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Electroluminescence properties of In-doped Zn_2SiO_4 thin films prepared by sol–gel process

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ABSTRACT

The effect of In doping on the electroluminescence (EL) properties of Zn_2SiO_4:In thin films was investigated. In-doped Zn_2SiO_4 thin films were deposited on $BaTiO_3$ substrates and their EL properties were characterized in this study. X-ray powder diffraction patterns of In-doped Zn_2SiO_4 powders revealed a single phase of Zn_2SiO_4 for In concentrations up to approximately 1.5 mol%, whereas a secondary phase of In_2O_3 was observed for In concentrations in the range of 2–10 mol%. The maximum luminance of thin film electroluminescent (TFEL) devices varied significantly with the amount of In doping. The highest luminance with blue emission was obtained when 2 mol% In was doped. The blue emission of In-doped Zn_2SiO_4 thin film may be related to the In substitution for Zn. The 2 mol% In-doped Zn_2SiO_4 thin film exhibited blue emission with CIE color coordinates of $x=0.208$ and $y=0.086$.

1. Introduction

The electroluminescence (EL) properties of oxide phosphors have been extensively investigated in recent years in relation to flat-panel displays. A variety of oxide phosphors have been characterized for use in oxide phosphor electroluminescent devices. Among these oxide phosphors, the silicate phosphors such as Zn_2SiO_4 and Y_2SiO_5 [1–3] are considered as some of the most promising candidates for commercial applications due to their EL properties and high chemical stabilities. Most studies have focused on characterizing their EL properties and developing processes for fabricating silicate phosphors using various transition-metal and rare-earth dopants as activators [4–6]. Minami et al. [1] reported the EL properties of Mn-doped Zn_2SiO_4 thin film which has green emission with an efficiency of 0.78 lm/W. Red emission at a wavelength of 610 nm has also been obtained from a Zn_2SiO_4:Eu phosphor [7]. Moreover, blue emission at a wavelength of 403 nm has been observed from a 1 mol% Ti-doped Zn_2SiO_4 phosphor prepared by radio-frequency sputtering [8], though the luminance of the phosphor is low in comparison with those of Mn- and Eu-doped Zn_2SiO_4. However, if the high luminance with blue emission is obtained for Zn_2SiO_4-based phosphors, the commercial application to the full color display by using Zn_2SiO_4 as a host material may be expected. Thus, the evaluation of EL properties of Zn_2SiO_4 doped with various kinds of activator, which show the blue emission, is important. In this study, Zn_2SiO_4 thin films with In concentrations ranging from 0 to 10 mol% were prepared by the sol–gel process and their crystalline phases, microstructures, chromaticities, and brightnesses were characterized.

2. Experimental method

Sintered $BaTiO_3$ (BT) substrates for thin-film electroluminescent (TFEL) devices were prepared from high-purity BT powders (Sakai Kagaku Co. Ltd., BT-05). BT powder mixed with polyvinyl alcohol was pressed into a pellet (12 mm in diameter and 1 mm thick) under a pressure of 100 MPa and sintered at 1250 °C for 10 h in air. The sintered pellets were polished and annealed at 850 °C for 2 h in air. The sol–gel process was used to prepare Zn_2SiO_{4-x} mol% In (Zn_2SiO_4:In) thin films in the In concentration range of 2–10 mol%. Tetraethylorthosilicate (TEOS, Sigma-Aldrich, 99.999%) and zinc nitrate hexahydrate ($Zn(NO_3)_2\cdot 6H_2O$, Sigma-Aldrich, 99.9%) were used as the starting materials. The commercial $Zn(NO_3)_2\cdot 6H_2O$ was dissolved in deionized water and ethanol at a molar ratio of $Zn(NO_3)_2\cdot 6H_2O$:C_2H_5OH:H_2O=1:2:5. After stirring for 1 h at room temperature, TEOS was added to the zinc solution; HNO_3 (70%) was simultaneously added as a catalyst. An appropriate quantity of indium nitrate oxide ($In(NO_3)_3\cdot xH_2O$) (Sigma-Aldrich, 99.99%) was added to the reacted solution and stirred for 24 h at room temperature to obtain chemically stable

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and highly transparent solutions. Solutions were prepared with molar percentages of In in the range 0–10% relative to the number of moles of Zn_2SiO_4. Each solution was deposited on a BT substrate by spin coating at 3000 rpm for 30 s in air. This process was continued two times to obtain the crystalline thin film. The thin film was dried at 200 °C for 30 min in air and sintered at a temperature of 1100 °C with the heating and cooling rates of 5 °C/min for 1 h in N_2 atmosphere. The In-doped Zn_2SiO_4 disks were also prepared via the conventional solid state reaction method to evaluate the electrical resistivity of the disks, using high purity ($\geq$99.9%) ZnO, SiO_2, and In_2O_3 powders. After mixing with ethanol, these powders were pressed into a disk (40 mm in diameter and 2 mm in thickness) and sintered at 1100 °C for 1 h in N_2 atmosphere. The sintered disks were polished and the dimension of the sample was approximately 30 mm in diameter and 1 mm in thickness. The electrical resistivity of the In-doped Zn_2SiO_4 disks was measured by using a resistance meter (8240A, ADCMT Ltd., Japan) under a dc voltage of 100 V. The crystalline phases of the thin films and the powders with different In concentrations were characterized by X-ray diffraction (XRD, RINT-2000, Rigaku Co., Japan) using Cu$K\alpha$ radiation. The lattice parameters of the In-doped Zn_2SiO_4 powders were determined in terms of the least squares method. The microstructures of the synthesized powders and thin films were investigated using a field-emission scanning electron microscope (FE-SEM, JSM-6330F, JEOL Ltd., Japan) equipped with energy-dispersive X-ray (EDX, JED 2200, JEOL Ltd., Japan) analysis. The EL properties of the thin films were characterized by fabricating TFEL devices (Fig. 1) by combining a BT substrate with an In-doped Zn_2SiO_4 thin film. The EL properties of the devices were measured using a SawyerTower circuit and a conventional luminance meter by applying ac voltage in the range 0–450 V with a frequency of 1 kHz.

3. Results and discussion

The XRD pattern of a Zn_2SiO_4 thin film with 2 mol% In doping deposited on a BT substrate was obtained by 2θ scan and the results are shown in Fig. 2. All the XRD peaks are corresponded to the diffraction from the Zn_2SiO_4 (JCPDS no. 37-1485) and no secondary phase was detected. The solutions of Zn_2SiO_4:In synthesized by the sol–gel process were dried and sintered at 1100 °C for 1 h in a N_2 atmosphere and the crystalline phases of samples with different In concentrations were identified by using X-ray powder diffraction (XRPD). The XRPD patterns of the In-doped Zn_2SiO_4 powders are shown in Fig. 3. In concentration range of 0–1.5 mol%, no diffraction peak which corresponded to the secondary phase was detected, whereas the presence of In_2O_3 (JCPDS no. 06-0416) was detected in the XRPD profiles as a secondary phase in the In concentrations range of 2–10 mol%. Thus, the Zn_2SiO_4:In powders with In concentrations up to 1.5 mol% are considered to be a single phase. For the In-doped $ZnGa_2O_4$, the presence of secondary phase was not observed up to 5 wt% In_2O_3 doping, and the In-substituted $ZnGa_2O_4$ and In_2O_3

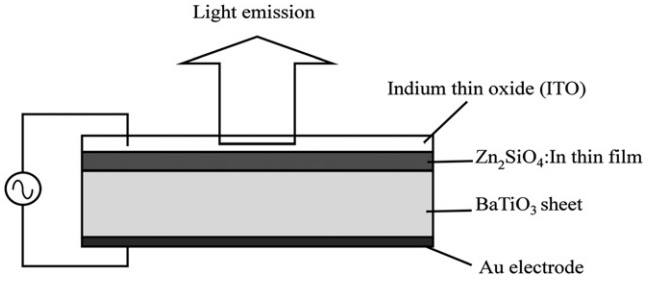

Fig. 1. TFEL device structure with a thick ceramic layer. The phosphor layer is approximately 1 μm thick. The $BaTiO_3$ substrate is approximately 0.3 mm thick.

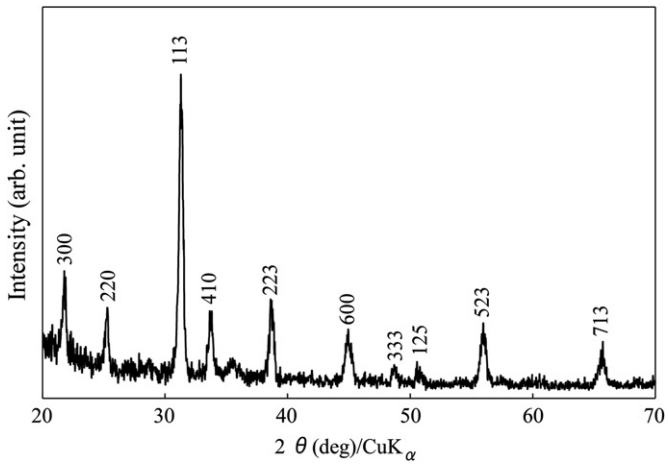

Fig. 2. Typical XRD pattern of Zn_2SiO_4 thin film with 2 mol% In doping deposited on a $BaTiO_3$ substrate. The diffraction data were collected by 2θ scan.

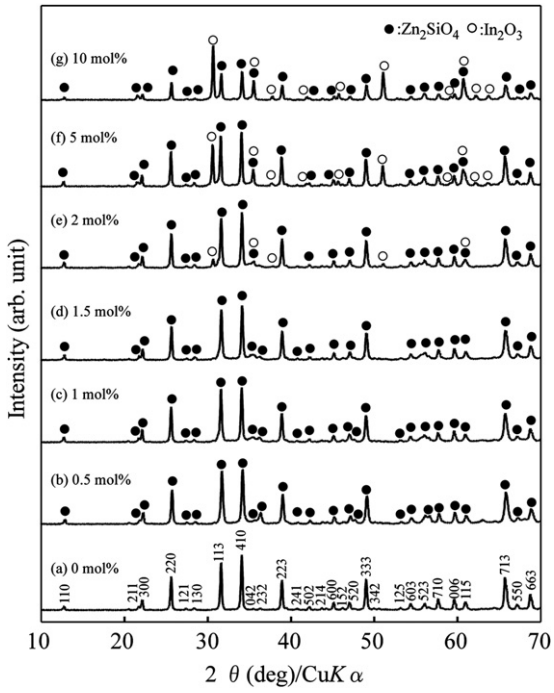

Fig. 3. XRPD patterns of In-doped Zn_2SiO_4 powders sintered at 1100 °C for 1 h in a N_2 atmosphere.

were detected at the In_2O_3 concentration higher than 5 wt% [9]. These results indicated that the Zn^{2+} cation in $ZnGa_2O_4$ was substituted by In^{3+} cation and the Zn^{2+} cation was interstitially substituted in the $ZnGa_2O_4$ in the range of 0–5 wt% In_2O_3 doping, resulting in oxygen vacancy in $ZnGa_2O_4$. On the other hand, in the case of In-doped ZnO film [10], similar results were also reported and no phases corresponding to indium oxide or other zinc–indium compounds were observed.

Based on the ionic radii of cations reported by Shannon [11], it is considered that the Zn site in Zn_2SiO_4 is partially occupied by In^{3+} cation and the Zn^{2+} cation may be interstitially substituted in the Zn_2SiO_4 as well as $ZnGa_2O_4$:In [9] and ZnO:In [10]. Thus, the lattice parameters of Zn_2SiO_4:In phosphors were determined in order to clarify the In substitution for Zn in Zn_2SiO_4 and the results are shown in Fig. 4. Both the lattice parameters of the In-doped Zn_2SiO_4 phosphors increased as the In concentration increased from 0 to 1.5 mol%, and these parameters were almost