Enhancement of photoluminescence in Sr_2CeO_4 phosphors by doping with non-rare earth impurities*

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Non-rare earth impurity doped Sr_2CeO_4:X (X =Zn, Hg, Al, Ag, Cr) phosphors are prepared by using the combustion method. The structural and photoluminescent properties of the as-prepared phosphors are investigated by X-ray diffraction (XRD) and photoluminescence at room temperature. Experimental results show that zinc addition and firing processing can effectively enhance the photoluminescence of Sr_2CeO_4 phosphors.

Keywords: Sr_2CeO_4 phosphor, photoluminescence, non-rare earth impurity

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1. Introduction

It is well known that the phosphors for field emission displays (FEDs) are required to have a high efficiency at low voltages, a high resistance to current saturation, a long service time and equal or better chromaticity than cathode ray tube (CRT) phosphors.[1] For full colour flat panel displays, unfortunately, it is difficult to find a suitable blue phosphor, because wide band gap materials are required, and the eye sensitivity is quite low in the blue spectral region.[2,3] Recently, Danielson *et al.*[4] have successfully synthesized an unusual luminescent rare-earth phosphor, Sr_2CeO_4, through the combinatorial method. The phosphor was found to exhibit an orthorhombic structure with one-dimensional chains of edge-sharing CeO_6 octahedra, and showed efficient blue-white luminescence centred at 485 nm with CIE (International Commission on Illumination) chromaticity coordinates $x = 0.198$ and $y = 0.292$, which was attributed to a ligand-to-metal Ce^{4+} charge transfer (CT). The Sr_2CeO_4 has gained increasing interest from the research community because of its potential applications as blue phosphors in commercial luminescent devices, such as electroluminescent panels, fluorescent lamps, cathode ray tubes, solid state lasers and X-ray medical radiography.

To date, considerable effort have been made to optimize the properties of Sr_2CeO_4 phosphors. Many synthesis methods, including the conventional high-temperature solid-state method,[5], co-precipitation,[6] the microemulsion method,[7] the hydrothermal method,[8,9] and citrate–gel,[10] sol–gel and solid-state reactions,[11] have been used to fabricate Sr_2CeO_4 phosphors emitting blue-white light. Jiang *et al.*[1] reported that Sr_2CeO_4 phosphor powder fired at 1200 °C for 2 h had a higher luminous efficiency at both 4 kV and 10 kV, indicating that the Sr_2CeO_4 phosphor had potential application in field emission displays. Several groups[12−14] have also investigated the rare earth (RE) impurity doping on Sr_2CeO_4 phosphors, the luminescence characteristics of doping RE ions and the energy transfer phenomenon in this compound. He *et al.*[9] even observed that the photoluminescence of Sr_2CeO_4 could be tuned by doping with Dy^{3+} ions. Whereas with excellent fundamental material properties as well as recent significant success in the growth of high-quality Sr_2CeO_4 phosphors for device applications, Danielson *et al.*[4] doubted that Sr_2CeO_4 was not suitable to be used as a commercial phosphor, because Ce^{4+} CT luminescence was easily quenched at 300 K, which made it impossible to improve the quantum efficiency (QE) at room temperature to above 50%. Indeed, at present, there are great challenges in improving the QE of the Sr_2CeO_4 phosphors.

The combustion method is a new synthesis method developed in recent years. Despite of its disadvantages, it presents some advantages compared with other methods: reagents are very simple compounds, no special equipment is required (pyrex containers are used), dopants can be easily introduced into the final

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product and the agglomeration of the powders remains limited. In this paper, we report the syntheses of non-rare earth impurity doped Sr_2CeO_4:X (X = Zn, Hg, Al, Ag, Cr) phosphors by using the combustion method. The photoluminscent properties are investigated. Our results demonstrate that the zinc doping and the sintering processing can effectively enhance the photoluminescence of the Sr_2CeO_4 phosphor at room temperature.

2. Experiment

All chemical reagents were of analytical grade, and were used without further purification. The Zn^{2+}-, Hg^{2+}-, Al^{3+}-, Ag^{1+}-, and Cr^{3+}-doped Sr_2CeO_4 powders were prepared through the combustion method. The dopant sources were $Zn(NO_3)_2$, $Hg(NO_3)_2$, $Al(NO_3)_3$, $AgNO_3$ and $Cr(NO_3)_3$. In a typical procedure, 5.7 mmol $Sr(NO_3)_2$, 3 mmol $Ce(NO_3)_3{\cdot}6H_2O$, x mmol dopant (for different doping concentrations) and 21 mmol $CO(NH_2)_2$ were added into 100 ml distilled water under vigorous stirring. The solution was then heated up to 500 °C in a muffle furnace. A gray precursor was obtained after the reaction of urea with $Ce(NO_3)_3$ or $Sr(NO_3)_2$. The as-prepared precursor was sintered at a temperature of 1100 °C for 4 h in a tube furnace, and then the phosphor was obtained. To investigate the effect of the sintering temperature on the luminescence, the obtained phosphor was fired at 800 °C–1250 °C. The phase structures of the phosphor powders were studied by using X-ray diffraction with Cu-K_α radiation at $\lambda = 1.5418$ Å. The room-temperature photoluminescence (PL) measurement was performed with a spectrofluorophotometer (PL, PerkinElmer LS55).

3. Results and discussion

The emission spectra of the pure Sr_2CeO_4 powders and the Sr_2CeO_4 powders doped with various non-rare earth metals (with X/Sr=0.10, (X = Zn, Hg, Al, Ag, Cr)) are showed in Fig. 1. The typical emission spectrum of the pure Sr_2CeO_4 powder measured at room temperature shows a broad emission peak centred at 467 nm, as reported by others. The emission spectrum is attributed to the charge-transfer transition from O^{2-} to Ce^{4+}.[4] It can also be seen from Fig. 1 that the luminous intensities of the non-rare earth metal doped Sr_2CeO_4 powders are each significantly different from that of the pure Sr_2CeO_4 powder, and vary with the doping species, while the shapes of the emission spectra of the doped Sr_2CeO_4 powders are similar to that of the pure Sr_2CeO_4 powder. This implies that the luminescent mechanism of the doped powder is the same as that of the pure Sr_2CeO_4 powder, so the emission spectra of the doped phosphors are also attributed to the charge-transfer transition from O^{2-} to Ce^{4+}, and the non-rare earth impurity doping does not change the active luminescent centre and the luminescent mechanism of the phosphor. It is found that the dopings with Hg, Al, Ag, and Cr can reduce the luminous intensities of the samples, and the photoluminescence of Sr_2CeO_4:Cr powders nearly quenches compared with that of the pure Sr_2CeO_4 powders. However, the luminous intensity of the Zn-doped Sr_2CeO_4 powder is found to be enhanced effectively. It has been recognized that the charge transfer transition is sensitive to the ligand environment. The substitution of Sr^{2+} by other ions may affect the luminescence of Sr_2CeO_4. Jiang *et al.*[1] claimed that doping Sr_2CeO_4 with some divalent alkaline earth elements (such as Ca or Ba) may improve its emission. However, Fu *et al.*[15] confirmed that the Ca/Ba doping did not evidently improve the emission of Sr_2CeO_4. In this study, we can see that doping with divalent element Zn can effectively enhance the emission of Sr_2CeO_4. However, with monovalent and trivalent element dopings, no emission improvement of Sr_2CeO_4 is observed. We think that the divalent state, the larger electronegativity and the smaller radius of the dopant each may play an important role in improving the emission of Sr_2CeO_4. However, the exact reason for this needs to be further investigated. The Zn-doped Sr_2CeO_4 powders emit strong blue-white luminescence at room temperature with excitation at 370 nm, which can be easily observed with the naked eye. Pieterson *et al.*[16] have investigated the luminous intensity of Sr_2CeO_4:Ca^{2+}, and observed a larger Stokes shift and a red shift of the emission, which was attributed to the expansion of the metal-to-ligand bonds in the excited state as a result of the presence of smaller Ca^{2+} ions on larger Sr^{2+} sites. In this study, Zn^{2+} is smaller than Sr^{2+}, but the red shift of the emission of the Sr_2CeO_4:Zn powders is not clearly observed as expected. The large Pauling electronegativity of Zn (Pauling electronegativity: 1.65) compared with that of Ca (Pauling electronegativity: 1.00) results in a stronger Zn^{2+}-to-ligand bond compared with the Ca^{2+}-to-ligand bond. Therefore, the red shift of the emission of the Sr_2CeO_4:Zn powder, which reflects the expansion of the metal-to-ligand bonds in the ex-

cited state, is not easily observed.

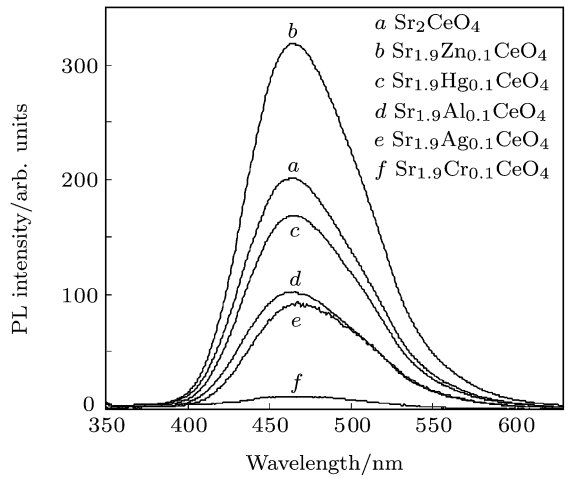


Fig. 1. Emission spectra (excitation wavelength: 370 nm).

In order to investigate the influence of Zn addition on the photoluminescence of the Sr_2CeO_4 powder, we have prepared $Sr_{2-x}Zn_xCeO_4$ powders with x varying between 0 and 0.20. The emission spectra of all the $Sr_{2-x}Zn_xCeO_4$ powders measured at room temperature are shown in Fig. 2. It can be seen that all the emission spectra are very similar in shape. However, the emission of the $Sr_{2-x}Zn_xCeO_4$ powder strongly depends on the doping concentration of Zn. It is found that the emission of the $Sr_{2-x}Zn_xCeO_4$ powder firstly increases with Zn concentration increasing, and then decreases with Zn content increasing as x exceeds 0.10, indicating that the optimum doping concentration x is around 0.10. The compound Sr_2CeO_4 belongs to the orthorhombic crystal system with space group *Pbam* and cell parameters $a = 0.6119$ nm, $b = 1.0350$ nm, $c = 0.3597$ nm.[17] The Sr_2CeO_4 is comprised of linear chains of edge-sharing CeO_6 octahedra running parallel to the [001] crystallographic direction. These chains are separated from and charge-balanced by seven-coordinated Sr^{2+} chains surrounding the octahedra chains. In a CeO_6 octahedra, there are two trans-terminal Ce^{4+}–O^{2-} bonds and four equatorial Ce^{4+}–O^{2-} bonds. The former are about 0.01 nm shorter than the latter. The $Sr_{2-x}Zn_xCeO_4$ possesses the same crystal symmetry as Sr_2CeO_4. However, the parameters of the unit cell are changed because of the Zn incorporation into Sr_2CeO_4. Hence, the emission from the charge transfer transition in Sr_2CeO_4 can be changed. We think that the Ce^{4+}–O^{2-}–Zn^{2+} in Sr_2CeO_4:Zn can attract the electrons of O^{2-} more strongly than the Sr^{2+} can because of the larger electronegativity and the smaller radius. Thus, the emission from the O^{2-} to Ce^{4+} transition is expected to be enhanced in Sr_2CeO_4:Zn. However, excessive Zn addition will increase the mutual interatomic interaction Ce^{4+}–O^{2-}–Zn^{2+}, which may result in the decreasing of the emission from the O^{2-} to Ce^{4+} transition.

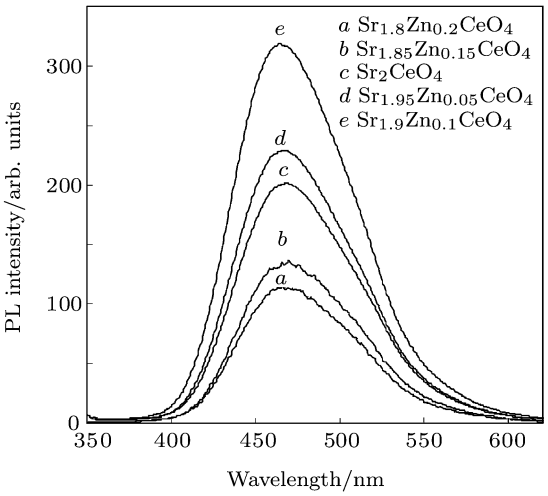


Fig. 2. Emission spectra of $Sr_{2-x}Zn_xCeO_4$ powder with various doping concentration x (excitation wavelength: 370 nm).

Figure 3 shows the excitation spectra of all the Zn-doped Sr_2CeO_4 powders recorded at room temperature. The excitation spectrum shows a broad band around 290 nm with a shoulder at 350 nm. As mentioned above, Sr_2CeO_4 has two kinds of Ce^{4+}–O^{2-} bonds. The two excitation bands observed in Fig. 3 are thus attributed to the two different charge-transfer transitions. There exists a tendency of the charge transfer band at higher energies for shorter metal-to-ligand distances.[18,19] The emissions at 290 nm and at 350 nm can be assigned to O^{2-} to Ce^{4+} transitions

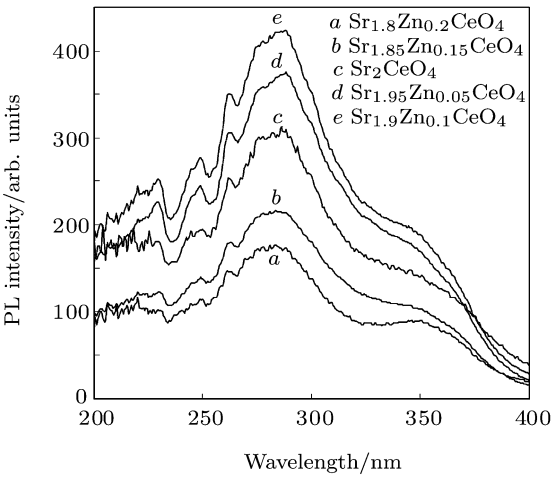


Fig. 3. Excitation spectra of $Sr_{2-x}Zn_xCeO_4$ powder with various doping concentration x (excitation wavelength: 370 nm).

in the trans-terminal Ce^{4+}–O^{2-} bonds and the equatorial Ce^{4+}–O^{2-} bonds, respectively. In addition, we

can find that the dependence of the excitation emission of the $Sr_{2-x}Zn_xCeO_4$ powder on the Zn content is very similar to that in the emission spectrum.

Figure 4 shows the emission spectra of the $Sr_{1.9}Zn_{0.1}CeO_4$ powders fired at different temperatures. It can be seen that the luminescence intensity first increases with the firing temperature increasing, then decreases when the firing temperature exceeds 1100 °C. The dependence of the luminescence intensity on the firing temperature is very similar to that reported by Liu *et al.*[20] The increase of the luminescence intensity with the firing temperature is probably due to the better crystallinity by the higher temperature firing. It is known that Sr_2CeO_4 is not stable above 1100 ^{o}C. Lu and Chen[11] found that the increasing of the heating temperature resulted in the decomposition of Sr_2CeO_4 to form $SrCeO_3$. Further raising the heating temperature leads to a greater decomposition of Sr_2CeO_4. So, the decrease in emission after firing above 1100 °C is probably related to the decomposition of Sr_2CeO_4. Firing at a temperature close to 1300 °C gives rise to a higher concentration of nonradiative defect centres, which results in a decrease of the luminescence intensity. In addition, the decrease in the luminescence intensity above 1100 °C may also result from the formation of larger agglomerates. It is known that hard agglomerates lead to a low packing density of the phosphors, which in turn causes a strong light scattering.[21] Consequently, the luminescence intensity decreases.

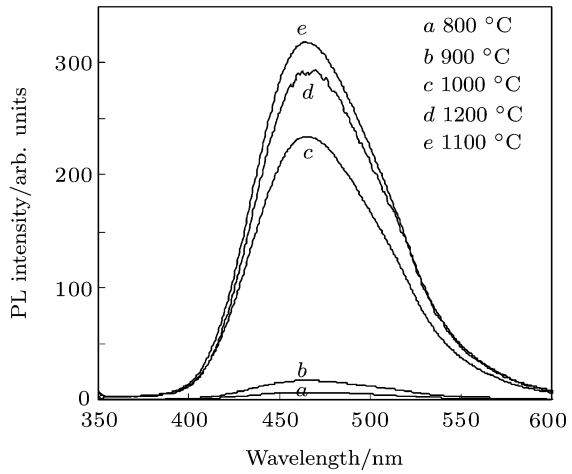


Fig. 4. Emission spectra of $Sr_{1.9}Zn_{0.1}CeO_4$ powders fired at different temperatures (excitation wavelength: 370 nm).

Figure 5 shows the XRD patterns of the $Sr_{1.9}Zn_{0.1}CeO_4$ powders fired at different temperatures. It can be seen from Fig. 5 that the samples fired at 900 °C do not have a pure phase. We can see Sr_2CeO_4 (Joint Committee on Powder Diffraction Standard card No. 50-0115), $SrCeO_3$ (Joint Committee on Powder Diffraction Standard card No. 47-1689) and other unknown phases presented in the XRD patterns. The undefined phase is probably $SrCO_3$.[11] With firing temperature increasing, the impurity phases decrease. The Sr_2CeO_4 powder typically exhibits an orthorhombic structure. The crystallinity of the Sr_2CeO_4 phase is improved by increasing the firing temperature below 1100 °C, which can be confirmed through the narrowing in the full widths at half maximum (FWHMs) of the diffraction peaks and the enhancements of all the diffraction peaks. However, all the diffraction peaks decrease when the firing temperature exceeds 1100 °C due to the poor thermal stability of Sr_2CeO_4 at higher temperature as discussed above. It can be seen that $SrCeO_3$ appears almost in all the patterns. However, we cannot accurately evaluate the change of the quantity of $SrCO_3$ due to the poor resolution of the XRD patterns.

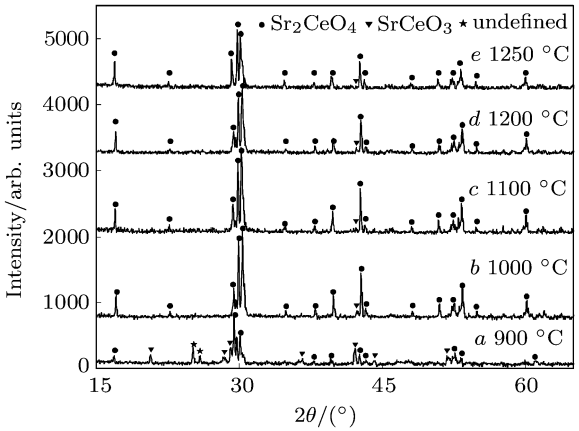


Fig. 5. XRD patterns of $Sr_{1.9}Zn_{0.1}CeO_4$ powders fired at different temperatures.

4. Conclusion

Orthorhombic non-rare earth impurity doped Sr_2CeO_4 powder phosphors are prepared by using the combustion method. The dependences of the photoluminescence on doping species, doping concentration and firing temperature are investigated. It is found that zinc doping with a concentration $x = 0.10$ and the post-thermal treatment can effectively enhance the photoluminescence of the Sr_2CeO_4 powder phosphor. This investigation provides a new way to enhance the luminescent properties of the Sr_2CeO_4 phosphor by using non-rare earth impurity doping. Thus, the presented results may be very useful for the application of the Sr_2CeO_4 phosphors in future field emission displays.

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