample was placed in an alumina crucible and subsequently fired at 1250 °C for 3 h in an air. At last the nominal compounds were obtained after the cooling down of programmable furnace and products were finally grounded into powder for characterizing the phosphors.

2.2. Measurement techniques

The Powder XRD pattern has been obtained from the Bruker D8 advanced X-ray powder diffractometer and the data were collected over the 2θ range 10°–80°. The morphological image of prepared phosphor was collected by the FESEM. Prepared phosphor was coated with a thin layer of gold (Au) and then the surface morphology of sintered phosphor was observed by FESEM; ZIESS Ulta Plus-55 operated at the acceleration voltage of 15 kV. An EDS spectrum was used for the elemental (qualitative and quantitative) analysis of the prepared phosphor. An FTIR spectrum was recorded with the help of IR Prestige-21 by SHIMADZU for investigating the finger print and functional groups region of prepared phosphor. FTIR spectrum was collected in the middle infrared region by mixing the potassium bromide (KBr, IR grade) with prepared $SrSiO_3:Eu^{3+}$ phosphor. The TL glow curve was recorded with the help of TLD reader 1009I by Nucleonix (Hyderabad, India Pvt. Ltd.). TL and ML spectrum was recorded with the help of different band pass interference (400–700 nm) filters. Excitation and emission spectrum was recorded on a Shimadzu (RF 5301-PC) spectro-fluorophotometer using the Xenon lamp (150 W) as the excitation source when measuring. The color chromaticity coordinates were obtained according to CIE 1931. The decay curve was obtained using a time resolved fluorescence spectroscopy (TRFS) from Horiba Jobin Yvon IBH to measure the fluorescence lifetimes of the prepared phosphor (pulsed lasers as excitation source). The ML measurement was observed by the homemade lab system comprising of an RCA-931A photomultiplier tube (PMT). The ML glow curve can be plotted with the help of SM-340 application software installed in a computer attached with the storage oscilloscope. All measurements were carried out at the room temperature.

3. Results and discussions

3.1. XRD analysis

The powder XRD pattern of prepared sample was investigated for the crystal structure confirmation. The typical XRD patterns of $SrSiO_3$ and $SrSiO_3:Eu^{3+}$ phosphors with JCPDS file was shown in Fig. 1(a). XRD patterns of prepared $SrSiO_3$ and $SrSiO_3:Eu^{3+}$ phosphors were consistent with JCPDS 24-1230 file [15]. In Fig. 1(b), the position and intensity of diffraction peaks of prepared $SrSiO_3:Eu^{3+}$ phosphor was matched and found to be consistent with the standard Crystallography Open Database (COD) card No. 96-200-6167 by MATCH 2 software. The figure of merit (FOM) while matching these was 0.8446 (85%) which illustrates that the phase of the prepared phosphor agrees with standard pattern COD card No. 96-200-6167. From the analysis of $SrSiO_3$ and $SrSiO_3:Eu^{3+}$ XRD patterns, it was found that the little amount of doped Eu^{3+} ions has no effect on the $SrSiO_3$ phase structure. From Fig. 1(b), it can be concluded that prepared samples were chemically and structurally strontium meta-silicate ($SrSiO_3$) phosphor.

The indexing and refinement of lattice parameters were investigated using software Celref V3. The crystal structure of discussing phosphor was a monoclinic structure with space group C12/c1. The lattice parameters of monoclinic $SrSiO_3:Eu^{3+}$ phosphor was founded as; a = 12.327 Å, b = 7.138 Å, c = 10.881 Å, α = 90°, β = 111.57°, γ = 90° and cell volume = 892.06 (Å)^3, Z = 12 is nearly same [a = 12.333 Å, b = 7.146 Å, c = 10.885 Å, α = 90°, β = 111.57°, γ = 90° and cell volume = 892.13 (Å)^3, Z = 12], with the standard lattice parameters which again signifies the proper preparation of discussing $SrSiO_3:Eu^{3+}$ phosphor. There are few extra peaks in an observed XRD pattern which could be due to the number of stacking faults induced by the presence of doping ions and also due to secondary phases and impurities formed during the elaboration process. The calculated spectrum confirmed the presence of monoclinic $SrSiO_3:Eu^{3+}$ phosphor.

3.2. FESEM study

FESEM study was carried out to obtain information about surface morphology, grain size, and shape of the synthesized phosphor. The morphologies of prepared $SrSiO_3:Eu^{3+}$ phosphor was also observed by means of FESEM in Fig. 2. The surface of discussing $SrSiO_3:Eu^{3+}$ phosphor has shown irregular shapes which mean the

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