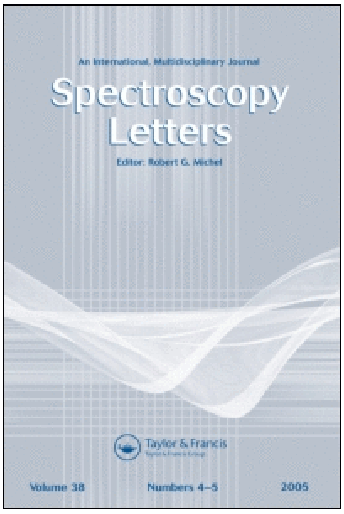

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Luminescence of Tb^{3+}-Doped Strontium Quinolinate

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To cite this Article Yuan, Liangjie , Sun, Jutang , Wang, Qingye and Zhang, Keli(1999) 'Luminescence of Tb^{3+}-Doped Strontium Quinolinate', Spectroscopy Letters, 32: 5, 867 — 873

To link to this Article: DOI: 10.1080/00387019909350033

URL: http://dx.doi.org/10.1080/00387019909350033

SPECTROSCOPY LETTERS, 32(5), 867–873 (1999)

LUMINESCENCE OF TB^{3+}-DOPED STRONTIUM QUINOLINATE

Keywords: Strontium, Quinolinic, Terbium, Luminescence, rheological phase reaction

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ABSTRACT

The Tb^{3+}-doped strontium quinolinate was prepared by rheological phase reaction method. The thermal stability, powder X-ray diffraction, infrared, emission and excitation spectra are investigated. The energy transfer mechanism from $C_5H_3N(CO_2)_2$ to Tb^{3+} ion and the influence of structure and heterocycle on the luminescence intensity were discussed. The energy $S_1\pi,\pi^*$ excited states of $C_5H_3N(CO_2)_2$ can be transferred to $^5D_4$ of Tb^{3+} ion to send out the $^5D_4 \rightarrow {}^7F_J$ transition emission of Tb^{3+}.The nitrogen heterocycle makes the excitation band of Tb^{3+} ion shift to short wavelength.

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INTRODUCTION

Many neat Tb^{3+} and Eu^{3+} aromatic carboxylate complexes had excellent luminescence properties [1-3]. Tb^{3+} and Eu^{3+}-doped benzoates, phthalates and pyromellitate, which had better luminescence properties than neat rare earth compounds could make use of luminescent materials [4-6]. In order to study luminescence behavior of Tb^{3+} in heterocycle carboxylate substrates, in the present paper, the Tb^{3+}-doped strontium quinolinate (SrQLT:Tb, QLT= $C_5H_3N(CO_2)_2$) was prepared by rheological phase reaction method. The thermal stability, powder X-ray diffraction data, infrared spectrum and luminescence properties were investigated. The energy transfer mechanism and relationship between luminescence intensity and structure were discussed.

EXPERIMENTAL

1.Preparation of the samples

Strontium carbonate and quinolinic are analytical reagent grade, terbium carbonate was prepared in our laboratory. Strontium carbonate, quinolinic and terbium carbonate were fully mixed by grinding in 1 : 1 : X (X=0.01~0.05) mole ratio and the rheological bodies were obtained by treating the above-mentioned mixture with a proper amount of purified water. The Tb^{3+}-doped strontium quinolinate was prepared from the rheological bodies in a closed container at ~140℃ for 3h and the products were dried at120℃, This method has been called semisolid reaction in the literature [7]. The elemental analyses and infrared spectra were consistent with the expected composition.

2.Measurements

The thermal stability of the prepared samples were studied with a Shimadzu DT-40 thermal analyzer in air (flow rate 40 mL/min) at a heating rate of 20 ℃/min. The powder X-ray diffraction data was obtained with a Rigaku D/MAX-RA model X-ray diffractometer with a graphite monochromator and Cu $K\alpha_1$ radiation (λ=1.5405Å). The infrared spectrum of the sample in KBr pellet was measured on a Nicolet 170SX FT-IR spectrometer in the 4000~400cm^{-1} region. The excitation and emission spectra were determined by a Shimadzu RF-5000 spectrofluorophotometer in the range of 200~700nm. All spectra were recorded at ambient temperature. The apparent density of the sample was measured by a pycnometric method using carbon tetrachloride as a displacing fluid.

RESULTS AND DISCUSSION

The thermal analysis shows no weight loss occurred for the solid sample from room temperature to 409℃.

The powder X-ray diffraction data from SrQLT:$Tb_{0.01}$ is listed in Table 1. The crystal structure is a monoclinic system and belongs to the C_2^1-$P2$ (No.3) space group with four molecules in the unit cell. The calculated lattice parameters are a=1.3082(1), b=1.2457(1), c=0.4946(1) nm, β=96.87(1)°,V=0.8002(4) nm^3 and d_{calc}=2.098(5) (d_{obs}=2.11) g/cm^3. The diffraction intensity of the (010) plane is about four times as strong as the second strong peak. It is suggested that the SrQLT:$Tb_{0.01}$ crystal exhibits a layered structure with metal ions located in the (010) plane and the QLT groups were situated on two sides of the metal ion plane.

The IR spectrum of the SrQLT:$Tb_{0.01}$ are shown in Fig.1. The very strong absorption band at 1395 cm^{-1} could be assigned to symmetric stretching vibration of the OCO group and the broad and very strong bands at 1568 and 1593 cm^{-1} to asymmetric vibrations. It is revealed that there are symmetrical and unsymmetrical bridging bidentate and chelateing coordination between the carboxylate group and the metal ion and the $C_5H_3N(CO_2)_2$ could bond with the Sr^{2+} ion through carboxylate groups to form a stable seven-membered ring [8].

The white solid SrQLT:Tb has very strong green emission when excited by 295 nm UV light. The excitation and emission spectra of the SrQLT:$Tb_{0.01}$ are

Table 1. The X-ray diffraction data from SrQLT:$Tb_{0.01}$

d_{exp}(nm)	I/I_1	d_{cal}(nm)	h	k	l	d_{exp}(nm)	I/I_1	d_{cal}(nm)	h	k	l
1.2988	10	1.2988	1	0	0	0.2454	4	0.2455	0	0	2
1.2475	100	1.2457	0	1	0	0.2379	3	0.2376	4	2	1
0.6232	9	0.6228	0	2	0	0.2243	2	0.2248	4	4	0
0.4913	4	0.4910	0	0	1	0.2111	1	0.2111	4	4	$\bar{1}$
0.4152	8	0.4152	0	3	0	0.2076	7	0.2076	0	6	0
0.3802	1	0.3795	1	2	$\bar{1}$	0.2009	3	0.2007	3	1	2
0.3487	1	0.3498	2	3	0	0.1975	1	0.1978	2	6	0
0.3324	1	0.3333	3	1	$\bar{1}$			0.1974	4	2	$\bar{2}$
0.3146	2	0.3142	4	1	0	0.1925	1	0.1928	0	4	2
0.3114	25	0.3114	0	4	0	0.1779	1	0.1780	0	7	0
0.2513	1	0.2518	4	1	1	0.1557	2	0.1557	0	8	0
0.2491	18	0.2491	0	5	0	0.1384	1	0.1384	0	9	0

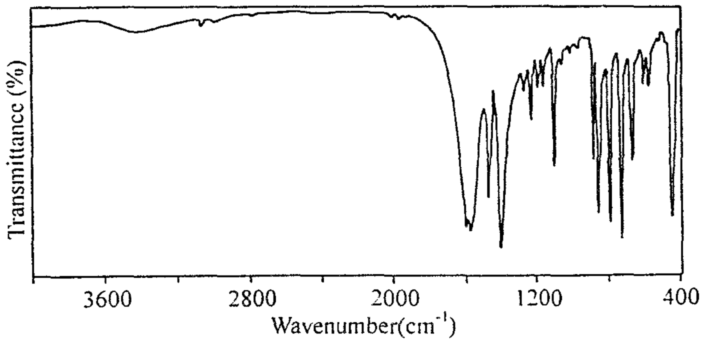

Fig.1 IR spectrum of SrQLT:$Tb_{0.01}$

shown in Fig.2. In the solid SrQLT:Tb, the $^5D_4 \rightarrow {}^7F_j$ (j=6, 5, 4, 3) transition emission from Tb^{3+} ion is observed at 488, 544, 582 and 618 nm, and the emission from $^5D_4 \rightarrow {}^7F_5$ is the strongest. The excitation band of Tb^{3+} ion emission is a broad band at 295nm and is consistent with the $\pi \rightarrow \pi^*$ transition absorption in the ultraviolet absorption spectrum of the aqueous solution of quinolinate. In solid samples, neither the $^5D_3 \rightarrow {}^7F_j$ emission of Tb^{3+} ion nor luminescence of quinolinate can be observed.

The excitation and emission spectra of strontium quinolinate in DMF are shown in Fig.3. The excitation band at 320 nm is ascribed to the $S_1\pi,\pi^*$ transition, and the broad emission band at 383 nm is due to the $T_1\pi,\pi^*$ transition in quinolinate.

From the above-mentioned results, it is seen that the $S_1\pi,\pi^*$ (31.3 × 10^3 cm^{-1}) and the $T_1\pi,\pi^*$ (26.1 × 10^3 cm^{-1}) energy levels of quinolinate are over the ^5D_j ($^5D_3$ 26.1 × 10^3, $^5D_4$ 20.50 × 10^{3}cm^{-1}) levels of Tb^{3+} ion [9]. So, the energy transfer and luminescence mechanism in SrQLT:Tb is proposed as follows。

Ligands with ultraviolet radiation are excited to the singlet excited state from the ground state. The energy of the $S_1\pi,\pi^*$ excited state of $C_5H_3N(CO_2)_2$ decays to the $T_1\pi,\pi^*$ level in $C_5H_3N(CO_2)_2$ and then relaxes directly to the $^5D_4$ level in Tb^{3+} ion through the intramolecular energy transfer to send out the $^5D_4 \rightarrow {}^7F_j$ transitions emission from Tb^{3+} ion. The dependence of emission intensity of Tb^{3+} ion on the Tb^{3+} concentration is measured. In the SrQLT:Tb, when the Tb^{3+} concentration is about 2 mol%, the highest emission intensity is twice as strong as that of solid neat terbium quinolinate.

In strontium quinolinate with a layered structure, the energy $S_1\pi,\pi^*$ excited states can be effectively transferred very far through the metal-oxygen bonding chains (-OCO-M-OCO-). That is to say, strontium quinolinate, as a

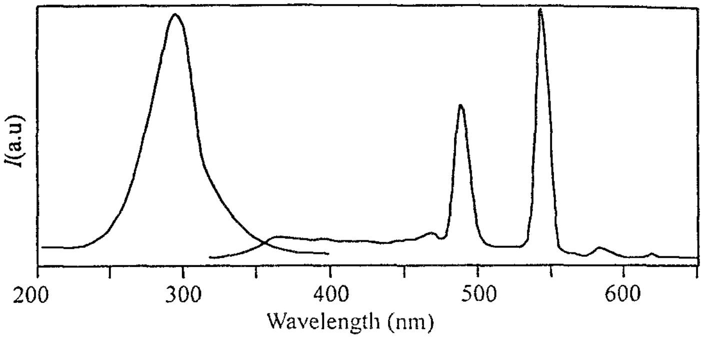

Fig.2.Excitation (left, λ_{Em}=544 nm) and **Emission** (right, λ_{Ex}=295 nm) spectra of solid SrQLT:$Tb_{0.01}$.

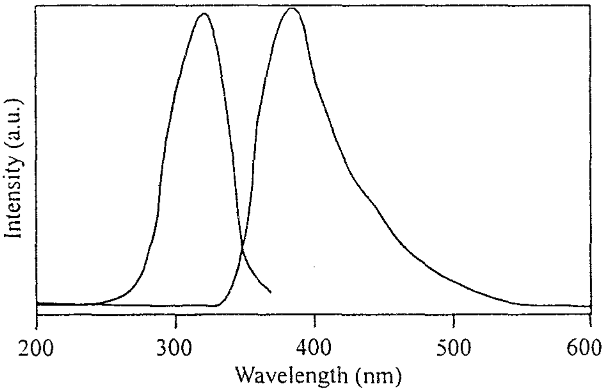

Fig.3.Excitation (left,λ_{Em}=383 nm) and Emission (right λ_{Ex}=320 nm) spectra of strontium quinolinate in DMF

substrate, can reduce the quenching effect of concentration and enhance greatly the luminescent efficiency of Tb^{3+} ion. This is due to the reduction of probability density of π electron cloud in the pyridine ring.. Therefore, the luminescence efficiency of Tb^{3+} ion in strontium quinolinate was weaker than that of strontium phthalate [4].

ACKNOWLEDGMENT

This study was supported by the National Natural Science Foundation of China.

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Date Received: January 15, 1999
Date Accepted: May 1, 1999