Low-Temperature Synthesis and Luminescence Properties of Alkaline-Earth Stannate Phosphors Prepared by Chemical Solution Process

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In this work, we present a Ca_2SnO_4:Eu^{3+} phosphor prepared by the sol-gel method at a low temperature using a soluble inorganic salt. The mixed solution was pyrolyzed at 500°C for 180 min in air, and final annealing was performed at 800°C for 180 min in air. The crystal structure and surface morphology were confirmed through x-ray diffraction analysis and field emission - scanning electron microscopy, and the photoluminescence spectra were measured with a fluorescence spectrophotometer. The sample annealed at 800°C exhibited an orthorhombic structure and showed a red emission at 613 nm.

Keywords: phosphor, sol-gel, red emission

1. INTRODUCTION

Luminescent materials have been studied widely for application in display devices. Great efforts have been made to discover host materials as well as activators with high performances for phosphor applications. To date, various types of inorganic materials have been developed as phosphors, including sulfides, aluminates, silicates, titanates, oxysulfides, nitrides, and so on, doped with various activators.[1-3]

Alkaline-earth stannates have received considerable attention over the past few years because of their potential applications in various fields, for example, as photocatalysts, ferromagnets, and anode materials for lithium ion batteries. Generally, the luminescent properties of phosphors are strongly dependent on the crystal structure of the host materials. SnO_4^{4-} anions are reported to be optically-inert, and could be a candidate as a host material.[4] Only two phases have been found in the CaO-SnO_2 binary system: $CaSnO_3$ and Ca_2SnO_4. Calcium stannate (Ca_2SnO_4) has an orthorhombic structure with the space group P*bam*; the lattice parameters a, b, and c are 5.753, 9.701, and 3.266 Å, respectively.[5]

Ca_2SnO_4:Re^{3+} (Re = Eu, Pr, Sm) phosphors have been synthesized through the solid-state reaction between SnO_2 and $CaCO_3$ at 1400°C for 12 h.[6,7] However, this synthetic method requires a higher thermal treatment temperature and produces a lower chemical homogeneity. As an alternative synthetic method, a chemical solution process was developed for the preparation of Ca_2SnO_4:Re^{3+} (Re = Eu, Sm) phosphors,

with calcination at 900°C for 6 h.[8] The chemical solution process is an efficient technique for the preparation of phosphors, and offers several advantages, such as good mixing of the starting materials, a relatively low reaction temperature, and more homogeneous products. To the best of our knowledge, there have been only a few reports on the successful preparation of Ca_2SnO_4:Eu^{3+} phosphors at low temperatures through the wet chemical route. In this paper, we report the red phosphor, Ca_2SnO_4:Eu^{3+}, prepared by using the chemical solution process at a lower temperature. The formation mechanism and luminescent properties are also investigated.

2. EXPERIMENTAL PROCEDURE

The starting materials used for the preparation of the phosphor were calcium nitrate tetrahydrate [$Ca(NO_3)_2$·$4H_2O$], tin (IV) chloride pentahydrate ($SnCl_4$·$5H_2O$), and europium (III) nitrate pentahydrate [$Eu(NO_3)_3$·$5H_2O$]. Eu^{3+}-doped Ca_2SnO_4 solutions (5 mol. %) were prepared. The details of the chemical solution process are as follows: Aqueous solutions (20 mL) were prepared by dissolving the above precursors in ethanol and stirring for 30 min. The transparent solutions were heated at 80°C for 3 h. The homogeneous gel powders were pyrolyzed at 500°C for 3 h in air, and then the precursors were finally annealed at 800°C for 3 h in air.

X-ray diffraction (XRD) of the sample was performed on a D-Max-1200 (Rigaku, Japan) with CuKα radiation (λ = 1.54056 Å). The morphology of the sample was examined with a field emission-scanning electron microscope (FE-SEM, S-4700, Hitachi, Japan). The excitation and emission

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spectra of the samples were recorded at room temperature with a fluorescent spectrophotometer (F4500, Hitachi, Japan) equipped with a Xenon lamp source.

3. RESULTS AND DISCUSSION

Ca_2SnO_4 has the Sr_2PbO_4-type structure, and is isostructural with Sr_2CeO_4.[9] In the Ca_2SnO_4 structure, SnO_6 octahedra are connected in a low-dimensional form, in which they share edges to form one-dimensional chains. The Ca^{2+} is seven-coordinate, and Sn^{4+} is six-coordinate.[9] The XRD patterns of $Ca_2SnO_4:Eu^{3+}$ sintered in air at 800°C are shown in Fig. 1. The XRD patterns reveal that the Eu^{3+}-doped Ca_2SnO_4 is chemically and structurally single-phase Ca_2SnO_4 (JCPDS No.46-0112). All the peaks in the XRD pattern of $Ca_2SnO_4:Eu^{3+}$ were indexed with orthorhombic cell parameters (space group Pbam). The diffraction peaks at $2\theta = 17.83°, 27.28°, 31.03°, 31.63°, 32.68°, 33.83°, 36.93°$, and $45.78°$ correspond to the diffraction faces (110), (001), (200), (130), (111), (021), (040), and (221), respectively. The calculated crystal cell parameters ($a = 0.5760$ nm, $b = 0.9728$ nm, $c = 0.3292$ nm for the Eu-doped sample) are a little larger than those ($a = 0.57538$ nm, $b = 0.97015$ nm, $c = 0.32669$ nm) for standard Ca_2SnO_4.

The ionic radii of Ca^{2+} and Eu^{3+} in seven-fold-coordination are 0.100 and 0.095 nm, respectively. These ionic radii are almost identical, so the Eu^{3+} ion has a pronounced tendency to occupy the Ca^{2+} sites. It was expected that all the Ca/Eu-O distances would decrease as a result of Eu^{3+} substitution. However, the positions of the peaks in the XRD profiles shifted to lower angles and some of the cell parameters increased. The extension of the lattice parameters may be due to the Eu^{3+} ions entering interstitial sites. Moreover, the Eu ions have a charge of 3^+, and hence, the entrance of doping ions into the Ca_2SnO_4 structure means that some charge compensation is needed.[6] One way in which the charge can be balanced is through the creation of a vacancy on the Ca^{2+} sub-lattice for every two Eu^{3+} ions incorporated into the structure. If the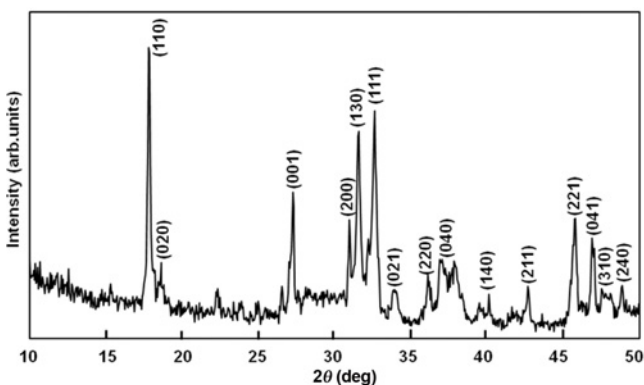 crystal structure maintains its overall stoichiometry, oxygen will be lost during the reaction at high temperatures.[6]

The FE-SEM technique was employed to determine the actual size and shape of the as-prepared samples. The FE-SEM observation of the powder indicated that the sample had a bar-like shape and exhibited a little aggregation, as shown in Fig. 2.

The photoluminescence (PL) emission and photoluminescence excitation spectra of the as-prepared $Ca_2SnO_4:Eu^{3+}$ phosphor were recorded at room temperature. The typical excitation spectrum from 200 to 500 nm at $\lambda_{em} = 613$ nm is shown in Fig. 3(a). As reported previously, the broad band at 275 nm comes from the charge-transfer bands (CTB) between the Eu^{3+} ions and the surrounding oxygen anions.[4] The sharp excitation peaks are assigned to transitions between the $^7F_0$ level and the ^5H_J, $^5D_4$, ^5G_J, $^5L_6$, and $^5D_{3,2}$ levels.

The PL emission spectrum of the $Ca_2SnO_4:Eu^{3+}$ phosphor annealed at 800°C for 180 min was measured under excitation with $\lambda_{exe} = 314$ nm at ambient temperature, as shown in Fig. 3 (b). The four emission peak bands situated at 589, 613, 652 and 695 nm correspond to the characteristic transitions of Eu^{3+} from $^5D_0 \rightarrow {}^7F_j$ ($j = 1, 2, 3$, and 4),[4] that is, to the

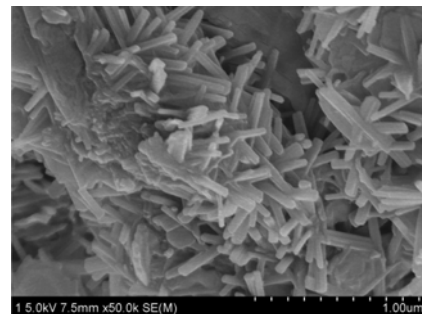**Fig. 2.** FE-SEM image of the $Ca_2SnO_4:Eu^{3+}$ powder annealed at 800°C.
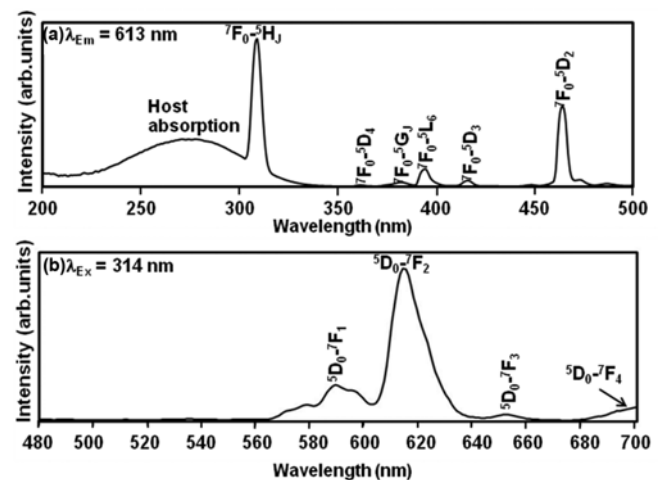

Fig. 1. XRD patterns of the $Ca_2SnO_4:Eu^{3+}$ powder annealed at 800°C.

Fig. 3. Typical excitation ($\lambda_{em} = 613$ nm) (a) and emission ($\lambda_{ex} = 314$ nm) (b) spectra of $Ca_2SnO_4:Eu^{3+}$ powder annealed at 800°C for 3 h.

$^5D_0 \rightarrow {}^7F_1$ (589 nm), $^5D_0 \rightarrow {}^7F_2$ (613 nm), $^5D_0 \rightarrow {}^7F_3$ (652 nm), and $^5D_0 \rightarrow {}^7F_4$ (695 nm) transitions, respectively. The emission peak at 589 nm is due to the $^5D_0 \rightarrow {}^7F_1$ magnetic dipole transition, which is insensitive to the site symmetry. The dominant emission peak, situated at 613 nm and showing a prominent, bright red light, is due to the $^5D_0 \rightarrow {}^7F_2$ electric dipole transition induced by the lack of inversion symmetry at the Eu^{3+} site, and is much stronger than that of the transition of the $^7F_1$ state.[4] Therefore, in the host material Ca_2SnO_4 crystal, the emitting center does not occupy a site with a center of symmetry. As a rule, the intensity ratio of ($^5D_0 \rightarrow {}^7F_2$)/($^5D_0 \rightarrow {}^7F_1$), known as the asymmetry ratio, reveals the degree of distortion from the inversion symmetry of the local environment of the Eu^{3+} ions in the host matrix.[10] The asymmetry ratio for the Ca_2SnO_4:Eu^{3+} phosphor is *ca.* 4.21, as calculated from Fig. 3(b).

In conclusion, through the sol-gel method, a Ca_2SnO_4-based red phosphor was obtained at temperatures as low as 800°C. Its intense luminescence properties make it a potentially good candidate for display applications.

4. CONCLUSIONS

Eu^{3+}-doped Ca_2SnO_4 samples were synthesized successfully through a chemical solution process, and their PL properties were examined. The precursor powders were crystallized into the orthorhombic phase as bar-like powders at a temperature as low as 800°C in ambient air. The emission peak at 613 nm, showing a prominent, bright red light under 314 nm-excitation, is due to the $^5D_0 \rightarrow {}^7F_2$ electronic dipole transition. The present work demonstrates that the chemical solution process at low temperatures is advantageous for the preparation of Ca_2SnO_4-based red phosphors.

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