PHOTOLUMINESCENCE PROPERTIES OF RARE EARTH IONS DOPED STRONTIUM TITANATE SOLID MATERIALS UNDER NEAR UV LIGHT

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The Sr₂TiO₄:Eu³⁺, Ce³⁺ phosphors were synthesized by sol-gel method. Multiple techniques including X-ray diffraction (XRD), scanning electron microscopy (SEM) were used to examine the surface morphology and structural properties of Sr₂TiO₄:Eu³⁺, Ce³⁺ phosphors. The optical properties were presented and discussed in terms of photoluminescence (PL), photoluminescence excitation (PLE) and ultraviolet-visible (UV-VIS) spectra. The as-obtained Sr₂TiO₄:Eu³⁺, Ce³⁺ phosphors showed higher PL emission intensity (at 588, 611 nm). These peaks were attributed to electronic transition (⁵D₀-⁷F₁, ⁵D₀-⁷F₂) of Eu³⁺. After being irradiated with ultraviolet light, the phosphor samples emitted white light with excitation at 394 nm. The UV-VIS absorption spectra showed strong absorption in the ultraviolet region, suggesting potential applications in many fields.

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1. Introduction

Inorganic photoluminescence materials has gained tremendous research interest in the past decade, due to they use as color or wavelength conversion materials in light-emitting diodes $(\text{LEDs})^{[1-3]}$. Commonly, white LEDs are based on the partial conversion of the blue emission of an (In, Ga)N LED by one or more phosphor materials. Not only blue or violet LEDs, but also nearultraviolet LEDs can be used as primary light sources ^[4,5]. In that case, all the emission of the LED chip should be converted to visible light to optimize the light output of the device. Since the excellent physical and chemical stability, titanates can be stably present in the epoxy or silicone encapsulating material. There is stronger absorption for TiO₄⁴⁻ at n-UV (< 400 nm), It can be able to efficiently absorb the excitation energy and pass it to the rare earth ion ^[6,7]. Particularly, when the central atom in anionic group and oxygen atom and rare earth ions which substituted the position of cations form a straight line, it is effective to transfer energy from anionic to rare earth which improving the luminous efficiency of rare earth ions^[8].

As rare earth ions, the outer electron structure of Eu is $5p^{6}6s^{2}4f^{7}5d^{2}$ ^[9]. As the lattice vibrations and lanthanides has the strong spin-orbit coupling, selection rule for atomic spectra was partially lifted. Some of the original transitions forbidden (f-f) also appears in the spectrum, so that the spectrum has a good color rendering. Within the Eu³⁺ magnetic dipole transition ${}^{5}D_{0}{}^{-7}F_{1}$ is always allowed, the emission peak located at 594 nm, its impact on the surrounding environment of Eu³⁺ is relatively weak, so the intensity changes was not obvious. The electric dipole transition ${}^{5}D_{0}{}^{-7}F_{2}$ transitions is ultra-sensitive. The impact of surrounded environmental is large, so its strength varies widely in different environments^[10,11].

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2. Synthesis and Characterization

2.1. Synthesis

 Sr_2TiO_4 : Eu^{3+} , Ce^{3+} phosphor was synthesized by sol-gel method. All of the chemical reagents used in this experiment were analytical grade. Eu_2O_3 was dissolved in dilute nitric acid to configure $Eu(NO_3)_3$ solution. Then $Sr(NO_3)_2$, $Ce(NO_3)_2$ and citric acid were weighted according to the stoichiometric ratio and mixed in distilled water. Afterwards, tetrabutyl orthotitanate was slowly dropped into the mixture solution under starting condition after alcohol thins. The resulting mixture was placed into water bath 80 °C stirred for 1 h. Then yellow-green gel precursor was obtained. The obtained precursor was placed in drying oven at 80 °C 4 h, in drying process the samples as a brown fluffy porous xerogel. Finally, the sample was calcined by a high temperature furnace to obtain the desired phosphor.

2.2. Characterization

The structures of the phosphor were established by X-ray diffractometer (Shimadzu, XRD-6000, Cu Ka target) and the morphology of the particles was observed by field emission scanning electron microscope (Sirion 200, Philip). The photoluminescence properties of the phosphors were studied on fluorescence spectrophotometer (Shimadzu, model RF-5301 PC).

3. Result and Discussion

3.1. Structural analysis

In order to analyze the crystal structure of the test sample, X-ray diffraction was performed to determine the crystal structure of the phosphors. Fig. 1 presented the XRD patterns of Sr_2TiO_4 : Eu^{3+} , Ce^{3+} which calcined at 1100 °C for 3 h and the standard PDF card. No impurity phases, such as TiO₂, SrTiO₃, Sr(NO₃)₂ were detected, which proofed that the samples pattern was in good agreement with JCPDS Card no. 39-1471. Sr_2TiO_4 crystallizes is tetragonal structure, space group I4/mmm, with lattice parameter a=3.8861 Å. These dopant ions Eu^{3+} and Ce^{3+} was expected to occupy the Sr^{2+} sites in the Sr_2TiO_4 host due to the close radii and identical valence of the ions.

3.2. Morphology analysis

Fig. 2 was the SEM micrographs of different calcining time. From the figure when the calcined time was 2 h, the phosphor began to form, and can preliminarily see relatively complete external morphology, but there were many fine particles. When calcined at 3 h, the phosphor particles crystal-type lattice tended to be completed, and the particle structure was complete, and particle size was uniform and at 0.5-1 μ m. When time at 4 h or 5 h, the over-burning phenomenon appeared, and the lattice was breakup and the crystalline was liquid, also the grain shape was irregular and there were many small and fragmented particles. With the increasing of the calcined time, the reaction was gradually complete. With the grain growing, crystal defect decreased and lattice tended to be complete. However, when the calcined time was too long, crystalline was liquid, we could not get the grain structure that we needed, and the appearance was affected. The SEM showed that when calcined time was 3h we get the optimal surface morphology of luminescent materials.



Fig. 1. The XRD patterns of Sr_2TiO_4 : Eu^{3+} , Ce^{3+} phosphors



Fig. 2. The SEM micrograph of Sr_2TiO_4 : Eu^{3+} , Ce^{3+} at different calcined time a)2h, b) 3h, c) 4h, d) 5h

3.3. Characterization of fluorescence properties

Fig. 3 was the ultraviolet absorption spectrum of the sample under the conditions of 200-800 nm. It can be seen from the spectra that under the conditions of 200-400 nm, the sample absorbance was clear, but lower between 400 and 800 nm. This indicated that the sample weakly absorbs the visible light and can absorb ultraviolet light, as UV excitation easy to achieve, through literature review, the UV absorption is mainly attributed to the O^2 -Ti⁴⁺.

In order to study and analyze the fluorescence properties of the phosphor, using the fluorescence spectrophotometer to test the material. Fig. 4 presented the excitation spectrum ($\lambda_{em} = 611 \text{ nm}$) and emission spectra ($\lambda_{ex} = 394 \text{ nm}$) of Sr₂TiO₄: Eu³⁺, Ce³⁺. As can be seen from the main excitation spectrum of narrowband excitation peak at 394 nm, the transition absorption belonged ${}^{7}F_{0}{}^{-5}L_{6}$ of Eu³⁺. There was excitation band width characteristic absorption in the ultraviolet region exhibit, which was due to O-Ti charge transfer.

Right side of Fig. 4 showed the Sr_2TiO_4 : Eu^{3+} , Ce^{3+} phosphor emission spectra at $\lambda_{ex} = 394$ nm conditions. There were three main peaks of the phosphor, which were located at 575 nm, 591 nm and 611 nm respectively and attributed to ${}^5D_0{}^{-7}F_1$ and ${}^5D_0{}^{-7}F_2$ transition emission. The peaks of 575 nm and 591 nm were attributed to the ${}^5D_0{}^{-7}F_1$ transition emission, mainly due to an asymmetric

substituted rare sites of Eu^{3+} in the crystal Sr^{2+} , which generated under the influence of the crystal field splitting of the diffraction peaks.



Fig. 3. The ultraviolet absorption spectrum of the sample



Fig. 4. The excitation ((λ_{em} =611 nm) and emission (λ_{ex} =394 nm) spectrum of phosphor calcined at 1000 °C, 3 h

While the ${}^{5}D_{0}{}^{-7}F_{1}$ and ${}^{5}D_{0}{}^{-7}F_{2}$ transition emission spectra can be found that the occurrence of the peak at 611 nm was dominant. That was because that ${}^{5}D_{0}{}^{-7}F_{1}$ correspond to the magnetic dipole transitions, and ${}^{5}D_{0}{}^{-7}F_{2}$ correspond to electric dipole transitions. But when the Eu³⁺ located in an asymmetric substituted rare sites of Eu³⁺ in the crystal, the electric dipole transitions was in a dominant position. This was consistent with the findings above.

Fig. 5 presented the emission spectra of luminescent materials with the calcination temperature from 900 $^{\circ}$ C to 1200 $^{\circ}$ C. When calcined at 900 $^{\circ}$ C, the emission was low. With the increasing of the temperature, the fluorescence intensity enhancement. As the temperature was over 1100 $^{\circ}$ C, the fluorescence intensity saturated and begin to gradually reduce. When at 1100 $^{\circ}$ C all the emission peak reached the maximum. It corresponded with SEM patterns from the Fig.2. With increased of calcination temperature, the fluorescence intensity increased at first, then gradually reduce. It's because with the increasing of calcination temperature, the degree of crystallinity increased at the same time, and had a uniform particle size. However, when the calcination temperature was too high, the phase was overburning and liquefaction phenomenon, thus leading the emission peaks luminous intensity decreased. The fluorescence intensity showed that the optimal calcination temperature was 1100 $^{\circ}$ C.

Fig. 6 was fluorescence intensity pattern of the phosphors that we made with the holding time of 2 h-5 h.



Fig. 5. The emission spectra at different calcination temperature



Fig. 6. The emission spectra at different calcination time

The pattern showed that the production's luminous intensity continuously enhanced with the increasing of holding time. Conform that the crystal grow when insulation. But when the holding time was too long, the phase over-burned and liquefaction phenomenon, leading the emission peaks luminous intensity decrease. Therefore, the optimal holding time was 4 h in this experiment.

Fig. 7 presented the emission spectra of different Eu^{3+} doping concentration and double doping Eu^{3+} and Ce^{3+} . As can be seen from the spectra, with the increasing of rare earth doping amount, the emission intensity increased. When the doping amount was 1 %, the light emitting of phosphor was not detected. It was due to the rare earth ions small amount doped into the phosphor, which was not form a light emitting center, and no significant luminescence. When the doping amount reached 3 %, there was a significant increase in fluorescence intensity because of the increasing of the amount of the luminescent center. But when the concentration continued to increase, the luminous intensity gradually became saturated. The trend was not linear growth which was due to doped miscellaneous excessive rare earth ions and the amount of luminescence centers did not continue to increase. The energy transfer between activator ions cause concentration quenching. When the concentration of Eu^{3+} was 7 %, fluorescence spectra appeared offset portion, which was due to sites of Eu^{3+} occupies a different variation of the crystal field. So 5 % doping concentration of Eu^{3+} was appropriate. Further, by adding 1 % Ce^{3+} , the fluorescence intensity increased again, and Ce^{3+} excitation peak was not observed. Ce^{3+} as sensitizer could transmitted the energy absorbed to Eu^{3+} to ulteriorly improve the luminous intensity.



Fig. 7. The emission spectra of Sr_2TiO_4 : X%Eu³⁺

4. Conclusions

The Sr₂TiO₄:Eu³⁺, Ce³⁺ phosphors were synthesized by sol-gel method. The XRD spectra showed that the phosphors was pure Sr₂TiO₄ (JCPDS 39-1471) and the phosphor was nearly spherical morphology and uniformity better. From the results of SEM and fluorescence intensity, the property of the light-emitting material were improved with the increasing of temperature. However, when the temperature was too high it will appear crushing grain and larger agglomeration. The optimum sintering temperature of this experiment was 1000 °C. The results of the fluorescence analysis showed that the best holding time of this experiment was 3 h. The asobtained Sr₂TiO₄:Eu³⁺, Ce³⁺ phosphors showed higher PL emission intensity (at 588, 611 nm). These peaks were attributed to electronic transition (${}^{5}D_{0}{}^{-7}F_{1}$, ${}^{5}D_{0}{}^{-7}F_{2}$) of Eu³⁺. The optimal doping concentration of Eu³⁺ was 5 %. Meanwhile the fluorescent properties can further improved by adding Ce³⁺. It was suggested to apply in many fields.

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