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Eu^{2+}-activated blue-emitting glass phosphor derived from Eu^{3+} exchanged USY zeolites by thermal treatment in reducing atmosphere

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ABSTRACT

In this work, we report a facile method to prepare Eu^{2+} activated blue-emitting glass phosphor via loading Eu^{3+} into USY ($Na_{28}Si_{168}Al_{28}O_{384}{\cdot}240H_2O$, Si/Al ratio = 6) zeolites' cavities followed by thermal treatment in reducing atmosphere. The zeolites powders containing Eu^{3+} were treated at different temperatures from 800 °C to 1200 °C in flowing 5%H_2 + 95%N_2 ambient. The photoluminescence properties were investigated on aspects of the emission and excitation spectra, internal quantum efficiency (IQE), thermal stability and the fluorescence lifetime. The XRD patterns showed that the sample calcined at 950 °C was of pure glassy state. Under the broad 200–430 nm excitation, a strong blue emission band peaked at 451 nm with a full width of half maximum (FWHM) value of 74 nm was observed for this sample. Under the 365 nm excitation, the samples treated at different temperatures showed monotone red shift in the emission peak wavelengths with the thermal treatment temperature increasing. Transparent glass sheets were obtained from the glass phosphor powders by spark plasma sintering (SPS) at 1200 °C, 1250 °C and 1300 °C. The optical transmittance and thermal conductivity of transparent glass sheets were measured. The results indicated that this glass phosphor may be a potential candidate material for white LEDs.

1. Introduction

Energy-saving and emission reduction have received more and more attention in recent years. In the field of lighting, traditional light sources such as incandescent lamp, fluorescent lamp and high intensity discharge (HID) lamp may no longer be adapted to the needs of twenty-first century due to their disadvantage of high power consumption. So the white light emitting diodes (wLEDs) emerge as the times require. wLEDs are considered as the next generation illuminating lamps for their superior features such as long lifetime, low power consumption, high luminous efficiency, and small size [1]. wLEDs have been widely used in various fields including urban landscape lighting, car lights, traffic lights, liquid crystal display(LCD) backlighting, indoor and outdoor general lighting [2].

Currently, there are mainly three ways to generate white light for solid state lighting [3–6] (1) Multicolor LEDs combination, which is to prepare white light by assembling red, green and blue LEDs together. This method may easily cause color difference for the light output of each LED decreasing differently with the temperature increasing. (2) Combining an InGaN-based blue chip with a yellow phosphor ($YAG:Ce^{3+}$) that can be excited efficiently by blue light. Part of the blue light is absorbed by the phosphor, which leads the phosphor to emit yellow light. The yellow light blends the remaining blue light from the LED with appropriate proportions, resulting in white light. However, this way is not enough satisfying either, such as high color temperature, unsatisfying color rendition, which is not suitable enough for indoor lighting as a result of the lack of a red light component. In addition, since blue and yellow light come from different matrices, the color stability is not ideal, and it will change with the driving voltage changing. (3) Near-ultraviolet (n-UV) LED chip excites red-green-blue (RGB) tricolor phosphors to obtain white light. Compared with the $InGaN/YAG:Ce^{3+}$ wLEDs, the wLEDs made up of n-UV chip and appropriate phosphors can provide a higher color rendering index (CRI). Another advantage of n-UV excitation is that because all the colors are determined by the phosphors, ultraviolet light can be completely absorbed, thus eliminating the harm of high-energy UV photons to human. Blue phosphor is an indispensable component of the scheme, so the research and development of blue phosphor has been a very important issue [7]. Therefore enormous investigations have been made to the development of blue phosphor which can be excited by n-UV LED chip. For example, (1) aluminate materials, the representative is Eu^{2+} activated $BaMgAl_{10}O_{17}$ (BAM) phosphor($BaMgAl_{10}O_{17}:Eu^{2+}$) [8,9]. (2)

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Eu^{2+} activated blue phosphor based on silicates, such as $Sr_2MgSi_2O_7$:Eu^{2+}, $Ca_2MgSi_2O_7$:Eu^{2+} and $Sr_2MgSi_2O_7$: Eu^{2+} + M (M = Dy^{3+}, La^{3+}, Na^{+}) [10–12]. (3) Eu^{2+}activated phosphate materials $NaBaPO_4$:Eu^{2+} and $KBaPO_4$:Eu^{2+} [13,14]. (4) Borate system, including $Ba_2CaB_6O_{12}$: Eu^{2+} phosphor and $Sr_2B_5O_9Cl$:Eu^{2+} phosphors [15,16].

However, these blue phosphors mentioned above may not be satisfying enough for practical application. For instance, the synthesis temperature of BAM phosphor is too high (more than 1600 °C) and its luminescent properties are easily deteriorated [17,18]. Silicate phosphors have better color rendering than BAM phosphors and relatively lower preparation temperatures, but it is easy to get miscellaneous phase when prepared with conventional solid-state reaction method. Phosphate phosphors and borate phosphors also have lower preparation temperature. However, the research on these two phosphors is still insufficient [19]. Aluminosilicate zeolites are a kind of crystalline microporous materials which has large surface area and low density. Due to their excellent loading capacities, they have been widely used as host materials for guest molecules, ions and nanomaterials [20]. In recent years, many kinds of phosphors derived from various kinds of zeolites have been reported. Yang et al. reported blue-emitting europium(II)-doped microporous zeolite 13X derivative glass phosphor with the emission peaked at 450 nm and a wide excitation band from 250 nm to 420 nm [21]. Lin et al. reported the reversible emission evolution of Ag activated zeolites A via the hydration/dehydration process in water vapor/vacuum [22]. Ye et al. studied the luminescence behaviours of Mn^{2+} and Yb^{3+} ions confined in zeolites-Y [23]. Gong et al. successfully synthesized an upconversion luminescence transparent glass from Er^{3+}/Yb^{3+} co-doped ZSM-5 zeolites powder [24]. Here we also chose zeolites as a matrix to prepare Eu^{2+} activated blue-emitting phosphor by loading Eu^{3+} into USY ($Na_{28}Si_{168}Al_{28}$ O_{384}·$240H_2O$, Si/Al ratio = 6) zeolites' cavities via ion-exchange and solid-state reaction in reducing atmosphere. In the process of synthesizing this kind of blue-emitting phosphor, the reaction temperature is also relatively low, which only needs about 950 °C. In addition, this kind of glass phosphor derived from USY zoelites has many advantages such as physical and chemical stability, high internal quantum efficiency (57%) and not easy to produce Eu^{2+} clusters due to separation of luminescent centers by USY zeolites' periodical porous structure. At the same time, the preparation method has the characteristics of high controllability, high consistency, low cost, no toxicity and no pollution.

2. Experimental

This blue-emitting phosphors were prepared by ion-exchange and solid-state reaction method. The raw materials were ultra-stable Y zeolites (USY zeolites, A.R.) and europium nitrate hexahydrate (Eu $(NO)_3$·$6H_2O$, 99.9%). The Si/Al ratio of the USY zeolites is 6 and the chemical formula is $Na_{28}Si_{168}Al_{28}O_{384}$·$240H_2O$. Firstly, the USY zeolite and Eu$(NO)_3$·$6H_2O$ powders were weighted. Then 100 g USY zeolites powder mixed with 25.1 g Eu$(NO)_3$·$6H_2O$ powder were immersed into deionized (DI) water in a beaker. The suspension was stirred at room temperature for 24 h for ion exchange. After ion exchange, the suspension is centrifuged and washed with DI water to remove excessive Na^{+} ions and Eu^{3+} ions on the zeolite powders' surface. Then, the Eu^{3+}-containing USY zeolite powders were calcined in a corundum crucible at different temperatures from 800 °C to 1200 °C for 3 h in a reducing ambient (5%H_2 + 95%N_2). Finally, the samples were cooled to room temperature and the Eu^{2+} activated blue-emitting phosphor were obtained.

The phase structure of the as-prepared samples was analyzed by X-ray diffraction (XRD) with Cu K_α λ = 0.15418 nm radiation at a scanning step of 0.01° in the 2θ range from 2° to 90° operated at 40 kV and 15 mA (Rigaku, Model MiniFlex600, Japan). The absorption spectra of the blue-emitting phosphor and the optical transmittance of the three transparent glass sheets were obtained by an ultraviolet-visible-NIR spectrophotometer (PerkinElmer, Model Lambda1050, U.S.A.). Photoluminescence excitation (PLE) spectra and photoluminescence (PL) spectra at room temperature were measured with a fluorescence spectrophotometer (HORIBA, DualUV-NIR, Japan) equipped with a xenon lamp as the excitation source. Morphology of the samples was investigated with a scanning electron microscopy (SEM) (HITACHI, S-4800, Japan). The elemental composition was evaluated by energy dispersive X-ray spectroscopy (EDS) equipped within the HITACHI SEM. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) (PerkinElmer, optima 5100DV, U.S.A.) was also employed to investigate the samples` chemical composition. The internal quantum efficiency (IQE) was measured with Edinburgh Instruments fluorescence spectrophotometer (Edinburgh Instruments, FLS980, U.K.). X-ray photoelectron spectroscopy (XPS) (ULVAC-PHI, PHI-5000, Japan) was carried out to investigate the valence state of europium. Thermal conductivity of the transparent glass phosphor sheet was measured using a laser flash apparatus (Netzsch, LFA447, Germany). Temperature-dependent PL spectra and fluorescence lifetime were measured by Fluorescence Spectrophotometer (Edinburgh Instruments, FLS980, U.K.).

3. Results and discussion

The XRD patterns of the prepared samples treated at different temperatures from 800 °C to 1200 °C are shown in Fig. 1. The diffraction peaks of the sample treated at 800 °C are in good match with the zeolites Y (JCPDS NO.75–1860), indicating that the framework of the

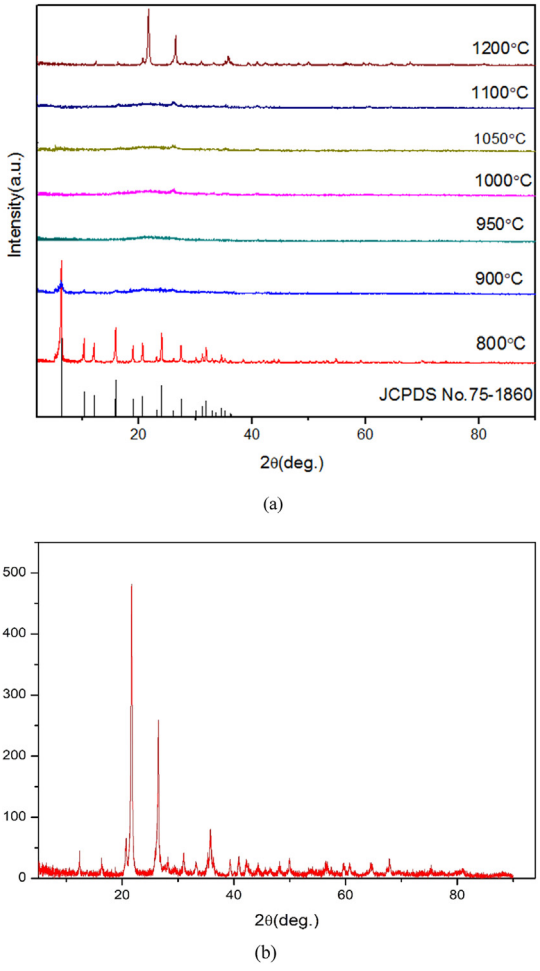

Fig. 1. (a) X-ray diffraction θ − 2θ scans of the Eu^{3+} exchanged USY zeolites powders thermally treated at different temperatures from 800 °C to 1200 °C. (b) An enlarged figure of the X-ray diffraction θ − 2θ scans of the Eu^{3+} exchanged USY zeolites powders thermally treated at 1200 °C.