Fluorescence Properties of BDD Molecules Doped in Si-Ti Binary Oxide Systems by the Sol-Gel Method

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The characteristics of the fluorescence spectra of 2,5-bis(4-diethyl-aminophenyl)-1,3,4-oxadiazole(BDD) doped in Si-Ti binary oxides by the sol-gel method were investigated as a function of time in its transitions from sol to gel to xerogel. The characteristic BDD excimer fluorescence was observed during the transition from gel to xerogel only in a mixture of TEOS and TPOT but not in pure TEOS, indicating that the presence of a tetrahedrally coordinated titanium ion species plays a significant role in the formation of the excimer.

One of the major applications of the sol-gel process for low temperature glass preparation is its ability to dope various organic molecules into inorganic glasses, especially to dope photo-functional and/or photo-sensitive organic dye molecules.[1,2] As a result, research into the room temperature polymerization of metal alkoxides has led to the preparation of materials of optical interest such as solid laser dye blocks and films,[3] photochromic glasses, hole-burning materials,[4] light guides and non-linear optical materials.[5-7] When guest molecules can be adequately selected and incorporated in the sol-gel starting solution, they act as probes to monitor the gelation process, providing information on the local viscosity, polarity, structural and chemical changes, and eventually, on the porosity of the final xerogel.[8-10]

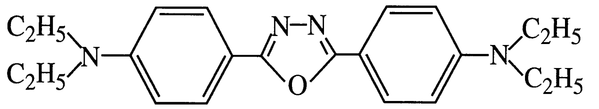

Figure 1. Molecular structure of BDD.

BDD (Figure 1) has been recognized as an important laser dye for the blue-green spectral region and there is much information on its photochemical and photophysical properties.[11] BDD has also been used on the charge transfer layers (CTL) in the excitation of photoconductors used in bilayer devices.[12] The photochemical stability of a dye in a dye laser system is the major criterion in determining its suitability and reliability as well as the lifetime of the laser. Although it has been reported that the laser dye doped in Si-Ti binary oxides can increase their photostability,[13] the fundamental photophysical and photochemical properties of doped BDD have yet to be studied in detail, especially during the sol to gel to xerogel transitions of the Ti-Si binary oxide systems. In the present work, we have measured the characteristic changes which take place in the fluorescence spectra of doped BDD during the sol to gel to xerogel transitions of such systems.

BDD was synthesized in the laboratory and purified by recrystallization from ethanol.[14] The structure of the dye was confirmed by elemental analysis, mass spectrometry and NMR. The starting reagent was a mixture of tetraethoxy-silane (TEOS), tetra-i-propoxy titanium (TPOT), and BDD/ethanol solution (1x10^{-4} M). Sample A did not include TPOT. The composition of sample B was TEOS:TPOT = 99:1. The fluorescence spectra were recorded with a Shimadzu RF-5000 spectrofluoro-photometer.

Figure 2 shows the changes in the fluorescence spectra of BDD observed in the TEOS (sample A) during the sol to gel to xerogel transitions. Just after mixing, the fluorescence bands can be observed at around 402 nm and 418 nm. In Figure 2, we can see that the fluorescence of the first stage (0~10 days) of the sol-gel chemical processes is assigned to the emission originating from the anionic species of BDD molecules. The peaks at 402 nm and 418 nm were assigned to the emissions from the monomer and dimer species, respectively.[14] Being in agreement with these observations, the two peaks at around 350 nm and 380 nm were observed in the absorption spectrum of the sample. Figure 2 also shows the change in the intensity of the fluorescence bands observed at 402 nm and 418 nm. At 10 days (gelation), the intensity of the fluorescence band at 418 nm gradually decreases with the gelation time. After 10 days, the intensity of the fluorescence band at 402 nm increases dramatically and then gradually decreases. The inset in Figure 2 shows the changes which can be observed with the main fluorescence bands with the gelation time. The distinct shift to shorter wavelengths can be seen as gelation proceeded.

With the gelation time, the solvent in the sample gradually evaporated so that the concentration of BDD became higher. As a result, the intensity of the fluorescence from the dimer species

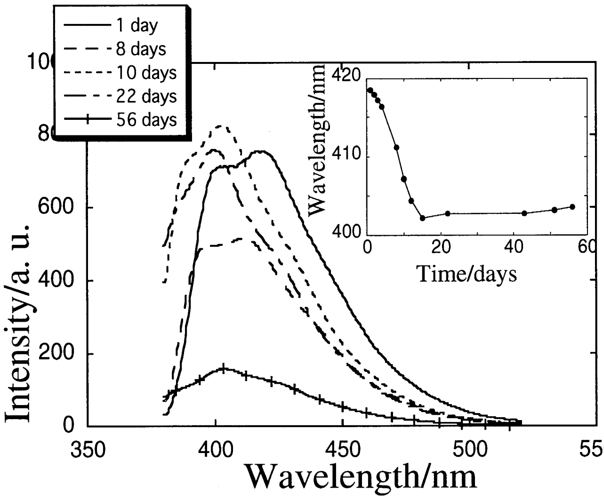

Figure 2. The changes of fluorescence of BDD in the TEOS (sample A) during the sol to gel to xerogel transitions (excition wavelength 370 nm). Inset: Changes in the position (λmax) of fluorescence spectra of BDD trapped in sol to gel to xerogel as function of the time.

was decreased due to a concentration quenching and shifted to shorter wavelengths. As gelation set in, the BDD molecules dispersed in the oxide systems of distorted (or fractral geometry) and smaller pores which were formed during the shrinkage of the systems. The BDD dimer molecules were trapped within the -O-Si-O- network structures. An increase in the shrinkage of the system led to an increase in the number of pores with a decrease in the diameter of each pore. This situation results in trapping BDD molecules in small pores in which BDD molecules are highly separated and dispersed on the gel surface as the monomer species in each pore. These processes which occurred during gelation caused the transformation of the fluorescence band from 418 nm (dimer) to 402 nm (monomer). However, further shrinkage of the system decreased the interaction of BDD with the gel surface leading to a gradual decrease in the intensity of the monomer emission.

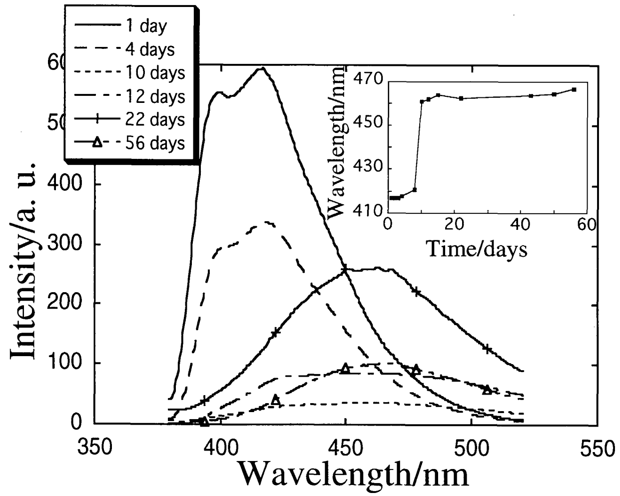

Figure 3. The changes of fluorescence spectra of BDD in the TEOS and TPOT mixed solutions during the sol to gel xerogel transitions (excitation wavelength 370 nm, Si:Ti=99:1). Inset: Changes in the position (λmax) of fluorescence spectra of BDD trapped in sol to gel to xerogel as function of the time.

Figure 3 shows the fluorescence spectra of BDD during the sol to gel to xerogel transitions of the TEOS-TPOT solution sample as a function of time. It is clear that with the starting TEOS-TPOT solution, two fluorescence bands can be observed at 402 nm and 418 nm, which can be assigned to the monomer BDD and dimer BDD, respectively.[14] As shown in Figure 3, the intensity of these fluorescence bands decreases with the gelation time. When the first stage of gelation is completed (10 days), the intensity of these bands at 402 nm and 418 nm decrease dramatically. At the same time, a new fluorescence peak appears at around 464 nm, and the intensity gradually increases during the passage of 10 to 22 days. This band at around 464 nm can be assigned to the BDD excimer which was not formed in the SiO_2 system (sample A) during the sol to gel to xerogel transitions. Only two bands at around 350 nm and 380 nm in the fluorescence-excitation spectrum were observed, showing an agreement with the absorption spectrum. The relative intensity of the fluorescence due to the excimer species becomes the strongest on the 22nd day, and after that gradually decreases.

In Figure 3, we can see that the fluorescence of the first stage (0~10 days) of sample B is similar to that of sample A. But from the 10th day, the intensity of band at 418 nm decreases dramatically while the peak at 464 nm appears and the intensity of the fluorescence spectra increases. During the gelation, an -O-Si-O-Ti-O- network spans completely over the inner site of the systems to form micro-pores. In the Ti/Si binary oxide, highly dispersed 4-fold coordinated Ti-oxide species were found to exist and play a role as effective adsorbing sites.[15-17] Therefore, when there are more than two BDD molecules in the same pore, it is possible to form "Bimolecular Ground State Associations" (BGSA's) or configurations.[18, 19] In the initial stage of gelation, some BDD molecules are doped in the pore together with H_2O, ethanol and isobutanol. However, with the gelation time, these solvent molecules evaporated making the effective concentration of BDD molecules gradually higher, which in turn caused the intensity of the fluorescence excimer to gradually increase. During the sol-gel reaction processes, the system shirkage resulted in the formation of smaller and distorted pores. Moreover, some BDD molecules that had been doped in the same pore were separated from each other while the excimer emission decreased in the xerogel state as the BGSA's were destroyed (22~56 days). Evidently the presence of Ti atoms leads to an excimer emission. Although the detailed reaction mechanisms behind the present reaction deserves further scrutiny, tetrahedral coordinated titanium oxide species highly dispersed in the SiO_2 matrices of the Ti-Si binary oxides were found to be highly effective and to play a significant role in the formation of an excimer under UV irradiation.

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