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Characteristics of Sr_2SiO_4:Eu^{2+} Green Phosphor Synthesized in the Presence of Nonthermal Plasma Discharge

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This work investigated the application of nonthermal plasma to the synthesis of Eu^{2+}-doped Sr_2SiO_4 phosphors. The effect of synthesis temperature and treatment time on the optical and structural properties of the phosphors was examined with a planar dielectric barrier discharge (DBD) reactor employed to create plasma. The X-ray diffraction patterns of the phosphors prepared by the present and conventional method were similar to each other. Despite relatively low synthesis temperature and short treatment time, the phosphors synthesized in the presence of nonthermal plasma were found to exhibit equivalent or higher photoluminescence intensities, compared to those synthesized by the conventional method.

Keywords Phosphor; nonthermal plasma; dielectric barrier discharge; synthesis temperature; photoluminescence; X-ray diffraction pattern

Introduction

One of the most important commercial applications of phosphors is the production of light emitting diode (LED) [1,2]. The LED is a semiconductor device that converts electrical energy into light energy. It is widely used in many fields such as aviation lighting, indicators, automotive lighting, headlights and traffic signals. It shows many advantages over existing incandescent and halogen/fluorescent lamps with respect to lifetime, energy efficiency, brightness, reliability and environmental friendliness [3–7].

The phosphors, also known as luminescent materials, consist of a host lattice, an activator and a sensitizer. Generally a host lattice sets an activator in it, absorbs externally supplied energy and transfers to an activator. An activator absorbs the excitation energy from a host lattice and then emits light, or directly absorbs the energy and emits light by itself [8,9]. Further, a sensitizer, which absorbs the energy and subsequently transfers to an activator, can be added when the activator ions show too weak an absorption.

Europium-doped silicates absorb ultraviolet (UV) and visible light and emit intense visible broadband light. Several methods, including solid state reaction, liquid reaction, sol gel, etc., have been used for the preparation of Sr_2SiO_4:Eu^{2+} phosphors. Conventionally,

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$Sr_2SiO_4:Eu^{2+}$ phosphors have been synthesized by solid state reaction and a sintering process at 1375°C for 2 h. This conventional process is quite expensive because it requires high temperature and long treatment time. In order to reduce treatment time and lower synthesis temperature as well as to enhance the emission intensity of Eu^{2+}, various methods such as co-doping and plasma treatment have been attempted [10–12].

Recently, there has been growing interest in applying plasma technology to the preparation of phosphor powder. Shi et al., [11] successfully prepared high quality of Eu^{2+} and Si co-doped aluminum nitride phosphors by plasma-activated sintering (PAS) process and concluded that the PAS is one of the potential techniques capable of reducing treatment time, costs and the energy required for the production of high quality Eu^{2+}-doped nitride phosphors. Significant improvement of photoluminescence intensity (PL) was observed in Yb^{2+}-doped α-SiAlON phosphors prepared with the spark plasma sintering (SPS) technique by Choi et al., [12]. Kim [13] also obtained higher photoluminescence properties of zinc sulfide with short treatment time by using glow and arc discharge techniques. In this work, $Sr_2SiO_4:Eu^{2+}$ phosphors were prepared by using solid state reaction and nonthermal plasma discharge with temperature and treatment time as variables. The structure, morphology and photoluminescence of the phosphors prepared by the present and conventional method were comparatively examined and discussed.

Experimental

$SrCO_3$ (Aldrich, 99.9%), SiO_2 (Aldrich, 99.995%), Eu_2O_3 (Aldrich, 99.99%) and NH_4Cl (Aldrich, 99.998%) were used as precursor materials for Eu^{2+}-doped Sr_2SiO_4 phosphors. A small amount of NH_4Cl was used as a flux to increase the reaction speed and to enhance the optical properties of the phosphors. The precursor materials were mixed thoroughly at the ratio of (2-x) $SrCO_3$, 1 SiO_2, (x/2) Eu_2O_3. The mixed precursor materials were pelletized into 10 mm (diameter) × 5 mm (thickness) tablets in a press.

The nonthermal plasma reactor used for this work was a dielectric barrier discharge reactor. As shown in Fig. 1 the plasma reactor was made up of 3-mm thick alumina plates and two planar molybdenum electrodes (100 mm × 30 mm), which was placed in a tube furnace. The distance between the two alumina-covered molybdenum electrodes was 8 mm. The upper molybdenum electrode was connected to alternating current (AC) high voltage (operating frequency: 60 Hz) and the lower one to the ground electrode.

$Sr_2SiO_4:Eu^{3+}$ was produced by a sintering process and then reduced to $Sr_2SiO_4:Eu^{2+}$ under a reductive atmosphere at temperatures of 1275, 1325 and 1375°C. Argon was used throughout this work to stabilize the plasma, and hydrogen was used as a reducing agent. The flow rates of argon and hydrogen were 400 and 100 $cm^3\ min^{-1}$, respectively. The electric power was controlled to 20 W by adjusting the applied voltage. As shown in Fig. 2, the voltage required to obtain an electric power of 20 W gradually decreased as the temperature increased.

As described in Fig. 3, the tube furnace where the reactor was placed was heated at a rate of 5°C min^{-1} up to 1275–1375°C, maintained for a while, and then cooled down slowly. To examine the effect of temperature on the optical and structural properties of the phosphors, the pelletized tablet samples were treated under different temperatures (1275, 1325 and 1375°C) with different treatment times of 0, 1, and 2 h. Here it should be noted that the treatment time stands for the period of time for maintaining the constant temperature. To create nonthermal plasma in the reactor, the AC high voltage was switched on when the temperature reached 600°C, and switched off at 600°C during the cooling-down stage.

The crystalline structures of the synthesized phosphors were investigated with X-ray diffraction analyzer (Model SPD-2000, Scinco, Korea), and the surface morphology was

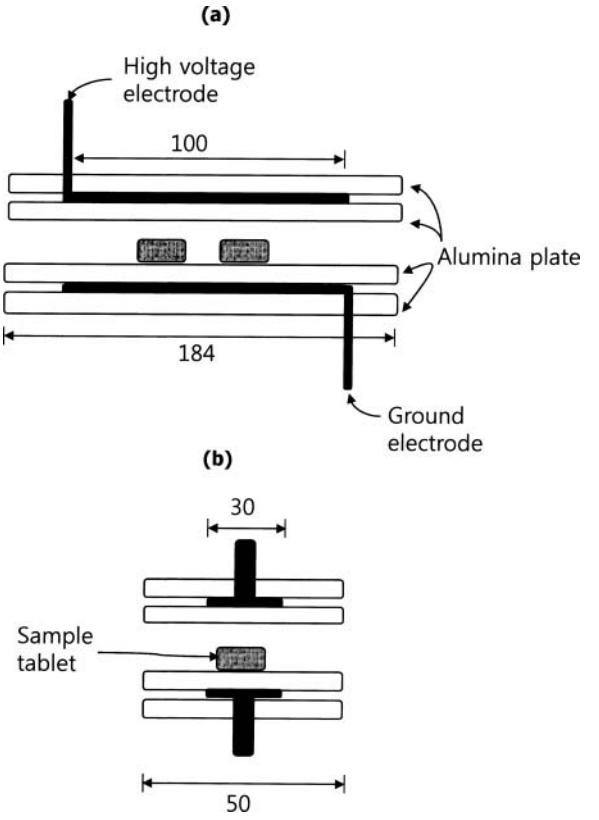

Figure 1. Schematic diagram of the plasma reactor (a) front view, (b) side view.

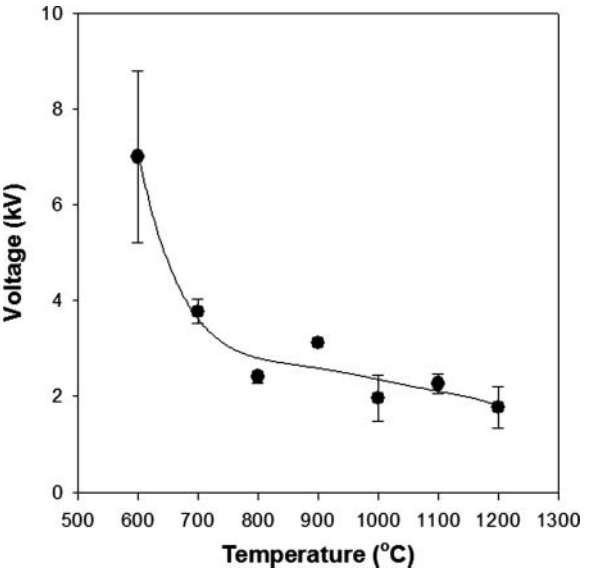

Figure 2. Voltages to obtain 20 W input power at various temperatures.

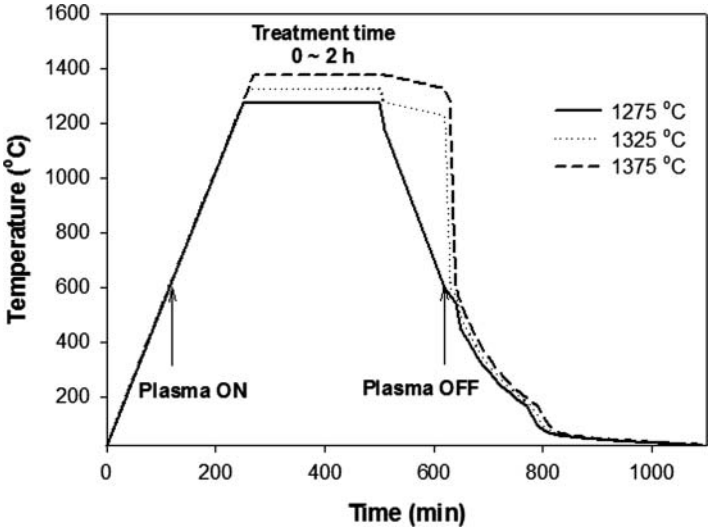

Figure 3. Temperature profiles of the furnace.

observed by a field emission scanning electron microscope (FE-SEM) (Model JSM-6701F, Jeol, USA). The luminescent properties of the phosphors were analyzed by a fluorescence spectrophotometer (Model F-4500, Hitachi, Japan).

Results and Discussion

Figure 4 presents the X-ray diffraction patterns of the standard α'-Sr_2SiO_4 (JCPDS 39-1256) and β-Sr_2SiO_4 (JCPDS 38-0271) as references, and Figure 5 shows the X-ray diffraction patterns of Sr_2SiO_4:Eu^{2+} phosphors synthesized in the presence and in the absence of nonthermal plasma discharge at various temperature (1275–1375°C) with different treatment times (0–2 h). Comparing the XRD patterns, almost all the peaks in the samples were matched well with those of the standard orthorhombic α'-Sr_2SiO_4 and monoclinic β-Sr_2SiO_4. The synthesized samples showed multiple phases of α'-Sr_2SiO_4 and β-Sr_2SiO_4.

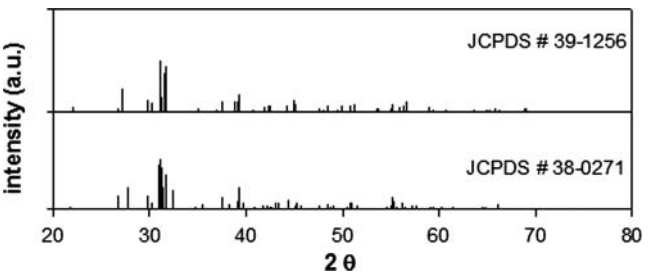

Figure 4. X-ray diffraction patterns for α'-Sr_2SiO_4 (JCPDS 39-1256) and β-Sr_2SiO_4 (JCPDS 38-0271).

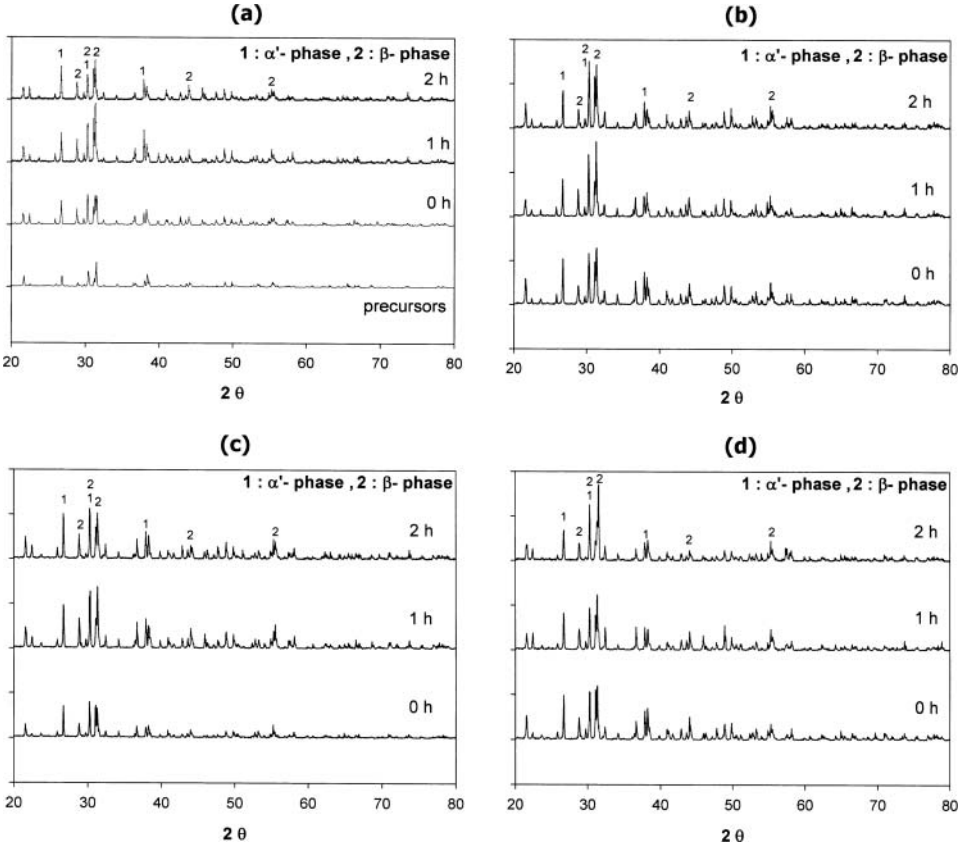

Figure 5. X-ray diffraction patterns for (a) precursor materials and $Sr_2SiO_4:Eu^{2+}$ synthesized by the conventional method at 1375°C, (b) in the presence of plasma at 1275°C, (c) in the presence of plasma at 1325°C, and (d) in the presence of plasma at 1375°C.

These two phases of Sr_2SiO_4 have similar peaks due to rearrangement of crystal structures. Different treatment times showed dissimilar effects on the structure of $Sr_2SiO_4:Eu^{2+}$. The plasma treated samples showed composed phases of α'-Sr_2SiO_4 and β-Sr_2SiO_4, and the β phase was more dominant. When increased the treatment time, the intensities of the diffraction peaks of the β phase gradually increased and then decreased with increasing the temperature. The introduction of Eu^{2+} ions into the Sr_2SiO_4 may replace the Sr^{2+} in the two kinds of unequivalent lattice sites in the Sr_2SiO_4. Xiaoyuan et al. [14] reported that the increase of Eu^{2+} concentration led to the phase transformation from β-Sr_2SiO_4 to α'-Sr_2SiO_4.

The SEM images of the phosphors synthesized in the presence of nonthermal plasma discharge and by the conventional method were depicted in Fig. 6. Before synthesis the sample showed many agglomerated particles without clear surface area (Fig. 6a). The plasma-treated sample (Fig. 6c) showed the particles were Fig. 7 small and well dispersed, clearly distinguishing the individual crystalline. The clean and large-sized surface of the phosphor powder shows higher photoluminescence intensities because of low surface defects [15]. The bigger size particles were shown during the conventional synthesized

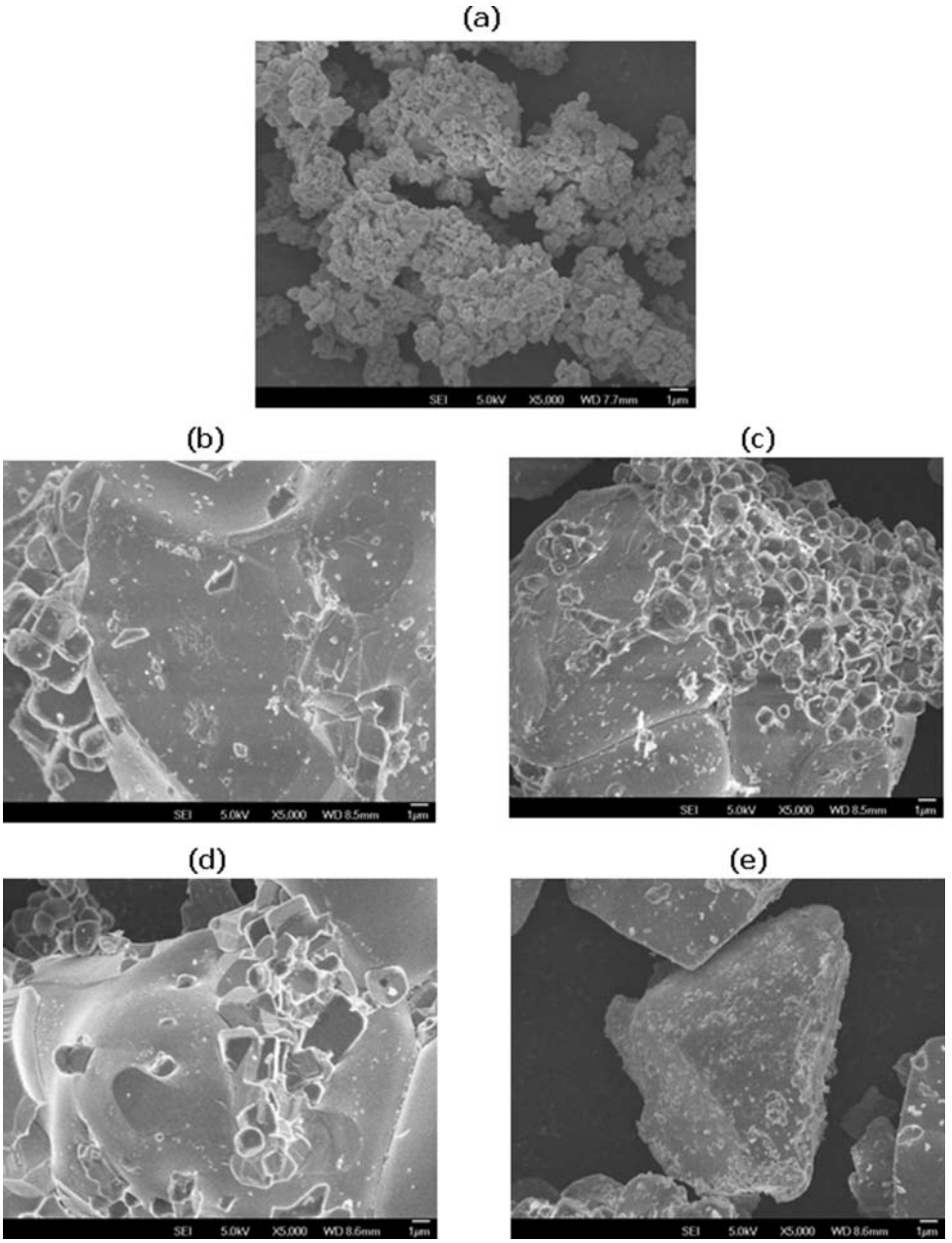

Figure 6. SEM images of (a) precursor material, (b) $Sr_2SiO_4:Eu^{2+}$ synthesized by the conventional method at 1375°C for 2 h, (c) in the presence of plasma at 1275°C for 1 h, (d) in the presence of plasma at 1325°C for 1 h, and (e) in the presence of plasma at 1375°C for 1 h.

method (Fig. 6b). However, increasing the temperature above 1325°C with plasma treatment, the particles grew quickly and aggregated to form secondary particles by sintering effect. In addition, some particle surfaces were smooth (Fig. 6e). The structural changes of the Sr_2SiO_4 may be in good agreement with the XRD patterns. As observed the phase

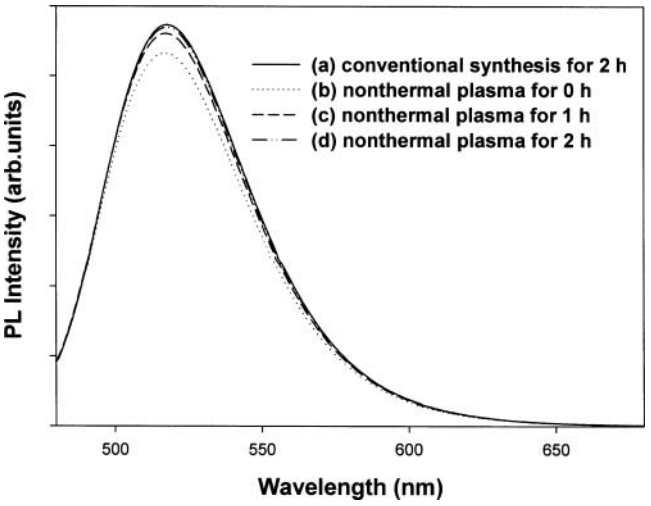

Figure 7. Photoluminescence emission spectra of $Sr_2SiO_4:Eu^{2+}$ phosphors synthesized (a) by the conventional synthesis method at 1375°C for 2 h, (b) with plasma at 1275°C for 0 h, (c) with plasma at 1275°C for 1 h, and (d) with plasma at 1275°C for 2 h.

transformation from the XRD, the changes of the crystal structure leads to modifying the morphologies of the Sr_2SiO_4 phosphor. Lee et al., [15] also reported that the phase transformation of Sr_2SiO_4 from β to α' leads to changing the structural characteristic of the phosphor from regular polyhedron shape to irregular shape. Plasma treatment at 1275°C indicates that the phosphors have a good dispersion and a relatively regular shape, which favors its practical applications.

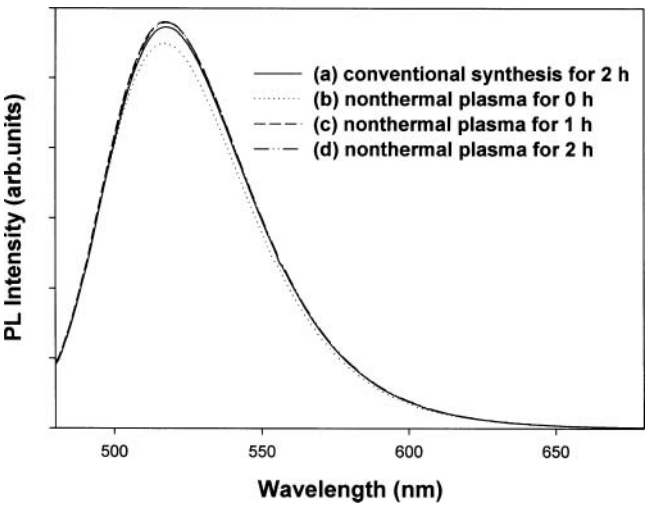

Figure 8. Photoluminescence emission spectra of $Sr_2SiO_4:Eu^{2+}$ phosphor synthesized (a) by the conventional synthesis method at 1375°C for 2 h, (b) with plasma at 1325°C for 0 h, (c) with plasma at 1325°C for 1 h, and (d) with plasma at 1325°C for 2 h.

Figure 7 depicts the comparison of the photoluminescence intensities of the phosphors synthesized by nonthermal plasma discharge at 1275°C and the conventional method at 1375°C. The phosphors showed a broad emission spectrum from 480 to 680 nm when they were excited by the energy at around 450 nm. The intensities of the phosphors synthesized at 1275°C by the present method were found to be similar to the phosphors synthesized by the conventional method at 1375°C, indicating that equivalent intensity can be obtained by the plasma treatment at lower temperatures. The same intensity at lower temperature may be due to the enhanced reduction in the presence of plasma. At a temperature of 1275°C, the intensity increased with increasing the treatment time (see Fig. 8) presents the photoluminescence for synthesized phosphor with the present method at 1325°C and the conventional method at 1375°C for 2 h. The highest emission intensity was observed in the phosphor synthesized with nonthermal plasma at 1325°C. The emission intensity of the plasma-treated phosphor at 1325°C was significantly enhanced, compared to the conventionally treated powder. The higher photoluminescence could be due to the stable luminescence centers of Eu^{2+} ions, because Eu^{3+} ions were easily reduced to Eu^{2+} ions in the presence of plasma, and Eu^{2+} ions were substituted in the places of cations of Sr_2SiO_4 crystals at high temperatures in the reductive atmosphere [16].

Conclusions

The Sr_2SiO_4:Eu^{2+} phosphors were synthesized in the presence of nonthermal plasma discharge. The structural and luminescent characteristics of the synthesized phosphors were investigated by X-ray diffraction patterns, SEM images and photoluminescence. The X-ray diffraction patterns of Sr_2SiO_4:Eu^{2+} synthesized by the present method showed multiple phases of α' and β. The plasma synthesized samples showed small and clean crystals well-dispersed and distinguished. The synthesized phosphors were excited by the energy of around 450 nm, and these had maximum photoluminescence intensity at about 518 nm. The phosphors synthesized in the presence of plasma discharge at lower temperature had similar or better luminescent characteristics to those synthesized by the conventional method at higher temperature, probably due to enhanced reduction.

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