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Short communication

Praseodymium-doped calcium stannates phosphor coatings prepared by electrostatic spray deposition

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Abstract

Ca_2SnO_4:Pr^{3+} phosphor coatings were prepared on silica glass substrates at a low temperature by electrostatic spray deposition using a soluble inorganic salt. The deposited films were pyrolyzed at 500 °C for 1 h in air. Final annealing was performed at 1000 °C for 1 h in air. Gels dried at 80 °C for 24 h were subjected to thermogravimetric analysis at 25–925 °C to analyze the thermal decomposition process. Crystal structure and surface morphology of the films were examined by X-ray diffraction analysis and scanning electron microscopy. Photoluminescence spectra were measured by a fluorescent spectrophotometer. The phosphor film annealed at 1000 °C showed orthorhombic structure and red emission at 626 nm.

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1. Introduction

Luminescent materials have been widely studied for application in display devices. Considerable efforts have been made to develop high-performance host materials and activators for phosphor applications. Different types of inorganic lattices, doped with various activators, have been developed as phosphors. Lattice materials tested include sulfides, aluminates, silicates, titanates, oxysulfides, and nitrates.

Alkaline-earth stannates have attracted considerable attentions over the past few years because of their potential application in various fields such as photocatalysis, ferromagnetics, and as anode materials for lithium ion batteries [1,2]. Generally, the luminescence properties of phosphors are strongly dependent on the crystal structure of the host material. SnO_4^{4-} anions have been reported to be optically inert and are therefore good candidates for host materials [3]. Only two phases, namely, $CaSnO_3$ and Ca_2SnO_4, have been observed in the CaO–SnO_2 binary system. Calcium stannate (Ca_2SnO_4) has an orthorhombic structure in the space group *Pbam*, where lattice parameters *a*, *b*, and *c* are 5.753, 9.701, and 3.266 Å, respectively [4].

Ca_2SnO_4:Re^{3+} (Re = Eu and Sm) phosphors have previously been synthesized using a solid-state reaction between SnO_2 and $CaCO_3$ at 1400 °C for 12 h [5,6]. The solid-state reaction is a well-known method of phosphor synthesis that requires high calcination temperatures and produces low chemical homogeneity in phosphor products. An alternative synthetic method, known as chemical solution processing, has been developed to prepare Ca_2SnO_4:Re^{3+} (Re=Eu, Sm) powder phosphor. This process involves a calcination step at 900 °C for 6 h [1,7]. Chemical solution processing is an efficient technique for preparing powdered phosphors and comes with several advantages such as efficient mixing of starting materials, relatively low reaction temperatures, and more homogeneous products.

Recently, a new spray pyrolysis technique called electrostatic spray deposition (ESD) has been used to prepare a range of coatings [8,9]. ESD has many advantages over conventional

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deposition methods, such as an inexpensive setup, high deposition efficiency, low-temperature synthesis, and easy control of the composition and surface morphology of the deposited coatings. However, there are few reports on the fabrication of red phosphor coatings using the ESD method.

This paper reports the fabrication of red phosphor Ca_2SnO_4:Pr^{3+} coatings at low temperatures by ESD. The formation mechanism and luminescence properties have also been investigated.

2. Experimental procedure

Starting materials used for phosphor coatings were calcium nitrate tetrahydrate [$Ca(NO_3)_2 \cdot 4H_2O$], tin (IV) chloride pentahydrate ($SnCl_4 \cdot 5H_2O$) and praseodymium (III) nitrate hexahydrate ($N_3O_9Pr \cdot 6H_2O$). In addition, Pr^{3+}-doped (5 mol%) Ca^2SnO_4 precursor solutions were prepared. Aqueous chemical solutions (20 ml) were prepared by dissolving the above precursors in ethanol followed by stirring for 30 min.

The working principle of ESD is described in detail in the literature [8,9]. The ESD setup consisted of three parts: an electrostatic spray unit, a liquid-precursor feed unit, and a temperature control unit. The electrostatic spray unit comprised a high DC voltage power supply (SHV120-30 K-RD, Convertech Co., Ltd., Korea), stainless steel needle (0.1 mm inner diameter), and a grounded and heated substrate holder. The liquid precursor feed unit consisted of a flexible silicon tube and syringe pump (KD200, KD Scientific Inc., U.S.A.). To obtain the con-jet mode of electrostatic atomization, 25 kV was applied between the needle tip and ground electrode. Silica glass substrates on a grounded electrode were heated at 80 °C for 40 min to vaporize organic compounds. A transparent precursor solution was pumped for 40 min (flow rate: 0.3 mL/60 min) through a nozzle placed 20 cm above the substrates. The deposited coatings were heated in a tube furnace to 500 °C for 1 h in air. Subsequently, the prefired coatings underwent final annealing at 1000 °C for 1 h in air. The thickness of the annealed film was approximately 0.8 μm, as confirmed by field emission-scanning electron microscope (FE-SEM, S-4700, Hitachi, Japan).

Thermogravimetric analysis (TGA, DTG-60, Shimadzu, Japan) of the gel dried at 80 °C for 24 h was performed using an α-Al_2O_3 reference and a heating rate of 3 °C/min. X-ray diffraction (XRD) analysis of the coatings was performed using a D-Max-1200 diffractometer (Rigaku, Japan) using CuKα radiation (λ=1.54056 Å). The morphology of the coatings was observed by FE-SEM. The excitation and emission spectra of the samples were recorded at room temperature using a fluorescent spectrophotometer (F4500, Hitachi, Japan) equipped with a Xenon lamp source.

3. Results and discussion

TGA of the dried gel for Ca_2SnO_4:Pr^{3+} precursor was performed to understand its pyrolysis behavior (Fig. 1). The TGA curve shows that the weight loss of the precursor gel increases on increasing the temperature from room temperature to 925 °C. Weight loss in the TGA curve below 120 °C accounted for 44% of the total loss, which was attributed to the evaporation of absorbed or residual gel solvent. Weight loss between 120 and 500 °C was attributed to the combustion of organic compounds. Weight loss between 500 and 600 °C was attributed to the nucleated crystal phase. Between these temperatures, the weight remains constant, which indicates that decomposition and combustion of organic compounds in the starting solution were completed below 600 °C. As shown in Fig. 1, the temperatures 120 and 500 °C correspond to the initial and final stage of the pyrolysis, respectively. The decrease in weight between 500 and 600 °C was approximately 6%. This value is much smaller than the $\sim$79% weight loss incurred by gradual heating from 120 to 500 °C. From Fig. 1, we can determine that most organic components have been vaporized by pyrolysis at 500 °C.

Ca_2SnO_4 with Sr_2PbO_4-type structure is isostructural to Sr_2CeO_4 [10]. In the Ca_2SnO_4 structure, SnO_6 octahedra are connected in a low-dimensional form. SnO_6 octahedra sharing edges with each other and form one-dimensional chains. Ca^{2+} and Sn^{4+} are seven- and six-coordinated, respectively [10]. The XRD patterns of Ca_2SnO_4:Pr^{3+} coatings sintered in air at 1000 °C are shown in Fig. 2(a). The XRD patterns showed that the Pr^{3+}-doped Ca_2SnO_4 coating is composed of single-phase

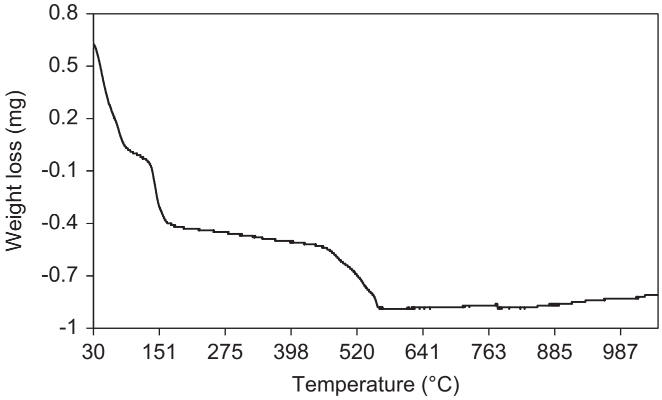

Fig. 1. TGA curve of dried gels for Ca_2SnO_4:Pr^{3+} precursor.

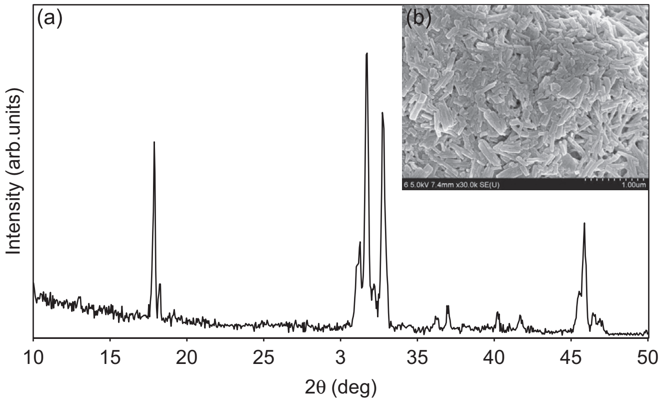

Fig. 2. (a) XRD patterns of Ca_2SnO_4:Pr^{3+} coatings and (b) FE-SEM image of the coatings after annealing.

Ca_2SnO_4 (JCPDS no.46-0112). All peaks in the XRD pattern of the Ca_2SnO_4:Pr^{3+} coating were indexed to orthorhombic cell parameters (space group *Pbam*). Peaks corresponding to neither the unstable intermediate $CaSnO_3$ phase nor any unknown phases were observed in the XRD pattern of Ca_2SnO_4:Pr^{3+}. The diffraction peaks at $2\theta = 17.63°$, $18.23°$, $31.28°$, $31.53°$, $32.48°$, $36.13°$, $36.93°$, $42.75°$, and $45.88°$ correspond to the diffraction planes (110), (020), (200), (130), (111), (220), (040), (211), and (221), respectively. The calculated crystal cell parameters ($a = 0.5750$ nm, $b = 0.9719$ nm, and $c = 0.3281$ nm for the Pr-doped sample) were slightly larger than those of standard Ca_2SnO_4 ($a = 0.5753$ nm, $b = 0.9702$ nm, $c = 0.3267$ nm).

The ionic radii of Ca^{2+} and Pr^{3+} in seven-fold coordination were 0.106 and 0.099 nm, respectively. As the ionic radii values are similar, the Pr^{3+} ion has a tendency to occupy Ca^{2+} sites. All Ca/Pr–O distances were expected to decrease upon Pr^{3+} substitution. However, the positions of peaks in the XRD profiles shifted to lower angles and some of the cell parameters, *b* and *c*, increased. The increase in the lattice parameter might be due to Pr^{3+} ions entering interstitial sites. Moreover, since Pr ions have a charge of 3+, some charge compensation is needed upon the entrance of doping ions to the Ca_2SnO_4 structure [5]. One way to balance charge is to create a vacancy in the Ca^{2+} sub-lattice for every two Pr^{3+} ions incorporated into the structure. If the crystal structure maintains its overall stoichiometry, oxygen will disappear at high temperatures [5].

FE-SEM was performed on the samples after final annealing at 1000 °C, as shown in Fig. 2(b). Ca_2SnO_4:Pr^{3+} phosphors took the form of a homogeneous bar-like layer on the silica glass substrate. Few visible cracks and pores were observed after final annealing.

The emission and excitation spectra of the Ca_2SnO_4:Pr^{3+} phosphor coatings were determined at room temperature. Fig. 3(a) shows the PL excitation spectrum of the sintered Ca_2SnO_4:Pr^{3+} coatings. When monitored at 626 nm, the excitation spectrum exhibited an excitation band ranging from 250 to 500 nm with peaks at approximately 314, 395, and 460 nm. The absorption peaks in the range 400–500 nm were likely due to the transitions of Pr^{3+} from the ground state $^3H_4$ to the excited state ^3P_J ($J = 0, 1, 2$) [10]. A 314 nm band was also observed and was assigned to fundamental host absorption. The presence of a fundamental host band at 314 nm in the excitation spectrum of the Ca_2SnO_4:Pr^{3+} coatings suggests that the energy transfer (ET) can occur from the host to the Pr^{3+} luminescence center.

The emission spectrum of Ca_2SnO_4:Pr^{3+} coatings excited by 314 nm at room temperature is shown in Fig. 3(b). Typical Pr^{3+} emissions, presumably induced by the excitation through the host, were observed. The emission spectrum for Ca_2SnO_4:Pr^{3+} phosphor coatings annealed at 1000 °C exhibited the narrow-line features of rare-earth ions, which consisted of two groups of peaks in the blue and green, and red spectral regions. The weak emission peaks at 488 and 540 nm were attributed to the $^3P_0 \rightarrow {}^3H_4$ and $^3P_0 \rightarrow {}^3H_5$ transitions, respectively. A strong emission peak at 626 nm was attributed to the transition $^1D_2 \rightarrow {}^3H_{4,6}$ in Pr^{3+} ions. The emission wavelength of Pr^{3+} ions depends strongly on the host lattice. The emission wavelengths might be blue or green when transitions occur at the $^1S_0$ or $^3P_0$ levels, respectively. On the other hand, red emission occurs at the $^1D_2$ level [11].

This study assessed red-emitting Ca_2SnO_4:Pr^{3+} phosphor coatings for flat-panel display applications, not only because oxide phosphors are chemically stable under high vacuums and under electron bombardment but also because thin-film phosphors offer high image resolution and strong adhesion to substrates.

Several methods have been used to produce phosphor coatings. A recently developed versatile technique for the

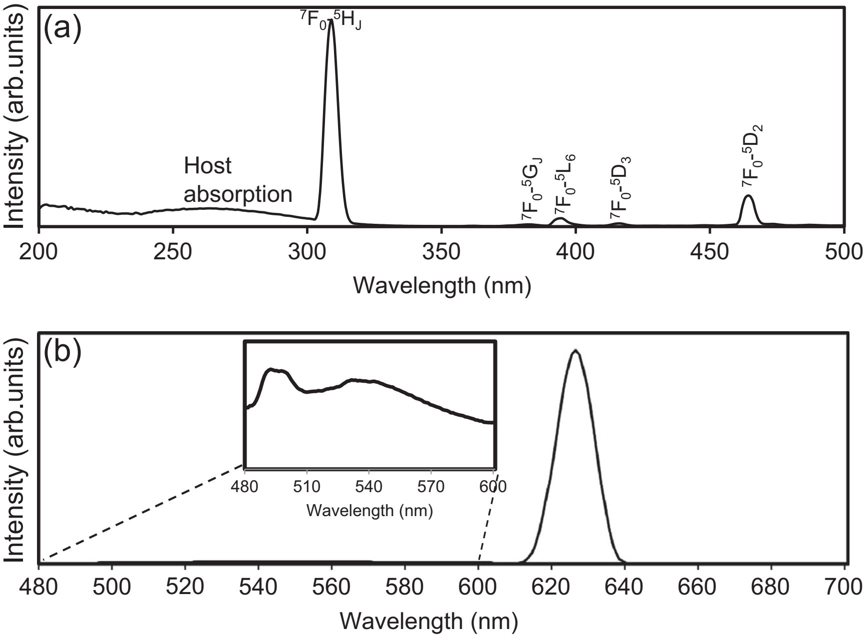

Fig. 3. Typical excitation ($\lambda_{em} = 626$ nm) and emission ($\lambda_{ex} = 314$ nm) spectra of annealed Ca_2SnO_4:Pr^{3+} coatings.

preparation of sol–gel coatings and aerosol–gel deposition has not yet been used to prepare such coatings. In this work, a red-emitting phosphor coating was successfully formed using ESD. The deposition mechanism of ESD is similar to the synthesis mechanism for a sol–gel process. In the case of the sol–gel process, metal ions mixed at the atomic scale exist in a sol precursor solution, and a dried gel precursor decomposes and crystallizes simultaneously by pyrolysis [12]. ESD normally atomizes a precursor solution containing metal ions into an aerosol, which is then applied to a heated substrate. In this study, films with desired properties were formed on a heated substrate by the simultaneous decomposition of precursor solution and synthesis of metal oxide and then subjected to prefiring and annealing.

In conclusion, combining the two methods makes it possible to achieve better mixing of elements and better reactivity of the mixture.

4. Conclusions

Pr^{3+}-doped Ca_2SnO_4 red phosphor coatings were prepared using ESD in order to examine the resultant crystal structure and photoluminescence properties. Precursor coatings were crystallized into an orthorhombic phase at temperatures as low as 1000 °C under ambient air, and FE-SEM confirmed that coatings were comprised of bar-like layers. The red emission peak at 626 nm under 314 nm excitation was assigned to the $^1D_2 \rightarrow {}^3H_{4,6}$ transition. The present study showed that ESD at low temperatures is advantageous for the synthesis of Ca_2SnO_4-based red phosphor coatings. This study demonstrates that the ESD technique is a simple and effective way to fabricate phosphor coatings from the structural, morphological, and luminescence analysis.

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