Preparation and optical properties of TPPS-doped metal–carboxylate-salts glasses

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Abstract

Li and Na carboxylate salts glasses with different number chains containing molecules of Tetraphenyl-porphine-tetrasulfonic acid (TPPS) were prepared by the melting method. TPPS doped in the glasses had the same form as the TPPS in the aqueous solutions. However the form of TPPS in the glasses changed because TPPS reacted with matrix glass during the melting process. Tetraphenyl-porphine (TPP) could not be incorporated into the Li and Na carboxylate salts glasses by the present melting method. The free base TPPS is important for photochemical hole burning (PHB) properties, and a mixed metal–carboxylate salts glasses containing free-base TPPS, which is the active form for PHB, were prepared by controlling the melting condition. It was found that a preparation condition such as holding time of the melts affects the formation of the complex of the TPPS and that in the mixed metal–carboxylate salts melts the TPPS formed a complex with Li but did not form a complex with Na. © 2001 Published by Elsevier Science Ltd.

Keywords: Optical property; Carboxylate glass; Porphine; Hybrids materials

1. Introduction

Inorganic matrices usually have the advantages of transparency, thermal durability and chemical and mechanical stability compared with organic ones. Some methods, for example, the sol-gel and conventional melting methods, are available for the incorporation of organic dyes into inorganic matrices. Using the sol-gel method, the hybrid materials can be synthesized easily at low temperature [1–9]. However, the gels are porous because of the limitation of the temperature of heat treatment. On the other hand, glasses obtained with the conventional melting method are rigid and dense. In order to avoid thermal dissociation of organic dyes, a low melting temperature is required.

Generally speaking, glasses obtained with low melting temperature usually have a rather poor chemical durability. Some studies on borax glasses doped with fluorescein, which have a large third-order nonlinear susceptibility $\chi^{(3)}$ value have been reported [10–14]. The SnF$_2$–P$_2$O$_5$–SnO–PbF$_2$ glasses, discovered by Tick, have not only a very low melting temperature but also a good chemical durability [15]. Some studies on their compositional dependence of several physical properties and their structure have been reported [16–23]. SnF$_2$–P$_2$O$_5$–SnO–PbF$_2$ glasses have been developed as matrices for organic dyes with optical properties [24–27]. A nonlinear optical property is one of the useful optical properties of organic dyes. Tompkin et al. have studied the SnF$_2$–P$_2$O$_5$–SnO–PbF$_2$ glasses doped with acridine yellow and acridine orange, which have large $\chi^{(3)}$ values [25]. Nasu et al. have studied the SnF$_2$–P$_2$O$_5$–SnO–PbF$_2$ glasses doped with organic dyes of stilbazolium group, which have large $\chi^{(3)}$ values [27]. Both of these studies have reported that the absorption spectra of glasses doped with organic dyes were typical of these dyes in liquid solvent.

Many studies on the photochemical hole burning (PHB) properties of some porphyrins in organic matrices have been reported [28–33]. The PHB properties have been studied because of the scientific interests and the possibility of the application to high-density optical data storage [28]. Some studies on the synthesis and spectroscopy of the gels with some porphyrins using the sol-gel process have been reported [6,8]. Since SnF$_2$–P$_2$O$_5$–SnO–PbF$_2$ glasses are more rigid and denser matrices than organic compounds and gels, it is expected that the optical spectra and PHB properties of SnF$_2$–P$_2$O$_5$–SnO–PbF$_2$ glasses doped with
porphyrins reflect more strongly the interaction between the porphyrins and the glass matrices.

The authors [29] reported that tetracyanophthalocyanine (TCNQ) and its Sn complex (TPPS–Sn) were incorporated into a low melting SnF$_2$–P$_2$O$_5$–SnO–PbF$_2$ glass system with a conventional melting method. From the absorption and luminescence spectroscopy, it was found that in the glass, the above organic dyes were not decomposed and the original structure of TPPS–Sn was maintained; however, the structure of TPPS changed from that in the aqueous solutions. The excitation spectra and the extraction of the dyes suggest that TPPS reacted with Sn during melting and TPPS–Sn, TPPS and TPPS–Sn with one pyrrole reduced were produced. This is supported by the result of PHB measurement. The free base form of TPPS is important for the PHB properties but complexes of TPPS were formed during the doping process.

Blair et al. [15] reported new family of low melting glasses of mixed metal carboxylate salts glasses. They have studied the glasses doped with photochrome which shows photochromism.

In this work optical properties such as absorption, excitation spectra of TPPS in the Na and Li carboxylate glasses with different number chains were studied to characterize the TPPS in the mixed carboxylate salts glasses.

Incorporation of TPPS of free base into this glass is expected to be possible in the alkaline matrix of Na and Li carboxylate salts glasses. In the sol-gel process we adopted a two-step process; that is acidic or basic conditions for preparation of amorphous silica containing free-base form TPPS, which is active for PHB properties [36,37].

2. Experimental

Reagent grade CH$_3$COOLi, CH$_3$ COOLi 2H$_2$O, CH$_3$COONa, CH$_3$(CH$_2$)$_2$COONa, (Wako Pure Chemicals Co.) CHCH$_2$COONa, CH$_3$(CH$_2$)$_2$COONa, CH$_3$(CH$_2$)$_3$COONa, CH$_3$(CH$_2$)$_4$COONa, (Tokyo Kasei Kougyo Co.), and doping dyes, TPPS (tetracyanophthalocyaninetetrasulfonic acid) or TPP (tetracyanophthaline) were used.

The molecular structures of TPPS and TPP are illustrated in Fig. 1. These chemicals were mixed thoroughly and heated in a glass beaker in a furnace fitted with a reflux condenser. The batches were melted at 240°C and poured into a brass mold. The melts were stirred carefully with an alumina bar. Some of the melts were held for 15 min and 240°C. After melting, the beaker was removed from the furnace and the melt was poured and quenched into glass. Metal–carboxylate glasses are not stable at high humidity atmospheres, thus the glass melts were poured into a brass holder with glass windows for optical measurements. Two series of samples were prepared. These compositions are as follows:

$$\text{CH}_3\text{COOLi} : \text{CH}_3\text{COONa} : \text{CH}_3(\text{CH}_2)_n\text{COONa} = 2n + 8 : n - 2 : 6 \quad (n = 2, 4, 5, 6)$$  \hspace{1cm} (1)

$$\text{CH}_3\text{COOLi} : \text{CH}_3(\text{CH}_2)_n\text{COONa} = 2 : 1 \quad (n = 0, 1)$$  \hspace{1cm} (2)

The (1) compositions are Li:Na = 2:1 and CH$_3$COO$^-$ : CH$_3$(CH$_2$)$_n$COO$^-$$n + 2$ (sum of the number of carbon is equal). For $n = 1$ the (1) compositions cannot be obtained by using the starting materials as above. Thus the (2) compositions were melted. In order to dope the dyes homogeneously the dyes were added with the glass powder containing the dyes, which was prepared by mixing the dyes and the fine glass powder in ethanol, drying and reducing to powder. Densities of glasses were measured using Archimedes method by using kerosene. Glass transition temperature, $T_g$ and melting temperature, $T_m$ were obtained using a DTA instrument (Rigaku Denki, TAS-100) at a heating rate of 5°C/min. Absorption spectra and fluorescence spectra were measured using a spectrometer (Hitachi, U-3410) and a fluorescence spectrometer (Shimazu RF-5000), respectively.

3. Results and discussion

3.1. Densities, glass transition temperature and melting temperature

Li and Na carboxylate salts glasses with different number
chains containing molecules of TPPS were prepared by the present melting method. Densities, glass transition temperature, \( T_g \), melting temperature, \( T_m \) of these metal carboxylate glasses are shown in Table 1. Densities of glasses decreased with the longer chain length of carboxyl of raw materials.

These effects of chain length on the density of carboxylic acids [15] have nearly the same trend with the densities of present glasses of which Na:Li is 1:1. Blair [15] also showed the same tendency for other ratios of Na, Pb. K and Ca. The \( T_g \) or \( T_m \) shows a decrease with the longer chain length that corresponds to an increase in the number of \( n \), as in Table 1.

3.2. Absorption spectra of metal carboxylate salts glasses containing TPPS

Absorption spectra of metal carboxylate salts glasses containing TPPS obtained by quenching the melt are shown in Fig. 2 as a function of \( n \) number. The absorption spectrum of the glasses doped with TPPS had an intense peak and some peaks in the 500–700 nm region. The shape of this absorption spectrum is characteristic of porphyrins [34]. The absorption spectra of the porphyrins have an intense band in the 400–450 nm region and two or four bands in the 500–700 nm region, which have been referred to as Soret and Q bands, respectively [34]. The porphyrins, which contain two and four hydrogens in the center position, are called free base and dication, respectively [35]. The absorption spectra of TPPS in the aqueous solutions are shown in Fig. 3. The Soret and Q bands had peaks at 414 nm and four peaks for the free base and at 434 nm and two peaks for the dication. In the region of the Q band, the wavelength of maximal absorption was at 515 nm for the free base, which was the highest energy band, and it was shifted to 645 nm for the dication which was the lowest energy band.

Absorption spectra in Fig. 2 as a function of \( n \) number are indicating that the TPPS was incorporated in these glasses without thermal decomposition. A peak at about 416 nm in the Soret band and four peaks at Q bands existed in these spectra, which shows the free base of TPPS in these glasses. TPPS doped in the glasses had nearly the same form as the TPPS in the aqueous solution, as shown in Fig. 3. However, the form of TPPS in the glasses changed a little from that in the aqueous solution, because TPPS reacted with matrix glass during the melting process. The shape of the spectra does not change much but the absorption intensity increased with increase in number of \( n \).

TPP could not be incorporated into the Li and Na carboxylate salts glasses by the present melting method. The reason for unsuccessful doping is not clear but TPP does not

Table 1

| \( n \) | Density (g/cm\(^3\)) | \( T_g \) (°C) | \( T_m \) (°C) |
|-------|----------------------|---------------|---------------|
| 0     | 1.35                 | 79            | 183           |
| 1     | 1.30                 | 66            | 191           |
| 2     | 1.28                 | 52            | 148           |
| 4     | 1.25                 | 59            | 162           |
| 5     | 1.21                 | 48            | 160           |
| 6     | 1.21                 | 55            | 161           |
have sulfonic acid bases and these may contribute to the reaction with matrix glass, which contains Na and Li ions.

3.3. Fluorescence spectra and excitation spectra of metal carboxylate salts glasses containing TPPS

In order to confirm the free base form of TPPS in the present glasses fluorescence and excitation spectra of metal–carboxylate salts glasses containing TPPS were observed and results are shown in Figs. 4–6. The excitation wavelength is 416 nm for Soret bands. The shape of the spectra shows as being nearly the same as that of the free base form of TPPS, indicating that most of TPPS existed in the form of free base. However, the shape of the spectrum is a little different from that of the aqueous solution. This is especially true for the peaks at longer wavelength, which shifts by about 15 nm and the shape changes a little. These are due to the difference of the matrix, that is glass and water, and also to the formation of a complex, which shows a weak peak at about 610 nm. Figs. 5 and 6 show excitation spectra at 716 and 608 nm, respectively. The change of shape of the spectra as a function of number of \( n \) was not observed. However, the peaks of the Soret bands in both excitations show a tendency to shift a little to a longer wavelength as the number of \( n \) increases. The existence of long chain carboxyl in the matrix decreases the density and also the number of carboxyl in the matrix. Electric dipole are localized around carboxyl and the decrease in the number of carboxyl means a decrease in the number of electricdipoles. Therefore, an increase in the number of \( n \) affects the shift of the Soret bands because of the decrease in the sum of electricdipoles that interact with TPPS. Nearly

Fig. 5. Fluorescence spectra of TPPS doped in the Na and Li carboxylate salts glasses with different number chains: (a) \( n = 0 \); (b) \( n = 1 \); (c) \( n = 2 \); (d) \( n = 4 \); (e) \( n = 5 \); and (f) \( n = 6 \), Excitation wavelength: 716 nm.

3.4. Effect of melting time on the formation of complex

By using the mixture of TPPS and \( \text{CH}_3\text{COONa} \) powder as

![Fluorescence spectra of TPPS doped in the Na and Li carboxylate salts glasses with different number chains: (a) \( n = 0 \); (b) \( n = 1 \); (c) \( n = 2 \); (d) \( n = 4 \); (e) \( n = 5 \); and (f) \( n = 6 \), Excitation wavelength: 416 nm.](image1)

![Fluorescence spectra of TPPS doped in the Na and Li carboxylate salts glasses with different number chains: (a) \( n = 0 \); (b) \( n = 1 \); (d) \( n = 4 \); (e) \( n = 5 \); and (f) \( n = 6 \), Excitation wavelength: 608 nm.](image2)
raw materials the melting time of batches (with \( n = 0, 4 \)) was held for 15 min and the melts were quenched to glasses.

Absorption spectra are shown in Fig. 7 together with that of the sample obtained by quenching the melt just after addition of the mixture and melting. The fluorescence spectra of these samples showed the formation of the complex. The metal carboxylate salts glasses contain both Na and Li. In order to confirm which cation the TPPS forms in the complex, the following experiments were conducted.

(a) By addition, the mixture of TPPS and \( \text{CH}_3\text{COOLi} \)

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powder as raw materials to the melt of \( \text{CH}_3\text{COOLi}\cdot2\text{H}_2\text{O} \) and melting time was held for 15 min and the melts were quenched and dissolved in water.

(b) By addition, the mixture of TPPS and \( \text{CH}_3\text{COONa} \) powder as raw materials to the melt of \( \text{CH}_3\text{COONa} \) and melting time was held for 15 min and the melts were quenched and dissolved in water.

The absorption spectra of both (a) and (b) samples are shown in Fig. 8 and indicating that the TPPS is free base form for (b) and TPPS forms the complex for (a). The Li complex solution was kept at room temperature for a week and the absorption spectrum was observed as Fig. 8(c). This spectrum indicates that the Li complex is unstable and decomposes partly to the dication form of TPPS. It is reported that the Li and Na forms a complex with porphine in the aqueous solution [34]. Thus, TPPS does not form a complex with Na in the carboxylate salts melt but forms a complex with Li in the carboxylate salts melt. Experiments (a) and (b) were repeated without holding the melt for 15 min at melting temperature for \( n = 0 \) composition. The absorption spectra is shown in Fig. 9. TPPS is almost free base form in the sample for Na carboxylate salts melt but TPPS forms a complex for Li carboxylate salts melt.

It was shown that in the carboxylate salts melts the TPPS formed a complex with Li but did not form a complex with Na.

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4. Conclusions

1. Li and Na carboxylate salts glasses with different number chains containing molecules of TPPS were prepared by the melting method. TPPS doped in the glasses had the
same form as the TTPS in the aqueous solutions. However, the form of TTPS in the glasses changed from that in the aqueous solutions, because TTPS reacted with matrix glass during the melting process.

2. TPP could not be incorporated into the Li and Na carboxylate salts glasses by the present melting method.

3. The free base TTPS is important for PHB properties, and the metal carboxylate salts glass containing free base TTPS was prepared by controlling the melting condition.

4. It was found that preparation conditions such as holding time of the melts affects the formation of the complex of TTPS.

5. It was found that in the carboxylate salts melts the TTPS formed a complex with Li but did not form a complex with Na.

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