



Luminescence spectra of stilbene-3 doped lead–tin–fluorophosphate glass excited by VUV–UV synchrotron radiation

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ABSTRACT

The stilbene-3 doped lead–tin–fluorophosphate glasses were successfully prepared and the luminescence spectra obtained from VUV–UV synchrotron radiation were investigated. The emission peaked about 440 nm from the undoped glass is observed at low temperature but quenches at room temperature. The doped glass exhibits strong characteristic emission of stilbenen-3 with 467 and 436 nm Gaussian bands under ultraviolet 250–330 nm excitation (characteristic excitation of stilbene-3) but weak emission under vacuum ultraviolet 190 nm excitation (host excitation). It is suggested that the energy transfer from host to the stilbene-3 dye can occur but the efficiency is still fairly low.

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1. Introduction

In the recent years, there has been an increased interest in the development of the low melting glasses doped with organic dyes (activators) as scintillators in the detection of X-ray, γ -ray or neutron in high energy physics and nuclear physics experiments [1–4]. Scintillators based on organic dye molecules doped in a glass host using sol–gel method with a low temperature for preparation have been reported [5]. Lead–tin–fluorophosphate glasses (Pb–Sn–P–O–F) have been extensively investigated as host of the scintillation glasses due to their relative high density of 4.5 g/cm³, low melting temperature, high optical quality and good water–durability [6–9]. They can be prepared below 500 °C, and have a viscosity low enough to dope organic dyes at about 300 °C, without thermal decomposition. They are transparent from the near ultraviolet to near infrared and can be easily fabricated into various shapes and sizes. Thus, lead–tin–fluorophosphate glasses could be ideal host materials for the organic dye-doped scintillation glasses. Organic compounds, such as *trans*-stilbene, *p*-terphenyl, POPOP, Rho-

damine 6G often exhibit fast decay on the order of nanoseconds and light yield proportional to energy deposition for the detection of particles [10]. Therefore, due to the combination of the characteristics derived from the glass host and the organic dopants, the glasses doped with organic dyes are becoming promising scintillators with fast decay and high light yield.

The scintillation mechanism for detecting high energy photons such as X-ray or γ -ray involves three processes [11]. During the first step the energy of the incident particle is converted into a number of electron–hole (e–h) pairs. These primary excited carries collide with other electrons and share their excess energy with them. The cascade-like process continues until the excess kinetic energy is too low to create more of them. The second step is the energy transfer from the excited host to the luminescence centers. This step can occur by means of carries diffusion through the lattice towards the centers. The last step is the emission of light from the luminescence centers. The total scintillation efficiency is essentially dependent on the individual contribution from the three processes. There are materials that emit efficiently under optical excitation but perform poorly when stimulated by ionizing radiation. This suggests that the two first steps of scintillation processes, conversion of the incoming particle to e–h pairs (host excitation)

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and the host-to-center transfer of energy, must be of great importance for the overall scintillation efficiency. For the scintillation glasses doped with organic dyes, the creating electron–hole (e–h) pairs under excitation and the emission processes from the organic dye are expected to be highly efficient, while the second step that the energy transfer process from the carriers to the organic dye (luminescence centers) is a crucial issue. Therefore, the study of the transfer process for the dye-doped scintillation glasses is important and helpful.

In this work, we prepared the lead–tin–fluorophosphate glass matrix (undoped) and the glass doped with organic dye stilbene-3 since stilbene-3 is extensively applied in the detection of neutron and γ -ray as an important organic scintillator due to its high light yield and short decay time [12–15]. The luminescence spectra of the undoped glass and doped glass excited by vacuum ultraviolet (VUV) and ultraviolet (UV) synchrotron radiation were measured and analyzed in order to understand the mechanism of luminescence and the energy transfer process. A spectral continuous VUV–UV light source is advantageous for the study of the energy transfer process since VUV photons can easily excite the glass host rather than directly excite the dye.

2. Experimental

The lead–tin–fluorophosphate glasses were prepared using reagent grade PbF_2 , SnF_2 , SnO and $\text{NH}_4\text{H}_2\text{PO}_4$. The composition of the glass is, in mol%, $52.2\text{SnF}_2 - 10.5\text{SnO} - 5.1\text{PbO} - 32.1\frac{1}{2}(\text{P}_2\text{O}_5)$. The glasses were prepared by melting the batch materials at temperature of 500°C , in an electric furnace for 30 min, and then the molten glasses were transferred to another furnace with temperature equilibrated at 340°C . Organic dye (stilbene-3) was added to the molten glass and the mixture was stirred until the mixture become homogenous and bubble free. The concentration of stilbene-3 doped in the glass is 1×10^{-7} mol/cm³. The samples used in the present work were an undoped glass (host glass) and a doped glass. The glasses were cut and polished to slices $5 \times 5 \times 3$ mm³ in size for measurement.

The excitation and emission spectra were measured at VUV Station of National Synchrotron Radiation Laboratory (NSRL), Hefei, China. The typical spectral resolution of the primary monochromator (1 m Seya-Namioka) and the secondary monochromator (Spectrapro-275) is 0.4 and 2 nm, respectively. The pressure in the vacuum chamber during the measurements was 1×10^{-4} Pa. The excitation and emission spectra were detected by a Hamamatsu H5920-01 photomultiplier. A 300 nm cutoff filter was used to prevent the incident light entering into the secondary monochromator. The excitation spectra were corrected for the photo flux of the excitation beam using the excitation spectrum of sodium salicylate as standard. The emission spectra were not corrected since the sensitivity of detection in the region of 300–650 nm is rather flat. The spectra were measured from 20 to 300 K.

3. Results

The temperature dependence of emission spectra as function of wavelength for the undoped sample excited at 190 and 306 nm is shown in Fig. 1. Under the excitation at 306 nm, the undoped sample exhibits a broad emission band peaked about 440 nm in the range of 350–650 nm and the emission intensity is rapidly decreased with the rising temperature and completely quenched at room temperature. A relatively weak emission band appears at 350–450 nm peaked at 400 nm excited by 190 nm. This emission shows to be less temperature dependent and even can be observed at room temperature despite of rather low intensity. The excitation spectra of undoped glass with the emission of 440 nm, shown in Fig. 2, exhibit two distinct regions of excitation, 250–330 nm band peaked at 306 nm with a shoulder at 290 nm and a weak band peaked at 190 nm. The former shows strong temperature quenching effect, whereas the latter shows weak temperature dependence.

The emission spectra of stilbene-3 doped glass under the excitation with 190 and 320 nm at the temperatures from 20 to 300 K are shown in Fig. 3. The emission spectra of doped glass show the typical luminescence from stilbene-3. The emission spectra are fitted into two Gaussian bands with the maxima at about 2.65 eV

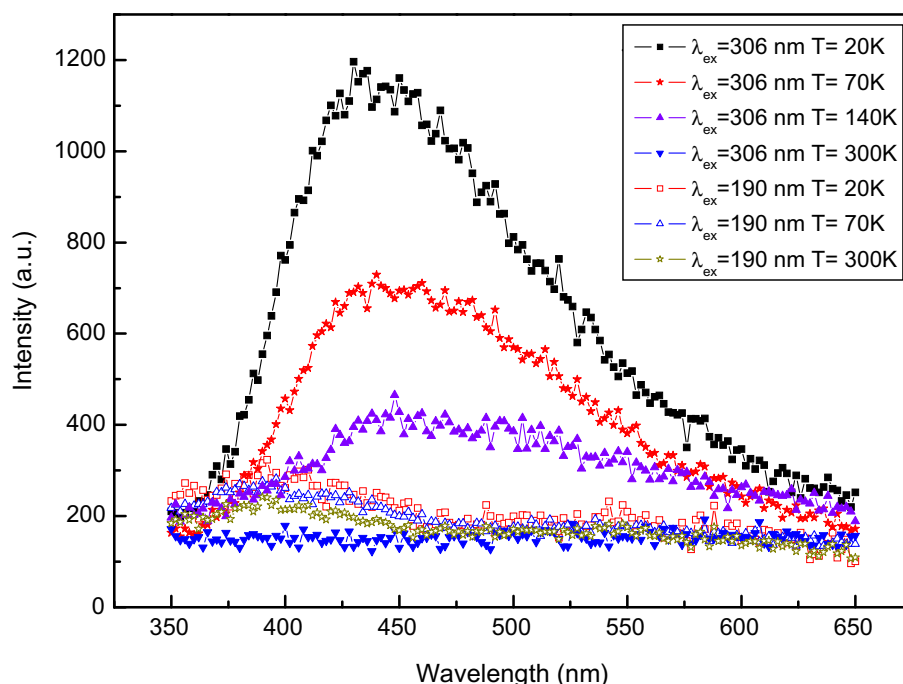


Fig. 1. Emission spectra of undoped lead–tin–fluorophosphate glass as a function of wavelength excited by 190 and 306 nm at the temperatures from 20 to 300 K.

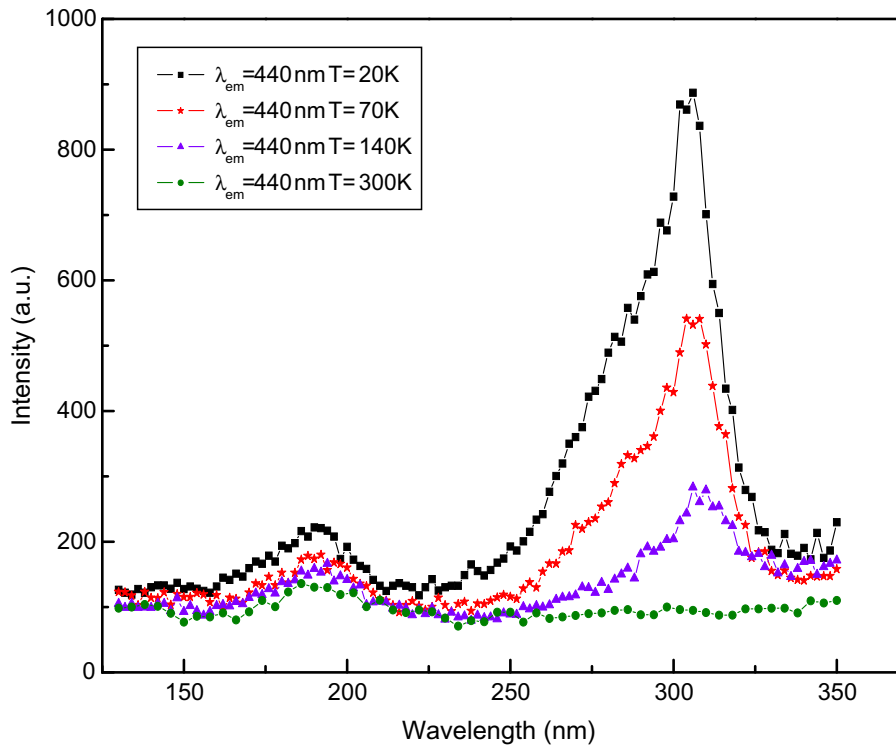


Fig. 2. Excitation spectra of undoped lead-tin-fluorophosphate glass with 440 nm emission at temperatures from 20 to 300 K.

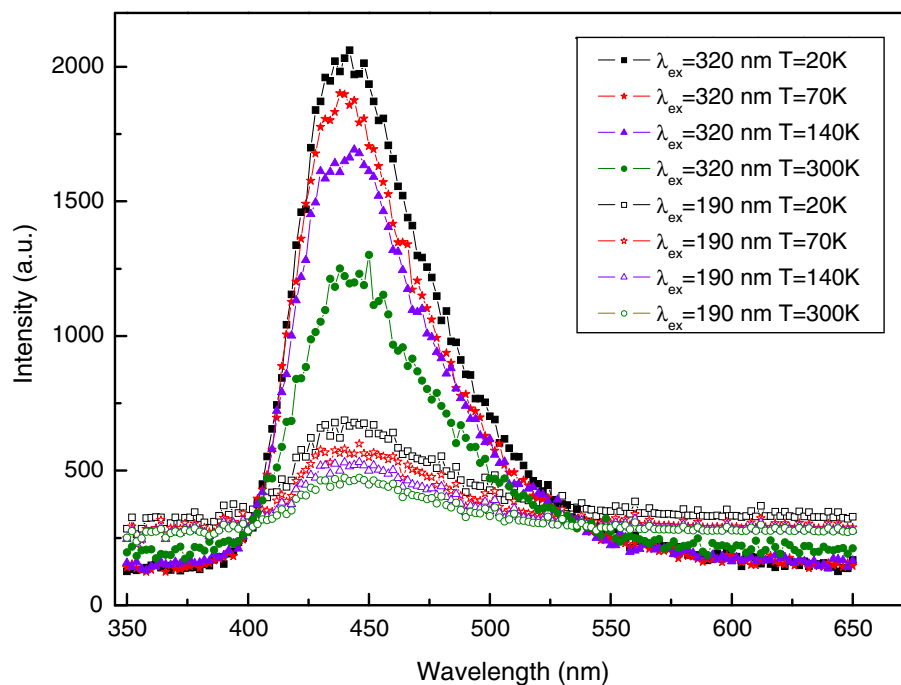


Fig. 3. Emission spectra of stilbene-3 doped lead-tin-fluorophosphate glass as a function of wavelength excited by 190 and 320 nm at the temperatures from 20 to 300 K. The emission intensities excited by 190 nm are multiplied by 2.

(468 nm) and 2.84 eV (436 nm), shown in Fig. 4. The emission spectra excited by 320 nm exhibits obvious temperature quenching effect and the intensity at 300 K decreases to the half that at 20 K, whereas the emissions excited by 190 nm show low intensity even at low temperature. The emission spectra at different temperatures are all well fitted into two Gaussian distributions with the results listed in Table 1. The two peaks are located at about 436 and

467 nm and the shift with temperature is less than 2 nm. It is explicitly found that with the rising temperature the emission intensity decreases, whereas the full width at half maximum (FWHM) increases, from 0.371 to 0.380 eV and 0.233 to 0.247 eV for bands of 467 and 436 nm, respectively. The spectral broadening with rising temperature originates from the thermal broadening of levels and can be described in the following equation [16]:

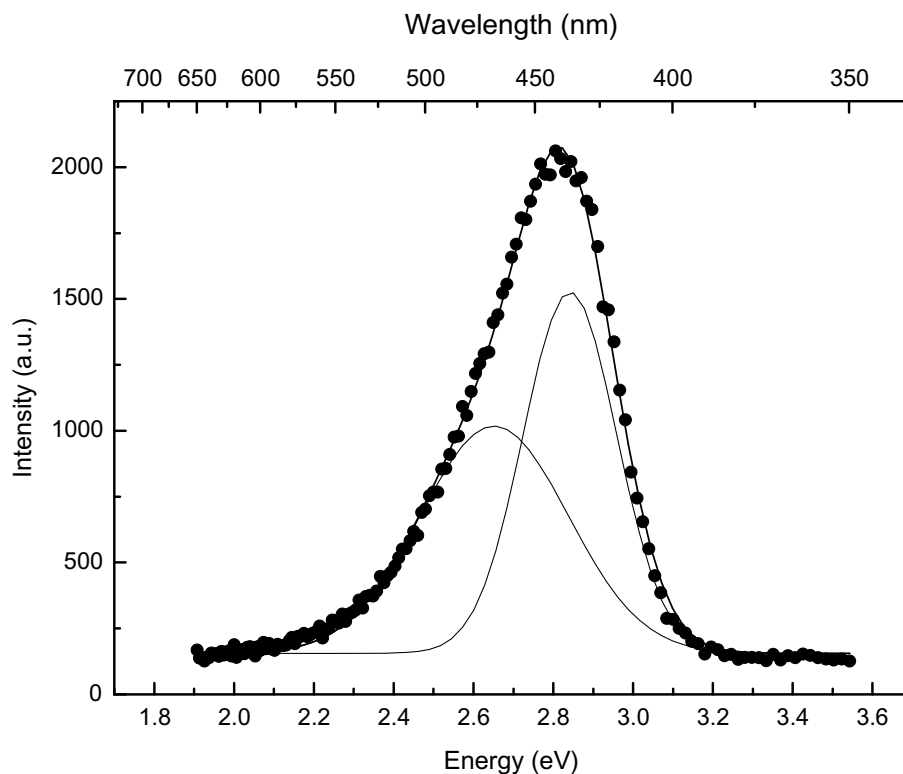


Fig. 4. Emission spectrum of stilbene-3 doped lead-tin-fluorophosphate glass excited by 320 nm at 20 K. The dots represent the experimental results and the solid lines represent the result of fit with two Gaussian components.

Table 1

Gaussian fitting results of emission spectra for stilbene-3 doped lead-tin-fluorophosphate glass excited by 320 nm at different temperatures, including emission peak, FWHM (full width at half maximum), phonon energies $h\omega$, integrated intensity, and ratio of intensity of two bands

Temperature (K)	Emission peak (eV/nm)	FWHM (eV)	$h\omega$ (cm^{-1})	Intensity (a.u.)	I_1/I_2
20	2.655/467.0	0.371	1050	406.3	1.03
	2.842/436.3	0.233	1098	396.4	
70	2.664/465.5	0.372	1206	362.4	1.03
	2.849/435.2	0.235	1242	353.0	
140	2.652/467.6	0.373	1212	310.8	0.92
	2.843/436.2	0.240	1283	338.3	
300	2.646/468.6	0.380	1450	205.8	0.90
	2.830/438.2	0.247	1495	228.8	

$$\Gamma(T) = \Gamma_0 \sqrt{\coth\left(\frac{h\omega}{2k_B T}\right)}. \quad (1)$$

Here $\Gamma(T)$ is the bandwidth at absolute temperature T . Γ_0 is the bandwidth at 0 K. $h\omega$ is the energy of the lattice vibration (or phonon) that couples with the electronic transition. k_B is the Boltzmann constant. The ratio of 467 and 436 nm bands is 1.03 at 20 and 70 K, whereas it decreases to 0.92 and 0.90 at 140 and 300 K, respectively. This suggests that the two emission bands have different temperature quenching speed. The involved phonon energies are in the range of 1000–1500 cm^{-1} , which is consistent with the experiments [17,18]. The excitation spectra of doped glass with 436 nm emission at 20–300 K are shown in Fig. 5. There are strong and broad UV excitation bands from 260 to 410 nm with the peaks at about 320 and 400 nm, which is the typical characteristic excitation of stilbene-3 [19]. The intensity of such characteristic excitation slightly decreases by about 5% from 20 to 140 K but

greatly lowers at 300 K with two-thirds of that at 20 K. It is also found that a weak excitation band appears in VUV region peaked at 190 nm but is less temperature dependent.

In Fig. 6, the transmission spectra of undoped and stilbene-3 doped lead-tin-fluorophosphate glass are shown. The absorption edges of are located around 320 nm and 420 nm for undoped and stilbene-3 doped glasses, respectively. The strong absorption in the region of 320–420 nm for doped glass is due to the characteristic absorption of stilbene-3. Such absorption corresponds with the effective excitation for stilbene-3 shown in Fig. 5.

4. Discussion

The optical process of stilbene-3 is involved with the transition between a bonding π orbital and an antibonding π^* orbital in a well-developed π -conjugated system [20]. The excitation and emission processes are due to the transition of $\pi \rightarrow \pi^*$ ($S_0 \rightarrow S_1$) and $\pi^* \rightarrow \pi$ ($S_1 \rightarrow S_0$), respectively, shown in Fig. 7. The two Gaussian emission bands origin from the presence of two vibrational states. The several excitation bands from 260 to 410 nm are also due to the multiple vibrational states of stilbene-3. The difference in energy of two emissions is about 0.19 eV (1530 cm^{-1}) which is in the range of the vibrational energy for stilbene-3 [17,18].

The emission about 440 nm of undoped glass may be due to exciton trapped at metal ion (Pb or Sn) or self-trapped exciton [21–24], which commonly appears in compounds with halide ions and is easy to be quenched with the rising temperature. The corresponding excitation is usually located in the UV region of 250–350 nm. In contrast, the excitation in the VUV region of 160–200 nm is probably due to the intrinsic excitation of host, i.e., the excitation from the valence band to conduction band. Therefore, the mobility gap may be estimated about 6.5 eV from

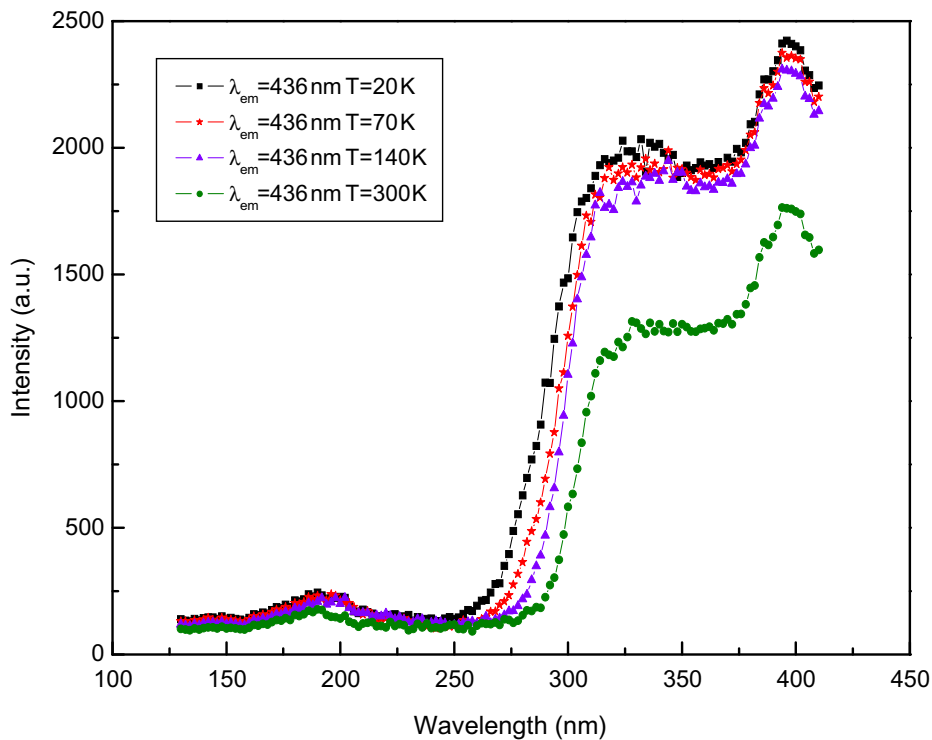


Fig. 5. Excitation spectra of stilbene-3 doped lead-tin-fluorophosphate glass with 436 nm emission at temperatures from 20 to 300 K.

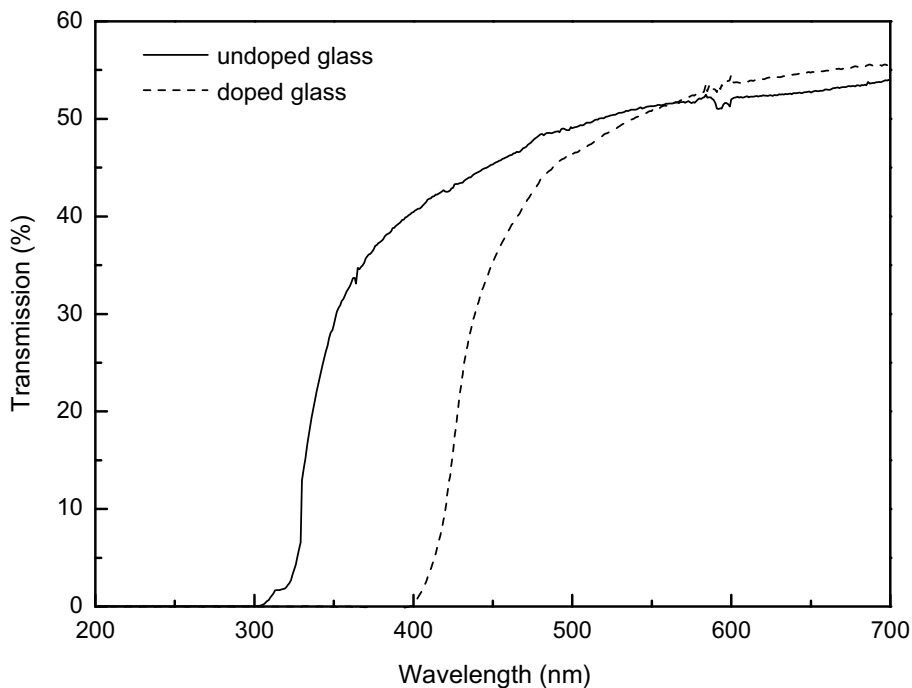


Fig. 6. Transmission spectra of undoped and stilbene-3 doped lead-tin-fluorophosphate glass.

the energy of the interband excitation. The emission at 400 nm band excited by 190 nm is related some unknown defects, which has a higher quenching temperature than room temperature.

The emission around 436 nm from stilbene-3 was observed under the excitation with 190 nm which belongs to the host excitation. Although the emission intensity excited by 190 nm is only about 10% of that under the direct excitation of stilbene-3, it is

explicitly indicated that the energy transfer occurs from the host to the dye. The excited carries (electron-hole pairs or exciton) created by the host excitation can mobile and transfer their energy to the luminescence center stilbene-3. The effective energy transfer from host to the organic dye is critical factor for the light yield, thus the application in the detection of high energy particles. However, the luminescent efficiency is still fairly low under the high

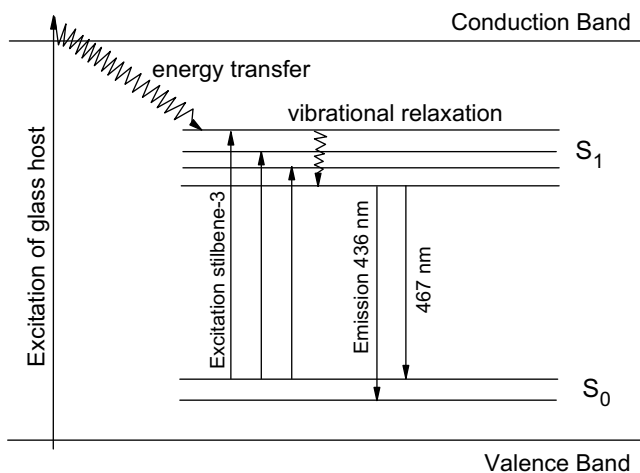


Fig. 7. The schematic explanation for the processes of absorption, energy transfer and emission by use of the energy state diagram for the stilbene-3 doped lead-tin-fluorophosphate glass.

energy excitation, and should be significantly improved. There are a variety of reasons responsible for the low transfer efficiency. The dye molecules may not be homogeneously doped into the glass network or become highly aggregative, thus the excited carriers may be hard to completely transfer their energy to each dye molecule. Another important reason is that the amount of defects in glass is large, such as impurities, structural defects and bubbles which can be introduced into the viscous melting during the doping process. Such plenty of defects can significantly influence the diffusion rate of the excited carriers to the dye molecules. Defects may also play the role of the nonradiative centers to dissipate their energy by emitting phonons (lattice vibration). Therefore, in order to improve the scintillation light yield of the dye-doped glass, it is necessary to optimize the fabrication technology to increase the concentration and homogeneity of doped dye in glasses and suppress the defects as possible.

5. Conclusions

Organic dye stilbene-3 was doped into lead-tin-fluorophosphate glass to prepare the scintillation glass. The host glass shows emission peaked about 440 nm at low temperature, but quenches

at room temperature. The doped glass exhibits strong characteristic emission of stilbene-3 with 467 nm and 436 nm Gaussian bands excited by ultraviolet 250–330 nm, but weak emission excited by 190 nm. The energy transfer from host to the dye can occur but with a low efficiency. It is important to improve the energy transfer efficiency in terms of practical applications.

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