Preparation and Third-Order Optical Nonlinearity of Organic Dye-Doped Glasses

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Organic dyes of stilbazolium group, such as 4'-dimethylamino-N-methyl-4-stilbazolium iodide (DMSI) and 4'-diethylamino-4-stilbazolium propylsulfate (DESPS) having large third-order nonlinear susceptibility $\chi^{(3)}$ values, were incorporated into a low melting PbF$_2$-SnF$_2$-SnO-P$_2$O$_5$ glass system with a conventional melting- and quenching technique. The dyes were mixed with the glass melts around 300°C. From the optical and infrared absorption spectroscopy, it was found that the original structure of each dye was maintained even in the glass. The $\chi^{(3)}$ of the dye-doped glass was evaluated from third-harmonic generation, and that of the glass containing DESPS was nearly twice as large as that of the base glass.

Key-words: Organic dye doped glass, Optical nonlinearity, THG, $\chi^{(3)}$, Low melting glass

1. Introduction

Recent remarkable development of high power laser has stimulated the study of nonlinear optical materials. Simultaneously, they have quite high potential for the photonic materials. On specific, they are thought to be applicable to optical switches, optical memories and optical branches etc. Generally, nonlinear electric polarization of materials ($P_n$) can be expressed as

$$P_n = \chi^{(2)} E \cdot E + \chi^{(3)} E \cdot E \cdot E + \cdots \quad (1)$$

where $E$ is the amplitude of electric field, $\chi^{(2)}$ and $\chi^{(3)}$ are second- and third-order nonlinear susceptibility, respectively. For instance, $\chi^{(2)}$ causes second harmonic generation or electrooptic effect, and on the other hand, $\chi^{(3)}$ results in third harmonic generation or optical Kerr effect. Of these effects, the optical Kerr effect, in other words, intensity dependent refractive index is a quite powerful candidate for a super high speed optical switch or shutter. To make the operation effective, large $\chi^{(3)}$ is naturally preferable. Some organic compounds have been known to have large $\chi^{(3)}$, but they are thermally unstable when exposed to high power laser beam for long time duration. Furthermore, they are powdery and frequently even difficult to be handled. Therefore, it is necessary to embed them in a stable matrix for extensive practical use. The oxide glasses have been commonly used as the laser system components such as mirrors and lenses because of their high transparency, high environmental durability and ease of fabrication to fibers, waveguides and so on. However, too low melting and boiling points or dissociation temperature of organic dye compared to the oxide glasses are frequently big barriers to use glasses as a matrix by the conventional melting- and quenching technique. So, in our previous paper, the sol-gel method was successfully applied to the incorporation of such organic dyes into SiO$_2$ gels. Although the structure of the dyes was unchanged in the gels and $\chi^{(3)}$ of the composites was higher than that of the base gel itself, the densification of the gels and the collapse of the pores were not sufficient resulting from the strict limitation for the heating temperature. In particular, the elimination of pores is very significant to avoid light scattering. Therefore, this study attempted the incorporation of organic dyes into glass matrix by the conventional melting- and quenching technique using very low melting PbF$_2$-SnF$_2$-SnO-P$_2$O$_5$ glass system found by Tick.

2. Experimental procedure

The commercial analytical grade SnO, PbF$_2$, SnF$_2$ and P$_2$O$_5$ (Nakarai Chemicals Co. Inc.) were weighed to the 8.3SnO·4.6PbF$_2$·31.4SnF$_2$·55.7P$_2$O$_5$ (mol%) in batch composition of 20 g in total. After mixing thoroughly, the powder was put into an aluminum crucible without any cap and melted in an electric furnace at 500°C for 20 min to obtain homogeneous melt. Then, the melt was cooled down to below the boiling point or dissociation temperature of the melts but to above the solidifying temperature of the melts. After removing the melt out of the furnace, the dyes of 0.005–0.15 wt% to the batch were added and stirred with an alumina bar until the melts were colored homogeneously. Subsequently, the melts obtained were poured on the stainless steel plate and sandwiched by another plate for quenching. All the above experimental procedure was carried out in the glove box filled with nitrogen. The organic dyes used were 4'-dimethylamino-N-methyl-4-stilbazolium iodide.
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...despite (DMSI), 4'-diethylamino-N-methyl-4-stilbazolium iodide (DESI), 4'-diethylamino-4-stilbazolium propylsulfate (DESPS) and 4, 4'-dimethylamino nitrostilbene (DANS), since they are known as non-resonant-type high $\chi^{(3)}$ materials ($\chi^{(3)} \approx 10^{-11}$ esu). Figure 1 shows the structure of each dye. The infrared, and visible and ultraviolet absorption spectra were measured by JASCO A-202 using KBr pellet method and by Varian CARP-14 with polished glass plates of 0.6-0.7 mm thickness, respectively. The spectra of dyes themselves were explored by JASCO UNIDE C-610 after dissolving them into various solvents using a SiO$_2$ glass cell. Non-resonant third-order optical nonlinearity $\chi^{(3)}$ of each dye-doped glass was evaluated by third harmonic generation at pump wavelength of 1.9 $\mu$m, and measurements were carried out at NTT Optoelectronics Lab., Tokai, Ibaraki. The details of the measurement setup and condition can be found elsewhere. DTA measurement was also performed to investigate the thermal change of the dyes.

3. Results and discussion

Prior to the incorporating into glass system, the dyes were subjected to DTA measurement to explore the appropriate temperature for mixing into glass melts without evaporation or dissociation. The melting points of DMSI, DESI, DESPS and DANS were 258$^\circ$, 225$^\circ$, 294$^\circ$ and 256$^\circ$C, and the boiling or dissociating temperature were 307$^\circ$, 308$^\circ$, 319$^\circ$ and 310$^\circ$C, respectively. Therefore, the temperature of about 300$^\circ$C seems to be reasonable for the mixing.

And, at such a temperature the dyes except DANS could be homogeneously incorporated into PbF$_2$–SnF$_2$–SnO–P$_2$O$_5$ melts by up to 5 wt%.

The color of the quenched dye-doped glass varied from bright orange to deep red with increasing its concentration.

Figures 2 (a), (b), (c) shows the visible and ultraviolet spectra for undoped base glass, dyes dissolved in ethylalcohol and glasses doped with dyes. From these figures, one can say that no significant peak can be seen for the base glass in the wavelength range from 400 nm to 700 nm. On the other hand, clear and broad peaks are observed for dyes in ethylalcohol and glasses doped with dyes. Although slight peak shift to low frequency is seen for DESPS-doped glass com-

![Fig. 1. Structural formula of stilbazolium group used.](image_url)

![Fig. 2. (a) Visible and ultraviolet spectra of base glass, DMSI-doped glass and DMSI dissolved in ethylalcohol, (b) Visible and ultraviolet spectra of base glass, DESI-doped glass and DESI dissolved in ethylalcohol, (c) Visible and ultraviolet spectra of base glass, DESPS-doped glass and DESPS dissolved in ethylalcohol.](image_url)
pared to that in ethylalcohol, the peak position (~500 nm) and shape of the dyes are basically unchanged between in ethylalcohol and in glass. Figure 3 illustrates the infrared spectra of base glass, 5 wt% DMSI-doped glass and DMSI powder. The peaks around 1100 cm⁻¹, 1000 cm⁻¹ and 850 cm⁻¹ for base and doped-glasses are ascribed to P-O-stretching, P-O-P stretching and P-F stretching vibration mode, respectively. Comparing the spectrum of DMSI-doped glass with that of DMSI powder, the structure of the absorption spectra in the range from 1200 cm⁻¹ to 1700 cm⁻¹ is quite similar to each other. The 1640 cm⁻¹ peak ascribable to trans C=C vibration and peaks at 1380 cm⁻¹ and 1470 cm⁻¹ both ascribable to –N(CH₃)₂ are also observable in the DMSI-doped glass, indicating that the original structure of DMSI is maintained even in the glass without dissociation nor cis–trans transformation. From the results and discussion thus far, it is emphasized that the organic dyes were successfully incorporated into the base glass without any thermal deterioration during the preparation process.

Table 1 tabulates the $\chi^{(3)}$ values obtained from base glass and dye-doped glasses. The $\chi^{(3)}$ value ($3.3 \times 10^{-12}$ esu) of the base glass itself is nearly 10 times higher than that of SiO₂ glass. For DMSI-doped glasses, no remarkable increase can be seen. On the other hand, the increase of the $\chi^{(3)}$ is detectable for DESI- and DESPS-doped glasses. The largest $\chi^{(3)}$ in this experiment is observed for 0.005 wt% DESPS-doped glasses and is $5.5 \times 10^{-13}$ esu, being nearly twice as large as that of the base glass. The $\chi^{(3)}$ values of the dyes in dimethylformamide ranged 0.3–2.0 $\times 10^{-13}$ esu, and thus $\chi^{(3)}$, in other words, nonlinear electronic polarization seems to be enhanced in the glass matrix. This may be attributed to the concentration of electric field by the high dielectric constant of the matrix glass (about 3.1) Tick et al. and He et al. reported quite large $\chi^{(3)}$ as $10^{-2}$–$10^{-3}$ esu for acridine yellow-or acridine orange-doped lead-tin fluorophosphate glasses. However, in those glasses the origin of the $\chi^{(3)}$ results from photochemical reaction, and thus it takes times in the order of nsec to show the $\chi^{(3)}$. In order to develop very fast all optical communication system, the response at least in psec order is required. In the case of stilbazolium group, $\chi^{(3)}$ originates from nonlinear electronic polarization, and thus the response time could be in the order of fsec. Therefore, from the viewpoint of developing photonic device, the present dyes seem to have higher potential than the acridine group.

4. Conclusions

Optical spectra and third order optical nonlinearity were investigated on stilbazolium group-doped low melting PbF₂-SnF₂-SnO-P₂O₅ glass system, and the results can be summarized as follows.

(1) DMSI, DESI and DESPS were homogeneously incorporated in the glass by up to 5 wt%. Depending on the dye concentration, the color varied from bright orange to deep red.

(2) From infrared, visible and ultraviolet spectra, the original structure of the dyes was found to be unchanged even during preparation procedure at about 300°C.

(3) The $\chi^{(3)}$ of DESI- and DESPS-doped glasses was higher than that of base glass, and the highest value was nearly twice as large as that of the base glass. The high dielectricity of the base glass may raise the nonlinear electronic polarization, resulting in effective increase of $\chi^{(3)}$.

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