Temperature Dependence of Luminescence Color of Mn^{2+}-doped $ZnCN_2$ Phosphor

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Abstract

Photoluminescent materials which show multi-wavelength luminescence have potential applications in temperature sensing device. In this study, Mn^{2+}-doped $ZnCN_2$ phosphor was prepared by ammonia nitridation of Zn-Mn oxalate precursors in the presence of carbon nitride. Upon UV excitation, it

showed photoluminescence band at 580 nm due to isolated Mn^{2+} ions as well as minor broad emission bands at 500 and 670 nm due to anion vacancies and Mn-Mn pairs in the $ZnCN_2$, respectively. Since the intensities of the luminescent bands had different temperature dependencies, and the total luminescence color changed from orange at 80 K to yellow green at 500 K.

Keywords: zinc carbodiimide; luminescence; phosphor; temperature sensor

1. Introduction

Photoluminescent (PL) materials have potential applications not only in lighting, but also in optical sensors. Temperature sensing using PL materials have been developed in organic molecules, metal-ligand complexes, and inorganic phosphors [1]. Phosphors, which show highly temperature-dependent quantum yield of luminescence and luminescence lifetime, can be explored for sensing temperature [2]. Different temperature quenching properties of two luminescent centers incorporated in phosphors change the total luminescence color depending on temperature [3]. Unit cell compression of host crystal structure of inorganic phosphors at low temperatures can modify the transition energy for *f-d* and *d-d* transitions, leading to temperature-dependent luminescence wavelength [4].

In inorganic phosphors, luminescence can be obtained not only from the metal ions in a normal crystallographic site but also from defect sites in the structure, such as local clusters, interstitial ions, and site vacancies. These defect site show luminescence at a different wavelength from the

luminescence center. Different temperature dependencies can be expected for defect-related luminescence. Several metal carbodiimides have been reported in the literature as phosphors doped with a Eu^{2+} or Mn^{2+} luminescence center [5,6]. Mn^{2+}-doped $ZnCN_2$ showed yellow luminescence under UV light irradiation [6]. Non-doped $ZnCN_2$ also showed a broad blue luminescence, which was attributable to lattice defect-related luminescence. The combined luminescence from the luminescent center Mn^{2+}, and defects of the host matrix can be used to make temperature-sensing phosphors, if the temperature dependencies of these luminescence intensities are different. Defect-derived luminescence is very important in actual applications and excellent multicolor luminescent properties can be expected when the luminescence from the doped meal ion and the defect site are generated simultaneously. In this study, Mn^{2+}-doped $ZnCN_2$ phosphors were prepared by the NH_3 nitridation method and the temperature dependence of PL properties were investigated.

2. Experimental procedure

Mn^{2+}-doped $ZnCN_2$ phosphors were prepared by nitridation of Zn-Mn oxalate precursors mixed with carbon nitride, as reported in the literature [6]. Aqueous solutions of $Zn(NO_3)\cdot 6H_2O$ and $MnCl_2\cdot 4H_2O$ were dropped into an aqueous ammonium oxalate solution, and the white precipitate was filtrated and dried to obtain Zn-Mn oxalate precursors. The Zn:Mn molar ratio was $1\text{-}x\text{:}x$ (x = 0, 0.01, 0.02, 0.05, 0.10). Carbon nitride (C_3N_4) was prepared by firing melamine at 500 °C in air [7]. The oxalate

precursor and C_3N_4 were mixed at a molar ratio of $Zn:C_3N_4$ = 1:4 similar to the previous paper [6]. The mixed precursors were nitrided at 600 °C for 1 h under 200 mL/min of NH_3 flow.

Crystalline phase of the products was characterized using X-ray diffraction (XRD; Ultima IV, Rigaku) with Cu-Ka radiation ($\lambda_{\alpha1}$ = 0.15406 nm and $\lambda_{\alpha2}$ = 0.15444 nm). The X-ray absorption near-edge structure (XANES) spectrum for the Mn K-edge was measured in the transmission mode at the BL-9C beam line of the Photon Factory at the KEK, Tsukuba, Japan. PL spectra of Mn^{2+}-doped $ZnCN_2$ (x = 0.02) were measured from 80 to 500 K under irradiation of a 340 nm LED light. The sample temperature was controlled using a cryostat (LT3 Helitran, ROCKGATE). Multichannel spectroscopy (Ocean Optics, QE65 Pro) was used for the luminescence spectrum measurement.

3. Results and discussion

Powder XRD patterns of the nitrided products were consistent with ICDD data ($ZnCN_2$, 01-070-4898). A single-phase $ZnCN_2$ was obtained in the nitrided products below x = 0.05 and a minor secondary phase appeared at x = 0.10 as shown in Fig. S1. The lattice parameters of the $ZnCN_2$ phase increased with increasing Mn content up to x = 0.05, because the ionic radius of Mn^{2+} (0.66 nm) is larger than that of Zn^{2+} (0.60 nm) [8]. The XANES spectrum for the Mn K-edge showed that the absorption energy for Mn-doped $ZnCN_2$ corresponded to that for the MnO reference, indicating that the oxidation state of the Mn in $ZnCN_2$ phosphor was 2+ as shown in Fig. S2. The apparent pre-edge peak at 6538 eV in

the XANES spectrum suggests that the Mn ion occupied the Zn site in the $ZnCN_2$ structure, which is a non-centrosymmetric tetrahedral site [9].

Upon excitation at 340 nm, Mn^{2+}-doped $ZnCN_2$ exhibited a strong luminescence band peaking at 580 nm, similarly to a previous report [6]. The highest luminescence intensity was observed for the product at $x = 0.02$. Two additional luminescent bands clearly appear at 500 and 670 nm in the spectrum at 80 K as shown in Fig. 1. The PL spectra were deconvoluted into three bands with respect to wavenumber by applying three Gaussian curves as shown in Fig. S3. The luminescence bands at 500, 580, and 670 nm are labelled peaks 1, 2, and 3, respectively. The 580 nm band (peak 2) has been reported in Mn^{2+}-doped $ZnCN_2$ and assigned to the $^4T_1 \rightarrow {}^6A_1$ transition in the Mn^{2+} luminescent center [6]. In the same literature, the band around 500 nm (peak 1) in non-doped $ZnCN_2$ was attributed to a defect-induced transition related to the anion vacancy. Origin of the anion vacancy is under investigation, but partial formation of cyanamide anion $[N\text{-}C{\equiv}N]^{2-}$ instead of carbodiimide anion $[N{=}C{=}N]^{2-}$ might be related to the vacancy inducing a local positive formal charge on N atom. A broad band at 670 nm has been reported in Mn-doped ZnS phosphor, which is attributed to a local Mn-Mn pair [10]. Luminescence intensity ratio (peak 3/peak 2) of Mn^{2+}-doped $ZnCN_2$ increased with increasing Mn doping concentration as shown in Fig. S4. This result also supports that the Mn-Mn pairs in the $ZnCN_2$ are the origin of the 670 nm band.

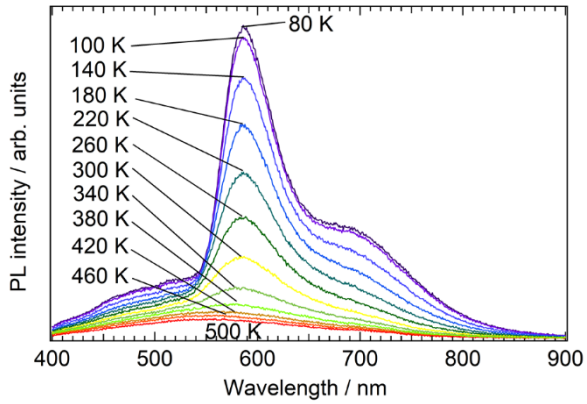

Figure 1 PL spectra of Mn^{2+}-doped $ZnCN_2$ (x = 0.02) depending on temperature.

Temperature dependences of the relative intensity and luminescence peak wavelength of the Mn^{2+}-doped $ZnCN_2$ phosphor at x = 0.02 are shown in Fig. 2. The luminescence peak wavelengths are almost independent of temperature between 80 and 500 K (Fig. 2(a)). The relative intensities of the luminescence peaks are plotted in Fig. 2(b). The Mn-related luminescence bands originating from the isolated Mn^{2+} and the Mn-Mn pair in the $ZnCN_2$ show larger temperature quenching than the anion-vacancy-induced luminescence (Peak 1). The rapid temperature quenching of peaks 2 and 3 are due to the increased non-radiative decay with increasing temperature. The Mn-related luminescence peaks (peaks 2 and 3) show similar temperature dependencies, while the intensity of the luminescence peak 1 due to anion vacancies is more stable at high temperatures. The stability of the luminescent intensity with temperature has also been reported in non-doped $ZnCN_2$, which shows an anion-vacancy-related luminescence around 500 nm [6]. The temperatures at which the luminescence intensity is reduced by 1/2 were approximately 337, 205, and 205 K for the luminescence peaks 1, 2, and 3, respectively. The

absolute sensitivity S_a for the optical temperature sensing based on the luminescence intensity ratio (I_{peak2}/I_{peak1}) was estimated according to the reference [12] and the details are shown in SI. The maximal S_a reached to 0.022 K^{-1} at 260 K, which is higher than the values of multi luminescent center doped phosphors [12].

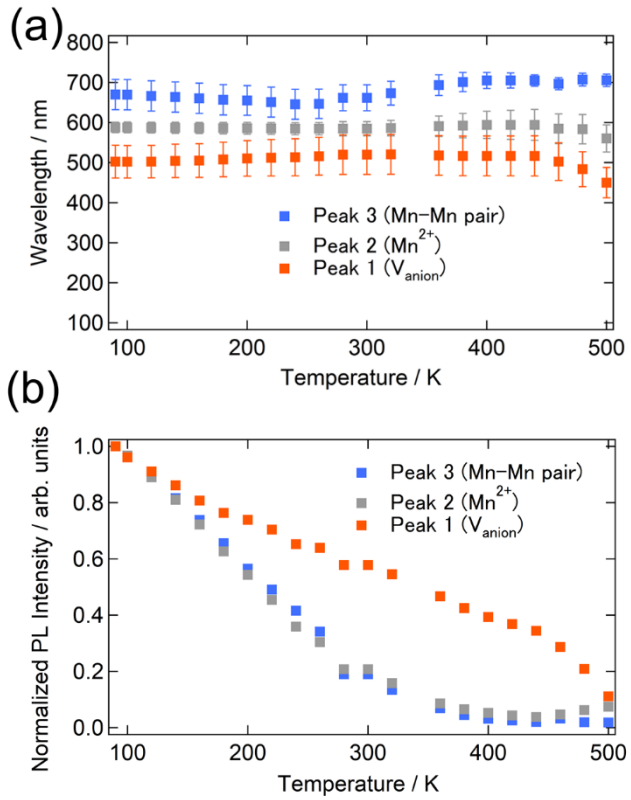

Figure 2. Temperature dependence of (a) luminescence peak wavelength and (b) normalized peak intensity of Mn^{2+}-doped $ZnCN_2$ phosphor.

The Commission internationale de l'eclairage (CIE) diagram in Fig. 3 depicts the variation in luminescence color of the Mn^{2+}-doped $ZnCN_2$ phosphor from orange at 80 K to yellow-green at 500 K. The corresponding CIE color coordinates changed from (0.49(2), 0.41(1)) at 80 K to (0.36(1),

0.41(a)) at 500 K. The photoluminescence spectra of single doped phosphors, such as Eu^{2+}-doped $BaCN_2$, exhibited temperature dependence, although the luminescence color did not change dramatically with temperature [4]. The local coordination around the luminescent center did not change very much with increasing temperature. Multi luminescent center doped phosphors of inorganic and metal-ligand complex compounds generally show a wide color change owing to the different thermal quenching properties of the luminescent centers [1,3]. Mn^{2+}-doped $ZnCN_2$ only has a Mn^{2+} luminescent center in the host lattice and a defect-related luminescence appears together with the luminescence from Mn^{2+}-center. Multi-color luminescence with different temperature dependencies enables the inorganic phosphor to be used as temperature sensor.

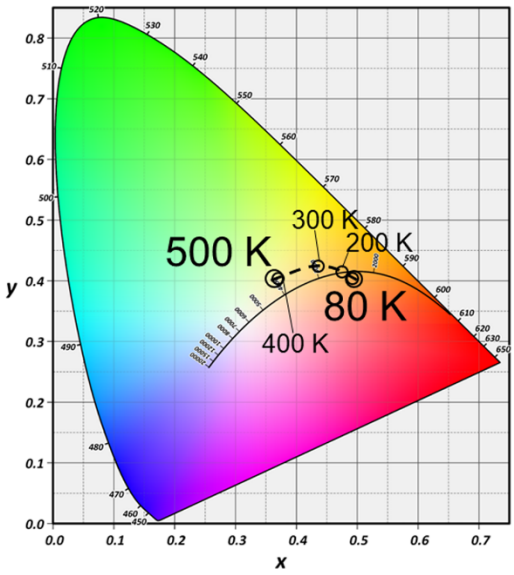

Figure 3. CIE chromaticity diagram of Mn^{2+}-doped $ZnCN_2$ phosphor (x = 0.02) at different temperatures.

4. Conclusion

Mn^{2+}-doped $ZnCN_2$ was prepared by NH_3 nitridation of a Zn-Mn oxalate precursor. A luminescence color variation with temperature was observed. Photoluminescent bands originating from the Mn^{2+} in the host lattice, anion vacancy, and Mn-Mn pair coexisted in the phosphor and showed different temperature quenching properties. Defect-related luminescence can produce temperature-sensing inorganic phosphors under a corporation of the photoluminescence from the luminescent center.

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