Optical Characterization of Eu^{3+} Doped and Undoped Sr_2CeO_4 Phosphors

İsrafil Şabikoğlu[1]*

[1]Celal Bayar University, Department of Physics, 90236 201 3126, sabikoglu@hotmail.com
*Corresponding author

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Abstract

The typical blue phosphor Sr_2CeO_4 material was prepared by different routes and also synthesized by different techniquies such as Pechini's method, high temperature solid–state reaction, citrate–gel/sol-gel method, microwave calcination method, combustion method, and microwave–accelerated hydrothermal method. The luminescent compound materials doped with Europium (Eu) have various luminescence features in different lattice parameters, which are important in fields of displays (FEDs), plasma display panel devices, lamps and cathode ray tubes (CRTs) etc. In this study, a rare earth material Eu doped Sr_2CeO_4 phosphors and undoped Sr_2CeO_4 were synthesized by the conventional solid–state reaction method and characterized by X–ray diffraction (XRD), scanning electron microscopy images (SEM) and radioluminescence (RL) measurements. The Undoped Sr_2CeO_4 has a broad band with a peak position around 500nm due to the charge transfer (CT) mechanism. The Eu is an excellent host lattice activator yielding a strong emission in comparison to the luminescence from the well–known Sr_2CeO_4. Strong red emission coming from the hypersensitive $^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+} ion suggested the presence of the dopant ion in a structurally disordered environment. From the XRD data, the average crystallite sizes of undoped and Eu doped Sr_2CeO_4, calculated using the Scherer's Formula are found to be 72nm and 73nm respectively.

Keywords –Radioluminescence (RL), Solid–State reaction method, inorganic compounds, Sr_2CeO_4, optical properties.

1 Introduction

The rare earth (RE) doped phosphor materials have interested for their well-described transitions intro-4f shell [1]. It is known that the Eu is a unique activator that giving both broad band and narrow band emissions as a dopant in a phosphor [2]. This property explains the prominent role played by Eu as luminescent probes. In the last decade the nanoscience and the nanotechnology has been made possible by the success in the synthesis of nanomaterials. The synthesis of nanomaterials includes the control of their size, shape and structure [3].

Over the past few years, nanoparticles (especially the powders) of ceramic materials have been produced on a large scale in terms of using by physical and chemical methods. In order to obtain an efficient phosphor, the notation between host and activator is a key factor. Most phosphors consist of a host composition and an activator, added in carefully controlled quantities. The activator itself will act as a substitutional defect and is subject to lattice phonon perturbations [4].

Recently, a new promising blue phosphor material, Sr_2CeO_4 was developed by combinatorial chemistry [5] and prepared by different routes. Sr_2CeO_4 was also synthesized by some other techniques such as Pechini's method [6], solid–state reaction [7], citrate–gel method [8], microwave calcination method [9], combustion method [10] and microwave–accelerated hydrothermal method [11].

The luminescence behavior of Eu involved in different host lattices has found applications concerned with its light emission, which are important in fields of displays (FEDs), plasma display panel devices, lamps and cathode ray tubes (CRTs)[12,13].

Sr_2CeO_4 phosphor material has an orthorhombic structure, which comprises of one–dimensional chains of edge–sharing CeO_6 octahedral coupled with strontium ions. This structure of Sr_2CeO_4 can absorb energy by itself and acts as a sensitizer to transfer the absorbed energy to the luminescence centers CeO_6 octahedral which are responsible for the occurrence of blue emission [14].

Unlike most other rare earth based oxide phosphor materials, the emission behaviour from Sr_2CeO_4 material is immense and has uncharacteristically long excited lifetimes. The luminescence of Sr_2CeO_4 is considered to originate from CT transition [15]. Sr_2CeO_4 phosphor material is 100% active center concentrated material, which means all CeO_6 octahedral bonding may be taken into account fluorescent centers and the quantum efficiency is so lofty. The Eu^{3+} as a rare earth material is the most prevalently studied. It can be used in commercial red phosphor due to luminescent behavior and spectral features.

In this study, the strontium cerate phosphors (undoped Sr_2CeO_4 and Eu doped Sr_2CeO_4) are prepared using the high temperature conventional solid–state reaction (CSSR) method. The luminescence features and microstructures of the powder materials are discussed. Furthermore, the RL properties of the powder materials resulting from electron transition and activators were investigated. The crystal structure and the surface structure of the powder materials were studied by employing XRD and SEM techniques, respectively.

2 Experimental

The CSSR method is the most commonly used method of preparing different components by diffusion of solid components at high temperatures. This method is frequently used for the synthesis of luminescent materials. Sr_2CeO_4:Eu was synthesized with Europium oxide (Eu_2O_3) doping by a CSSR for comparison reasons. The powder form, strontium carbonate ($SrCO_3$), cerium oxide (CeO_2), and europium oxide (Eu_2O_3) of high purity chemicals (99.999%, Sigma–Aldrich) were used as–precursor materials to prepare Sr_2CeO_4 host material and Eu doped phosphors.

The powder $SrCO_3$, and CeO_2 in stoichiometric proportions of Sr:Ce as 2:1 is weighed and mixed in agate mortar to create a host material. In addition, another host material, 0.1mol% Eu_2O_3 doped Sr_2CeO_4 material was synthesized as well. All the processes were performed in a nitrogen–filled glove box. The ground samples were placed in an alumina crucible and fired at 1100°C for 3h in a muffle furnace with a heating rate of 5°C/min. The samples were then allowed to cool room temperature over a period of approximately 20h. Note that this slow cooling provides for the formation of the ceramic structure, in opposite situation the fast cooling can be converted the material to the glassy form. Philips–Xpert Pro XRD spectrometer equipment is used for the phase formation and crystal structure of the phosphor materials using Cu K_α line (λ=0.15418nm). The microstructure of the samples was studied using SEM (Philips XL–30 SFEG, SEM). All the spectra were recorded at room temperature.

The Machlett OEG–50A X–ray tube with a W target which is integrated with RL equipment system was used for excitation of the material. Approximatly the 0.5Gy/s X-Ray radiation dose rate was applied on the material. Emited light come from the material was collected with JobinYvon spectrometer integrated with liquid nitrogen cooled charge–coupled device (CCD).

All the spectral data are plotted in ′′arbitrary units of intensity (a.u.)′′.

3 Results and Discussion

XRD measurements were showed the impurities in the structure and the phases of different composition from Sr_2CeO_4. A typical XRD pattern of the resultant $Sr_2CeO_4:Eu^{3+}$ is shown in Fig. 1(a, b, c). The XRD pattern for the parent Sr_2CeO_4 is also given for comparison. From the Fig.1, the Sr_2CeO_4 phase is formed in the structure. The diffraction peaks are well indexed on the basis of JCPDS card no 50–0115. The structure of Sr_2CeO_4 is orthorhombic according to spectrum; also Sr_2CeO_4 is quite compatible with the previous studies [5, 20, 22]. However, some previous work indicates that the crystal structure of Sr_2CeO_4 is triclinic [6, 23]. Even though it has been described with different crystal structures in literature, the obtained pattern results are similar. The pattern results show a crystallized pure Sr_2CeO_4 phase, especially for materials synthesized by the solid–state method at higher temperature (as in this study, ~1100°C) [8, 23]. On the other hand, the crystalline size was determined using the Scherrer equation $D = k\lambda/\beta\cos\theta$, where k is the constant (0.94), λ

is the wavelength of the X–ray (0.15418nm), β is the full–width at half maxima (FWHM) and θ is the Bragg angle of the XRD peak. The calculated average crystal size of Sr_2CeO_4 is about 72nm. No other product of the starting material was observed, the phase composition of materials is low–temperature monoclinic phase (α–phase). In addition Eu^{3+} ions in the material (structure) have no obvious affect on the host lattice.

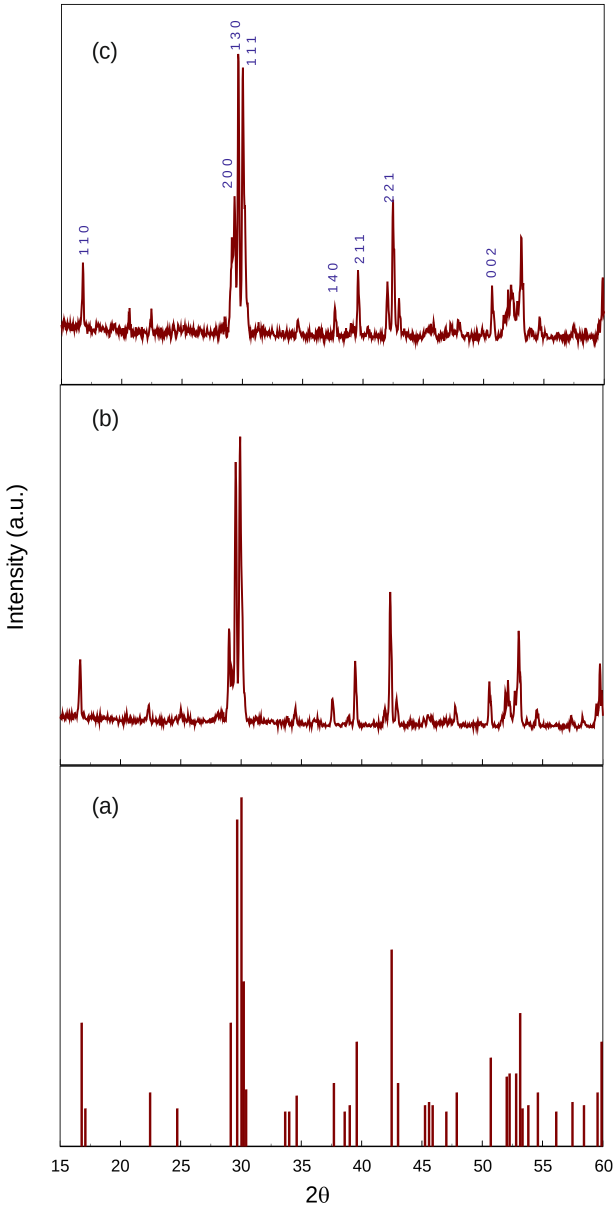

Figure 1. The XRD spectra of (a) JCPDS card no 050-0115, (b) undoped Sr_2CeO_4 and (c) Eu doped Sr_2CeO_4.

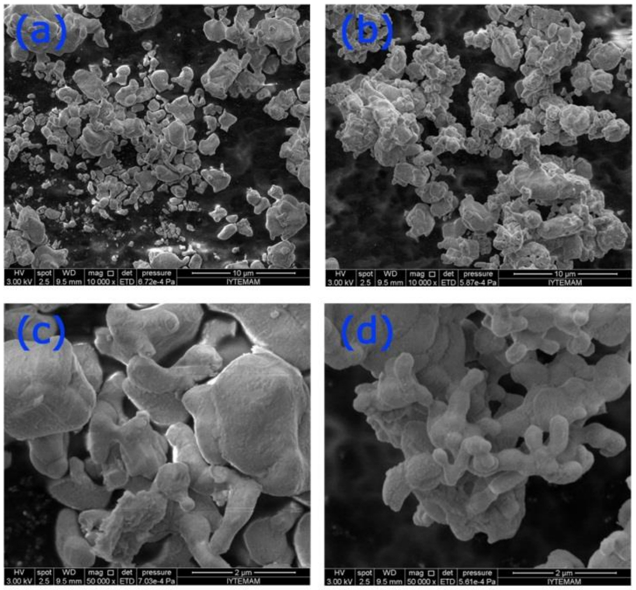

Figure 2. SEM micrographs of host material Sr_2CeO_4, (a) 10µm (c) 2µm and Eu doped Sr_2CeO_4 (b) 10µm (d) 2µm sized.

Fig. 2 shows the SEM images of undoped host material Sr_2CeO_4, Fig.2(a) at 10µm, Fig.2(c) at 2µm sized, and Eu doped Sr_2CeO_4 phosphor Fig.2(b) at 10µm, Fig.2(d) at 2µm sized. Although there is no obvious difference between the undoped and Eu doped–Sr_2CeO_4, it can be said that Eu doped Sr_2CeO_4 has a smaller grain size. In addition, the SEM images disclose that the morphology of the material is not uniform and they have different shape varies from round to irregular. This formation shape may be owing to the synthesis technique. On the other hand, the same shaped form can be obtained by using ball mill mixing equipment after the synthesis procedure. This result is commonly expected in CSSR methods since these materials are developed at high temperatures with grain sizes in an order of micron and cannot have a uniform structure.

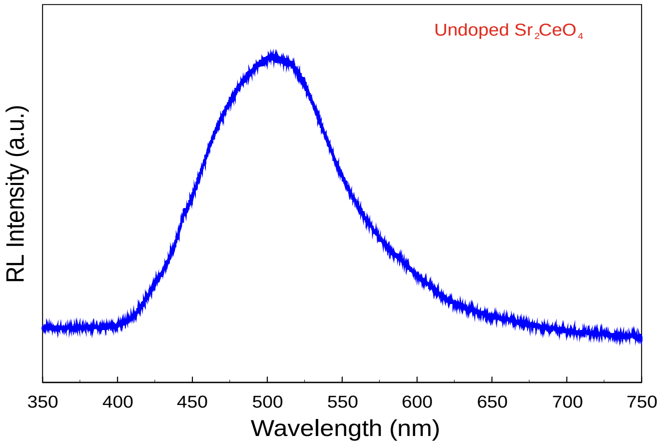

Figure 3. RL spectrum of host material Sr_2CeO_4 at room temperature.

Fig. 3 shows that a RL emission spectrum of undoped Sr_2CeO_4 is maintained around 500nm. The luminescent mechanism of this phosphor is mainly based on ligand–to–metal CT from O^{2-} to Ce^{4+} [5, 15] and does not arise from Ce^{3+} defect centers. This emission is attributed to the change from metal to ligand CT excited states, to the ground state [21]. The emission band observed in this case is at a slightly higher wavelength compared to the reported value of ~500nm for the same compound. All the known cerium–based phosphor materials are owing to bounded Ce^{3+} excited states, because of the luminescence comes from d–f transitions. The cerium ions are in the 4+ state in this case, and these ions have long excited state luminescence life time with an uncharacteristically, however the excited state of the Ce^{3+} ions may not have luminescence lifetime as others [5]. The emission of the Eu^{3+}ion, usually consists of sharp lines in the red spectral region. The sharp emission lines arise from the f–f transition of the Eu^{3+} ions. These emission lines have found an important application in lighting and display technology (color television). A simple electronic energy level diagram of Eu^{3+} illustrates the transitions from the singly degenerate excited state $^5D_0$ to the different sublevels within the terminal states ^7F_j (j=0 to 6), which correspond to different emission lines [24]. The $^5D_0 \rightarrow {}^7F_0$ emission is forbidden by electric dipole order and so it is not observed. Since $^5D_0$ level is not split by the crystal field (because j=0), the splitting of the emission transition yields crystal field splitting of the ^7F_j [25]. In addition, the emission from higher D–states ($^5D_1$, $^5D_2$ and $^5D_3$) may also be observed. The $^5D_0 \rightarrow {}^7F_j$ emission is very suitable to survey the transition probabilities of the sharp spectral lines of the Eu^{3+} ion.

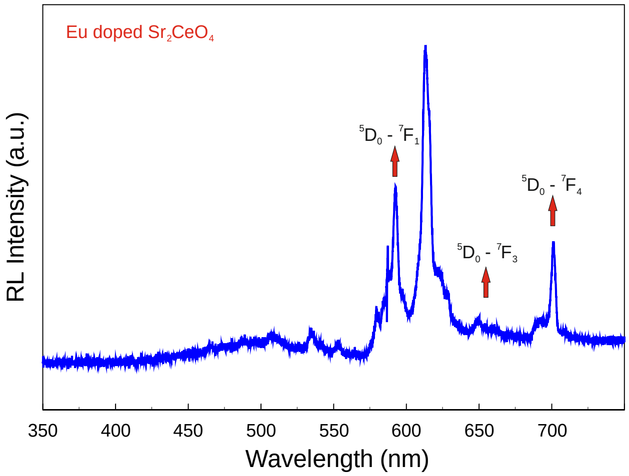

Figure 4. RL spectrum of Eu doped Sr_2CeO_4 at room temperature.

In the Fig.4, the resulting emission spectrum can be seen. The emission lines of the Eu^{3+} ion are defined by well-known $^5D_0 \rightarrow {}^7F_j$ (j=0, 1, 2, 3…), especially the strong emission at ~615nm is due to $^5D_0 \rightarrow {}^7F_2$ transition. In our case, the intermediate state is thought to populate the lowest $^5D_0$ state leading to the emission at 615nm, in addition the 590, 650 and 700nm peaks were observed too. The peak at 615nm band is predominant and there is no inversion symmetry at the site of the Eu^{3+} rare earth ion. On the other hand the electric dipole transition of the site is dominant. This behavior shows that the Eu^{3+} ions exist in central symmetric sites. Furthermore, the possibilities of all transition in any symmetry are based on the selection rules. The electric dipole transitions can be seen relating to $\Delta J = \pm 2$ as selection rules, this description is related to no center of inversion symmetry. Nevertheless, only the magnetic dipole transitions are permitted and selection rules of $\Delta J = \pm 1$ are acceptable, if the Eu^{3+} ion is a center of inversion symmetry in the lattice. The $^5D_0 \rightarrow {}^7F_1$ transition is forbidden, but permitted as magnetic dipoles. It might be said that the all lines corresponding to these transitions split into number of components recognized by the local symmetry. The second option is more probable for our results. It can be sait that the emission lines at 590nm correnspondss to $^5D_0 \rightarrow {}^7F_1$transition, also the peaks at 650, and 700nm correspond to $^5D_0 \rightarrow {}^7F_3$ and $^5D_0 \rightarrow {}^7F_4$ transitions, respectively. As shown in the Fig. 4, the emission spectra of $Sr_2CeO_4{:}Eu^{3+}$ phosphor material indicates the transition emissions from the higher energy levels to lower as $^5D_1$ and $^5D_2$. The presence of emission lines for higher excited statesis ascribed to the low vibration energy of CeO_4^{4-} groups. Multiphonon relaxation by CeO_4^{4-} is not able to bridge the gaps between the higher energy levels and the $^5D_0$ level of Eu^{3+} completely, resulting in weak emission from these levels [26].

4 Conclusion

Pure undoped Sr_2CeO_4 phosphor and Eu doped Sr_2CeO_4 phosphors were successfully synthesized via high temperature CSSR. The emission spectrum of undoped Sr_2CeO_4 phosphor displays that the broad band comes from the CT transition and d–f energy level transition of the Sr_2CeO_4. The effect of Eu^{3+} on the RL emission spectra of Sr_2CeO_4 was also studied. The optical characteristic of Sr_2CeO_4 materials in blue emission was predominated in favor of the red emission of Eu^{3+} ions. In the host lattice the europium has to be close cerium ions for energy transfer. We suggest that this may be because the crystal behaves as a host donor to transfer the energy; in addition the Eu ion plays a role as a receptor of that energy. We found that the emission transition of $^5D_0 \rightarrow {}^7F_2$ at peaks of ~615nm was the most intense among the main lines by studying the optical properties of Eu^{3+}. The emission from $^5D_{1,2}$ transition due to the low–energy vibration of the host lattice was also observed. Experimental results show that Sr_2CeO_4 and $Sr_2CeO_4:Eu^{3+}$ are good materials for field emission displays as well as use in fluorescent lamps.

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