Photoluminescence properties of CaO:Ce³⁺,Na⁺, a non-garnet yellow-emitting phosphor under blue light excitation

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ABSTRACT

A yellow-emitting phosphor, CaO:Ce³⁺,Na⁺ is synthesized by solid-state reaction. The photoluminescence spectra, fluorescence decay curves and the temperature-dependent luminescence are investigated. The results show that CaO:Ce³⁺,Na⁺ can be excited by blue light, which matched well with the emission wavelengths of blue InGaN LED chips. When excited at 474 nm, in the range of 480–700 nm, CaO:Ce³⁺,Na⁺ exhibits a strong yellow emission band located around 555 nm. The temperature-dependent luminescence behavior of this phosphor indicates that CaO:Ce³⁺,Na⁺ exhibits better thermal stability than commercial YAG:Ce³⁺.

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1. Introduction

The spectroscopic properties of Ce³⁺ in different host lattices have been widely investigated due to the large absorption cross section of the parity allowed f–d transitions of Ce³⁺ ion, therefore, appear as intense bands in spectra [1–4]. It is well known that Ce³⁺ doped garnet phosphor YAG has been used as the yellow component in InGaN-based white LEDs. It can absorb blue light and convert it into yellow emission. By blending the yellow and the penetrated blue light, white light can be generated [5–7]. However, YAG:Ce³⁺ has little red component and poor thermal stability, and those induce a low color rendering index and poor color stability of white LEDs. Therefore, it is important and necessary to fabricate some non-garnet phosphor with more red component and better thermal stability.

The luminescence properties of CaO-phosphors containing 17 different activators were reported by Lehmann in 1973 [8]. Although CaO is chemically relatively unstable in air, reacting with atmospheric moisture to non-luminescent Ca(OH), it can be experimentally improved by coating with a protecting layer of CaF₂ [8]. It is important to note that Ce³⁺ doped CaO cannot be excited by 254 or 365 nm ultraviolet but can be excited by visible blue light. Despite CaO:Ce³⁺ is excitable by blue light, data on the basic characteristics of the Ce³⁺ luminescence in CaO host are sparse [3]. This prompts us to perform a detailed study of powder samples with compositions CaO:xCe³⁺, xNa⁺ (0<x≤0.02). The photoluminescence properties of CaO:Ce³⁺, Na⁺ are studied in this letter. The effects of Ce³⁺ concentration on the crystal structure, luminescence and fluorescence decay behavior of CaO are also investigated.

2. Experimental

CaO:Ce³⁺,Na⁺ were synthesized via solid-state reaction. The original materials were CaO (99.99%), CeO₂ (99.99%), and Na₂CO₃ (99.5%). Codoping Na⁺ helps to incorporate the Ce³⁺ into Ca²⁺ sites by compensating the different charges between Ce³⁺ and Ca²⁺. After the homogenization, the mixtures were placed in crucible boat and fired under reducing atmosphere of 5%H₂ + 95%N₂ at 1300 °C for 4 h.

A Bruker D8-Focus X-ray diffractometer (XRD) was employed to check the phase of the phosphors. The photoluminescence (PL), and photoluminescence excitation (PLE) spectra were measured by Hitachi F-4500 spectrometer equipped with a 150 W-xenon lamp under a working voltage of 700 V. Diffuse reflection (DR) spectra were obtained using BaSO₄ as a reference. The fluorescence decay curves of Ce³⁺ were measured by a FL920 fluorometer (Edinburgh Instruments Ltd.). All of the measurements above were performed at room temperature. A thermostat (Omega CN76000) was used to obtain the temperature-dependent photoluminescence (25–235 °C) spectra which were performed via Hitachi F-4500 spectrometer.

3. Results and discussion

CaO crystallizes in the space group $Fm\overline{3}m$ with lattice constants a = 4.810 Å [9]. Because the ionic radius of Ce³⁺ (1.03 Å) is close to that of Ca²⁺ (0.99 Å), it is expected that Ce³⁺ could be doped into the host substituting for Ca²⁺ by codoping Na⁺ to compensate the different charges between Ce³⁺ and Ca²⁺. Fig. 1 gives the XRD
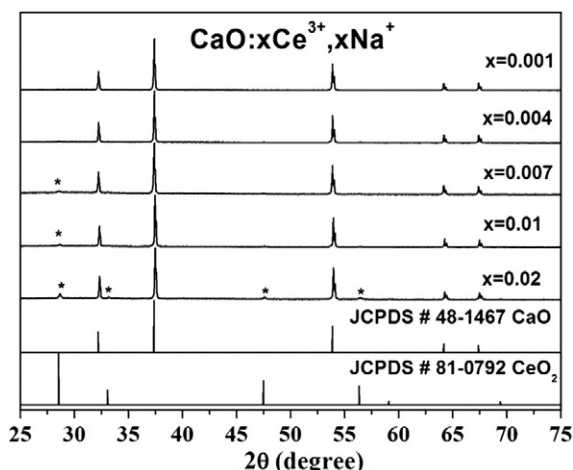
Fig. 1. XRD patterns of CaO:xCe^{3+},xNa$^+$ and the standard patterns of CaO and CeO$_2$.

Fig. 3. Fluorescence decay curves of CaO:xCe^{3+},xNa$^+$ (x = 0.001, 0.004, 0.007, 0.01 and 0.02) (a). Making natural logarithm to the decay curves (b).

patterns of CaO:xCe^{3+},xNa$^+$ (x = 0.001, 0.004, 0.007, 0.01 and 0.02) phosphors with the standard JCPDS cards of CaO and CeO$_2$ included. The results show that the XRD peaks of CaO:xCe^{3+},xNa$^+$ match quite well with those of the cubic CaO phase (JCPDS No.48-1467). This indicates that the obtained samples have a single phase and the codoped Ce^{3+} and Na$^+$ do not induce any impurity phase. However, a small amount of non-reduced CeO$_2$ phase (marked with asterisk) appears when the concentration of Ce^{3+} is more than 0.4 mol%, and this implies the occurrence of solubility saturation of Ce^{3+}. It is experimentally found that this CeO$_2$ phase cannot be reduced under any strong reducing atmospheres. This impurity phase could influence the photoluminescence behavior of CaO:Ce^{3+},Na$^+$, as will be discussed in the following section.

Fig. 2 gives the PLE and PL spectra of CaO:xCe^{3+},xNa$^+$ (x = 0.001, 0.004, 0.007, 0.01 and 0.02) phosphors. The PLE spectra consist of a single band located around 474 nm, with a broad band width ranging from approximately 400 to 530 nm. This peak position matches quite well with the emission peak position of InGaN-based blue LEDs, suggesting that the phosphor is very suitable for down-converting blue LED lights. When excited at 474 nm, CaO:xCe^{3+},xNa$^+$ exhibits a strong asymmetric yellow emission band located around 555 nm in the wavelength range of 480–700 nm. This emission peak originates from the transition of Ce^{3+} from the 5d excited state to the $^2F_{5/2}$ and $^2F_{7/2}$ ground states. It can be well fitted by two Gaussian profiles centered at 543 nm (18,416 cm^{-1}) and 596 nm (16,778 cm^{-1}). The energy difference of those two peaks is about 1638 cm^{-1}, which is

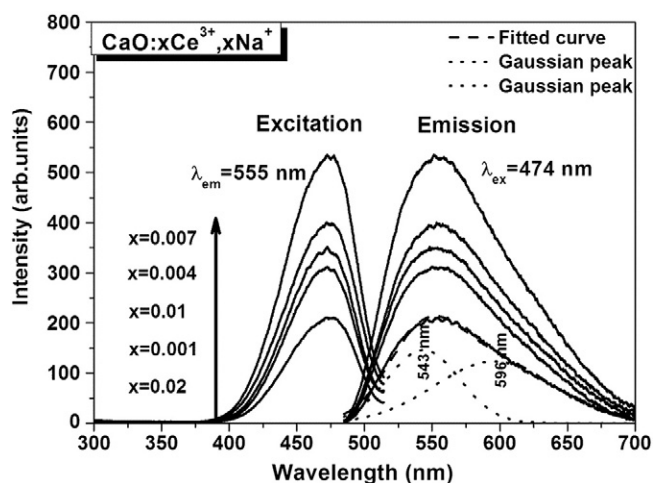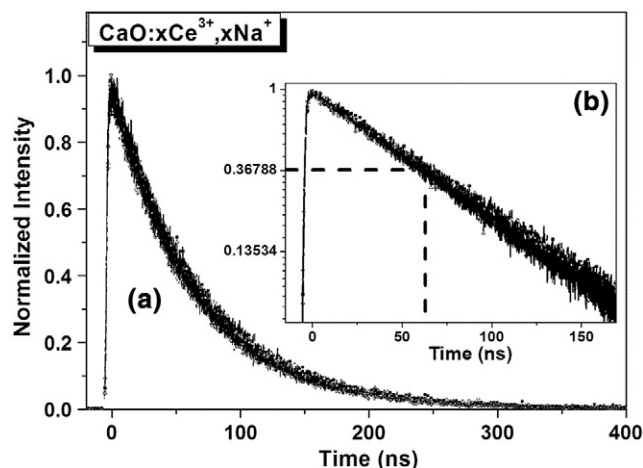close to the energy separation between $^2F_{5/2}$ and $^2F_{7/2}$ levels [10, 11]. From this figure, it can be seen that the PL intensity initially goes up with increasing the Ce^{3+} concentration from 0.1 mol% up to 0.7 mol% and further decreases gradually when the concentration is higher. The optimum doping concentration of Ce^{3+} is 0.7 mol%. Generally, this behavior of the PL intensity is ascribed to the concentration quenching of activators due to the spectral overlap between the emission and excitation. It can be further understood by the fluorescence decay study of Ce^{3+} with different concentrations. Fig. 3 gives the fluorescence decay curves of CaO:xCe^{3+},xNa$^+$. In Fig. 3(a), it shows that all the decay curves overlap with each other and exhibit a single exponential function, and does not produce any nonexponential function even when the concentrations of Ce^{3+} are high (x = 0.2). It is further confirmed by taking the logarithm of those curves, and linear lines are obtained as shown in Fig. 3(b). The exponential decay behavior of this phosphor implies that the nonexistence of Ce^{3+} concentration quenching phenomenon within the range of Ce^{3+} concentration of interest in this work. In principle, the PL intensity is in direct proportional to the absorption and the luminescent efficiency of the activator. As shown in Fig. 3(b), the fluorescence lifetime, the time at which the intensity has decayed to $1/e$ of the original value, behaves nearly unchanged around 63 ns, suggesting that the luminescent efficiencies of Ce^{3+} in CaO are almost invariable under different concentrations. Therefore, it is convinced that the variation of the PL intensities with different Ce^{3+} concentrations is due to the numbers of the excitation photons absorbed by Ce^{3+} ions.
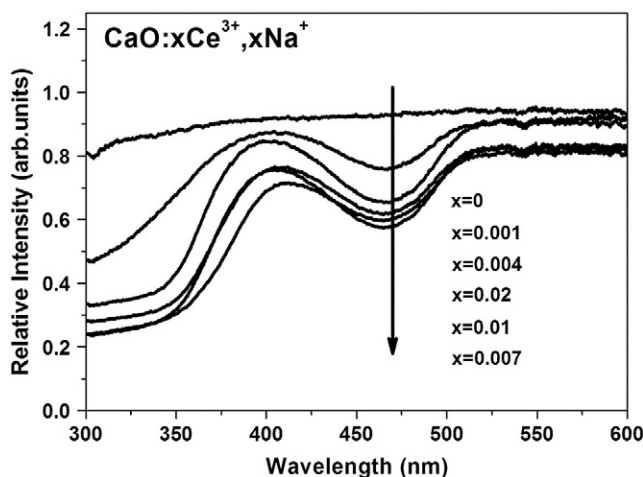

Fig. 2. PL and PLE spectra of CaO:xCe^{3+},xNa$^+$ phosphors.
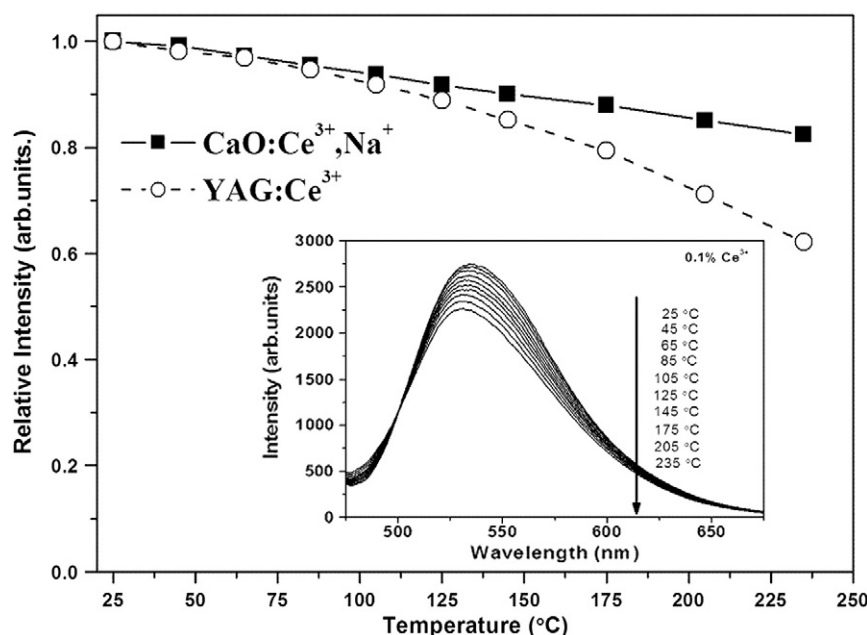

Fig. 4. DR spectra of undoped and Ce^{3+},Na$^+$ codoped CaO phosphors.

Fig. 5. The relative PL intensities of CaO:0.001Ce^{3+},0.001Na$^+$ and YAG:Ce at various temperatures in the range of 25–235 °C.

The diffuse reflectance spectra reflecting the absorption have been measured and shown in Fig. 4. The absorption of excitation photons increases as the Ce^{3+} concentrations up to 0.7 mol% and further decreases gradually, which matches quite well with the variation of the PL intensity of Ce^{3+} in CaO. Therefore, the variation of the PL intensity can be understood by the variation in number of absorbed excitation photons. The further decrease of absorption intensity may arise from the CeO$_2$ impurity phase (shown in Fig. 1) which induces absorption in visible light region and competes with Ce^{3+} for absorption of excitation lights.

Fig. 5 shows the thermal quenching of luminescence spectra of CaO:Ce^{3+},Na$^+$ under different temperatures in the range of 25 to 235 °C. The relative peak intensity of CaO:Ce^{3+},Na$^+$ decreases slightly with temperature. When the temperature is 150 °C, the relative peak intensity decreases 10% of the initial value, and even when the temperature is as high as 235 °C, the decrease in relative peak intensity is only 15%. It also can be seen from this figure, the thermal stability of CaO:Ce^{3+},Na$^+$ (solid square connected with solid line) was better than that of commercially available YAG:Ce phosphor (open circle connected with dashed line). The small decrease in the emission intensity indicates stable thermal ability of CaO:Ce^{3+},Na$^+$ phosphors.

4. Conclusions

A non-garnet yellow-emitting phosphor, CaO:Ce^{3+},Na$^+$, were synthesized and their PL properties were investigated. The excitation band of CaO:Ce^{3+},Na$^+$ matched well with the radiation of InGaN-based blue LEDs in the wavelength range of 400–530 nm. When excited at 474 nm, CaO:Ce^{3+}, Na$^+$ presented a yellow emission band located around 555 nm in the wavelength range of 480–700 nm.. Furthermore, the CaO:Ce^{3+},Na$^+$ phosphor had a better thermal stability than the commercial YAG:Ce phosphor. Our study of CaO:Ce^{3+},Na$^+$, as a non-garnet phosphor, may provide a new way toward the fabrication of yellow phosphor for blue LED chips based white LEDs.

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