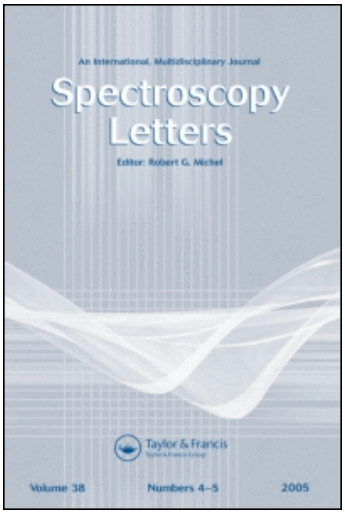

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Luminescence Properties of Salicylate Doped Zinc Benzoate

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LUMINESCENCE PROPERTIES OF SALICYLATE DOPED ZINC BENZOATE

Key words: Luminescence, zinc, salicylate, benzoate, semisolid reaction.

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ABSTRACT

The salicylate-doped zinc benzoates $Zn(Bzo)_2$:Sal are synthesized by means of the semisolid phase reaction method. The excitation and emission spectra are investigated, and compared with $Zn(Sal)_2$, A-Zn(o-$OC_6H_4CO_2$) and B-Zn(o-$OC_6H_4CO_2$). For $Zn(Bzo)_2$:$Sal_{0.05}$, the luminescent intensity is mainly dependent on the efficiency of n,π^* transition emission, the peaks of excitation and emission bands are at 328 and 384 nm, respectively. The emission intensity of $Zn(Bzo)_2$:$Sal_{0.05}$ is 3 times as strong as that of $Zn(Sal)_2$, 1.6 times A-Zn(o-$OC_6H_4CO_2$), and 6 times B-Zn(o-$OC_6H_4CO_2$).

INTRODUCTION

Our previous works revealed that the rare earth ions doped lanthanum, zinc and alkali earth metal aromatic carboxylate had better luminescence properties than pure rare earth complexes [1~4]. These phosphors have been made use of luminescent film and transducer material of X-ray microphotographic camera et.al. But the luminescence properties about anion doped aromatic carboxylate are not well known to us. Today the salicylate, as an activator, was used in the zinc benzoate. It is found

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that the luminescence properties of the salicylate doped zinc benzoate are also very interesting. In order to get some luminescent information on salicylate activator, three kinds of solid zinc salicylates are prepared by means of the semisolid phase reaction and thermal decomposition method. Their luminescence properties and mechanism are investigated.

EXPERIMENTAL

1. Preparation of Salicylates

Salicylic acid and zinc oxide are used as raw materials. The semisolid phase mixture are obtained by grinding the above-mentioned reagent together in accordance with a proper proportion, then treated with proper water.

The $Zn(HOC_6H_4CO_2)_2$ and the zinc monosalicylate, A-$Zn(OC_6H_4CO_2)$ are synthesized by the semisolid phase reaction method from zinc oxide and salicylic acid in 1:2 and 1:1 mole ratio in a closed container at 80~110℃, respectively. Zinc monosalicylate, B-$Zn(OC_6H_4CO_2)$, can be obtained by the thermal decomposition of $Zn(HOC_6H_4CO_2)_2$ at 200~280℃ under an inert atmosphere. The salicylate-doped zinc benzoate $Zn(Bzo)_2$:Sal are synthesized from zinc oxide, benzoic acid and salicylic acid in 1:2:x (x=0.01~0.1) mole ratio with the same method as the $Zn(HOC_6H_4CO_2)_2$. The composition and structure were identified by elemental analysis, infrared spectra and the powder X-ray diffraction.

2. Spectra Measurements

The excitation and emission spectra of solid samples were examined with a Shimadzu RF-5000 spectrofluorophotometer in the range of 200~600nm.

RESULTS AND DISCUSSION

The elemental analysis, infrared spectra and the powder X-ray diffraction showed that the composition of A-$Zn(OC_6H_4CO_2)$ is the same with B-$Zn(OC_6H_4CO_2)$ and their structures are completely different.

The solid zinc salicylates can produce blue emission under ultraviolet radiation excitation. In this kinds of salicylates, the excited levels of the first singlet S_1n,π^* and $S_1\pi,\pi^*$ of Sal are located in 315 and 340nm, the emissive levels from the lowest triplet T_1n,π^* and $T_1\pi,\pi^*$ to ground state lie in 387 and 430nm, respectively.

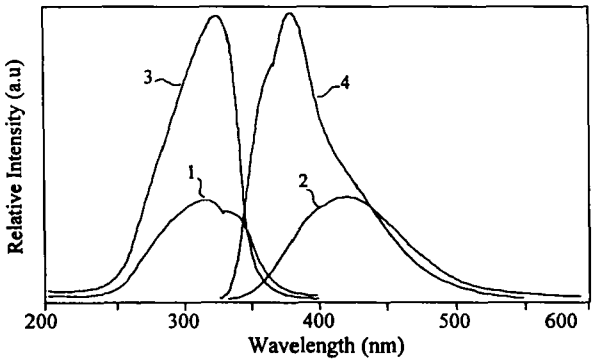

FIG.1. Excitation and emission spectra of $Zn(Sal)_2$ (1,2) and $Zn(Bzo)_2:Sal_{0.05}$ (3,4)

1, Excitation, λ_{Em}=425nm; 2, Emission, λ_{Ex}=317nm;

3, Excitation, λ_{Em}=384nm; 4, Emission, λ_{Ex}=328nm

$Zn(Sal)_2$ has very strong blue emission when excited by long wave UV light. The excitation and emission spectra are shown in Fig.1 (curve 1 and 2). The broad bands in the 200~600nm region are attributed to the transition excitation and emission of n,π^* and $\pi,\pi^*$of salicylate. The peaks at 317 and 425nm are assigned to the transition excitation and emission of π,π^*, the weak shoulder peaks at 340 and 395nm to the transition excitation and emission of n,π^*, respectively. The broad excitation band resulted from interoverlap of transition from ground state to S_1n,π^* and $S_1\pi,\pi^*$. The interoverlap of emissive transition from T_1n,π^* and $T_1\pi,\pi^*$ to ground state resulted in the broad emission band. The excitation and emission spectra of B-$Zn(OC_6H_4CO_2)$ are consistent with $Zn(Sal)_2$ in shape, but the relative intensity is only 45% that of $Zn(Sal)_2$.

The very strong blue emission can be observed when the solid $Zn(Bzo)_2$:Sal are excited by long wave UV light. With an increase of salicylate concentration, the emission bands of were not prominently changed, the relative intensity increased, but when the doped salicylate concentration was about 5 mol%, the relative emission intensity was the highest, it is twice as strong as that of $Zn(Bzo)_2:Sal_{0.01}$. The excitation and emission spectra of $Zn(Bzo)_2:Sal_{0.05}$ are shown in Fig.1 (curve 3 and 4). The excitation and emission of $Zn(Bzo)_2$ disappeared completely. The peak of excitation at 328nm occurred red shift clearly compared

with that of $Zn(Sal)_2$ and the emission band occurred blue shift, the peak is located in384nm. The relative intensity is 3 times as strong as that of $Zn(Sal)_2$. The excitation and emission spectra of A-$Zn(OC_6H_4CO_2)$ are consistent with $Zn(Bzo)_2:Sal_{0.05}$ in shape, but the relative intensity is about 63% that of $Zn(Bzo)_2:Sal_{0.05}$.

As above mentioned, in the zinc salicylates, the relative intensity of salicylate doped zinc benzoate $Zn(Bzo)_2:Sal_{0.05}$ is the strongest. The emission spectra showed that the increase of luminescent relative intensity is mainly dependent on the increase of efficiency of S_1n,π^* transition emission. In $Zn(Bzo)_2$, the excitation bands of S_1n,π^* and $S_1\pi,\pi^*$ are located in 239 and 315nm, respectively. It exhibits that benzoate made less contribution to the luminescence of salicylate. Therefore, in $Zn(Bzo)_2$:Sal, $Zn(Bzo)_2$ play a role of substrate, which reduced quenching effect of concentration and enhanced greatly luminescent efficiency of salicylate. The different structure of A-$Zn(OC_6H_4CO_2)$ and B-$Zn(OC_6H_4CO_2)$ resulted in the difference in luminescent efficiency. The detailed study on their structures will be reported soon.

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