Scintillating glass doped with organic activator p-TP and/or POPOP

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Abstract. Two organic activators, p-TP(p-terphenyl) and POPOP (1,4-bis(5-phenyloxazol-2-yl) benzene), which are normally used to prepare the scintillating plastic, were doped in tin fluoroarsenophosphate glasses to develop a serial of scintillating glasses with different concentrations. The fluorescence spectra and the transmission spectra of some scintillating glass were explored and the actual concentration organic in scintillating glass was estimated by comparing the extracted solution from glass with standard solution. Results show that the organic materials can be doped into inorganic glass, however, the actual concentration of organics doped in the glass is very low. Compared with scintillating plastic, the emission peak of scintillating glasses move towards the longer wavelength and POPOP is not wavelength shift any more.

Keywords: Scintillating glass, doping, organic activator, concentration

1. Introduction

New colliders for high-energy physics studies require that the scintillators have high density, short decay time, good radiation hardness, and low cost. The present scintillators can not meet all the requirements no matter they are inorganic or organic materials, therefore, more and more attention is paid in how to prepare a kind of scintillators which have not only the advantages of plastic scintillators but also the scintillating glass. Nogues[1] developed a fast, Radiation–Hard Scintillating silica glass through sol-gel method, providing a new idea that doping organic materials in glass to prepare the scintillating glass. The development of low-melting[2] lead-tin-fluorophosphate glass make it possible to dope organic scintillating materials into bulk inorganic glass. The following investigations[3-4] of doping organic laser-dye in the lead-tin-fluorophosphate glass is also the evidence that organic materials can be doped into the glass. Based on the above results, Hongsheng Zhao[5] developed a scintillating glass doped with organic activator p-TP(p-terphenyl), which is normally used in the scintillating plastic. Although the light yield of prepared glass is low, the results show that doping organic activators in inorganic glass is a promising method to prepare scintillating glass.

In this paper, a serial of scintillating glasses are developed using low-melting tin-fluorophosphate glass as the matrix through doping organic activators p-TP and/or POPOP (1,4-bis(5-phenyloxazol-2-yl) benzene),( p-TP and POPOP are often used as the activators in scintillating plastic and POPOP is believed to be the wavelength shifter in the plastic.[6,7])The fluorescence spectra, transmittance of scintillating glass are explored and the actual concentration of organic material in glass is estimated.

2. Experiment

The raw materials were mixed well according to a certain ratio and melted in a alumina crucible at 500°C for 30min. Then took out the crucible and introduced the organic activator in the melt at ~300°C. After stirred the melt for a few minute, poured out the melt in a carbon steel mold and quenched the sample at the temperature 10°C above the glass transition temperature (T_g). The batch amount of organic activators in different samples glasses doped is listed in Table 1.
Table 1 Designed concentration of different dopants in scintillating glasses

| Sample | Concentration designed/wt% |
|--------|----------------------------|
|        | p-TP | POPOP |
| 1      | 0.2  | 0.2   |
| 2      | 0.1  | 0.1   |
| 3      | 0.05 | 0.05  |
| 4      | 0.2  | 0.2   |
| 5      | 0.1  | 0.1   |
| 6      | 0.06 | 0.02  |
| 7      | 0.12 | 0.04  |
| 8      | 0.06 | 0.01  |

The as-made glasses are polished into the thin plates in the size Φ20mm×3mm for the measurement of transmission and fluorescence. The transmission spectra of samples are studied in ultraviolet and visible region by using a UV - VIS spectrophotometer with the error bar of 0.3% in transmission and ±0.3nm in wavelength. The fluorescence spectra are measured with a Hitachi-850 fluorescence spectrophotometer. The range of wavelength is 200-900nm and the scanning rate is 60nm/min.

The concentration of organic activator doped in the glass is determined by comparing the intensity of fluorescence spectrum of standard solution and the solution dissolving the glass using same solvent. The sample to measure is crushed into powder first and then dissolved in the dense muriatic acid completely. Then the solution is extracted using chloroform and the fluorescence spectrum of the extracted solution is measured and compared with the standard chloroform solution to estimate the concentration of organic activator in scintillating glass.

3. Results and discussion

3.1 Fluorescence spectrum of glasses

![Fluorescence spectra](image)

Fig.1 Fluorescence spectra of sample 5: A absorption spectrum(λ_m=530nm) B emission spectrum(λ_E=367nm)
Fig. 1 shows the fluorescence peak of sample 5, which doped with 0.2wt% POPOP. Table 1 lists the absorption peak and emission peak of POPOP in different matrix. From Fig. 1, we can see that the absorption peak of the glass is at ~367nm, which is almost the same as that of toluene solution dissolving some POPOP [7]. There are two peaks in the emission spectrum at 420nm and 540nm, respectively. The peak at 420nm is very close to that of pure POPOP [6] and its fluorescence intensity is weaker than that of the peak at 540nm. The Stoke shift between the absorption and emission spectra is about ~177nm.

The fluorescence spectra of sample 2 doped with 0.2wt% p-TP was given in Fig. 2. It can be found that the fluorescent intensity of absorption and emission spectra of this glass were much weaker than that of sample 5 as shown in Fig. 1. Unlike sample 5, two peaks appear in the absorption spectrum of sample 2: one is at 290nm with very weak fluorescence intensity, while the other peak is at 355nm with relatively strong fluorescence intensity. There is only one peak for the emission spectrum (~610nm). It can be seen that the glass exhibits a large Stokes shift (~255nm) between the absorption spectrum and emission peak. Compared with the emission peak of p-TP in SiO₂ glass [2] prepared by sol-gel method (~360nm) and that in polythene plastic (~340nm) [6], the emission peak of sample 2 move obviously toward the longer wavelength.

![Fig. 2 Fluorescence spectra of sample 2: A absorption spectrum(λₐ=610nm) B emission spectrum(λₑ=355nm)](image)

Fig. 3 gives the fluorescence spectra of sample 8, which doped with 0.12wt% p-TP and 0.04wt% POPOP. There are two peaks for the absorption spectrum. One peak (~290nm) is very close to the first absorption peak of sample 2 as shown in Fig. 2, therefore, it is believed that a certain amount of p-TP do exists in the sample 8. The other peak at ~370nm, which is almost same with the only absorption peak of sample 5 as shown in Fig. 5, maybe corresponds to the existence of POPOP in the glass. It ca also be seen that the emission spectrum of sample 8 is almost the same as that of sample 5. Although the actual concentrations of the organic activators are unknown because of the evaporation of organics during preparation of sample, it is believed that there do be some p-TP and POPOP doped in the sample 8 and they produce the fluorescence together when excited. POPOP is not the wavelength shifter in the sample 8 any more, because the emission peak of p-TP and POPOP both move toward the longer wavelength in the scintillating glass compared to that of p-TP and POPOP in scintillating plastic. In summary, all the scintillating glass doped with organic activators p-TP and POPOP exhibit a relatively large Stoke shift between absorption and emission spectra. And the strongest absorption and emission
peak for each glass both shift to longer wavelength, which is attribute to the interaction between the organics and matrix glass\textsuperscript{[3,4]}.

![Graph showing fluorescence spectra]

**Fig. 3** Fluorescence spectra of sample 8: A absorption spectrum($\lambda_{em}=530$nm) B emission spectrum($\lambda_{e}=360$nm)

3.2 Actual concentration of organic activator in scintillating glass

![Graph showing comparison of emission spectra]

**Fig. 4** Comparison of emission spectra for extracted solution (B) from sample 5 and standard solutions A ($10^{-5}$mol/L) and C ($10^{-6}$mol/L)

Fig. 4 gives the comparison of emission spectra for extracted solution C from sample 5 and two standard solutions A and C. The concentration of POPOP in standard solution A is $10^{-5}$mol/L and that in solution C is $10^{-6}$mol/L. As shown in Fig.5, the change of concentration of POPOP in solution does not change the location of emission peak in the spectra, but the intensity of fluorescence. The fluorescence intensity of extracted solution from sample 5 is between those of standard solution, indicating that the concentration of POPOP in the extracted solution is between those of standard solution. The calculated results show that the concentration of POPOP in
extracted solution is about $1.7 \times 10^{-6}$ mol/L, and the calculated volume concentration of POPOP in glass 5 is about $1.1 \times 10^{18}$ molecule/cm$^3$, means that there are about $1.1 \times 10^{18}$ molecule doped in every cubic-centimeters scintillating glass. Although the concentration is lower than that reported in reference [9], it is in the same order as that reported. Compared with the concentration of organic activators in scintillating plastic [6], the actual concentration of organic in scintillating glass is much lower and the lower concentration of organics in glass will weaken the ability of glass to yield light. Therefore, how to increase the concentration of organic activators in the scintillating glass is the second key point to prepare scintillating glass with better properties.

4 Conclusions
Organic activators, p-TP and POPOP, both can be doped into tin fluorophosphate glass to prepare the scintillating glass, however, the actual concentration of organic activators in glass is very low due to the evaporation of organics during preparation of glasses. Compared with the scintillating plastic, the emission peak of scintillation glass doped with organics moved toward to the longer wavelength. POPOP in the glass is not the wavelength shifter anymore and it produces fluorescence directly. The key point to get better scintillating glass is to increase the concentration of organics in glass and avoid the evaporation of organics during preparation of glasses.

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