Photochemical Hole Burning in Optical Materials

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Photochemical hole burning (PHB) is a topic of attracting increasing interest from spectroscopic viewpoints as well as from the practical prospects for ultra-high-density frequency-domain optical storage. Recent advances in PHB study are reviewed mainly focusing on the effects of chemical structure of guest ions and molecules as well as host matrices on the efficiency of hole formation and its temperature dependence, low energy excitation modes and Debye-Waller factors in amorphous matrices, and the mechanism of photon-gated PHB.

Key-words: Photochemical hole burning (PHB), Homogeneous width, Low energy excitation modes, Debye-Waller factor, Hole, Zero-phonon line, Phonon-side band, Optical storage, High temperature PHB, Photon-gated PHB, Electron-phonon interaction

1. Introduction

Photochemical hole burning (PHB) is a phenomenon in which site-selective and persistent decrease of absorption or a hole is created in the absorption band of molecularly dispersed photoreactive guests in host matrices at low temperatures. The phenomenon of PHB was discovered by two Russian groups.\textsuperscript{1,2} The word “chemical” distinguishes this phenomena from the so-called hole burning phenomenon due to saturated absorption observed in laser materials. In PHB, a hole in the spectral range exists persistently after the laser irradiation. This persistency is attained mainly by the photochemical change or rearrangement of guest molecules. Sometimes the term “photochemical hole burning” is restricted to the hole formation through the former process, and “persistent spectral hole burning” (PSHB) is used in order to include the hole formation through both processes. But since the boundary between “photochemical” process and “non-photochemical” process is not so clear, there is the case that the word “photochemical” represents the persistency of a hole and points to general hole formation phenomena.

The PHB technique eliminates the inhomogeneous broadening of the system and therefore it can be used as a good tool for high resolution spectroscopy.\textsuperscript{3,4} A hole profile gives much information on the microenvironment around the guest molecules. The PHB is used as a sensitive microprobe for the electron-phonon interaction.\textsuperscript{5,6} In the early stage of the investigation on PHB, the nature of a zero-phonon line (e.g., optical dephasing) and local structural relaxation around guest molecules or spectral diffusion which is explained with the two-level-system (TLS) model\textsuperscript{7,8} in amorphous hosts have attracted much interest in the physical field. The information as to homogeneous width obtained by the PHB measurements has been compared with the results of photon echo measurements\textsuperscript{9–11} and fluorescence line narrowing measurements.\textsuperscript{12}

The PHB phenomenon has been reported for a variety of organic and inorganic materials. As the general discussion as to these phenomena is presented in excellent review articles,\textsuperscript{3,4} the recent advances of PHB investigation especially in polymer systems will be discussed in the present article. The effect of chemical structures of guest molecules and host matrices on the efficiency of hole formation is given in Section 2. Thermally activated structural relaxation monitored by PHB is discussed in Section 3. The low energy excitation modes probed with PHB measurements which affect the electron-phonon interaction is discussed in Section 4 as an example of usage of PHB as a microprobe for molecular dynamics of polymers.

PHB is expected as a possible means for ultra-high-density frequency-domain optical storage as well as a tool for high-resolution spectroscopy.\textsuperscript{3,4,12}
If a hole corresponds to a data bit, the frequency-domain optical storage can be constructed. The storage density is supposed to be $10^{13} - 10^{14}$ times as large as that of ordinary optical memory systems (e.g., a magneto-optic disc system) due to frequency domain multiplexing in addition to spatial domain. Its density corresponds to $10^{11} - 10^{12}$ bit/cm$^2$. But there are many problems which should be solved for the application of PHB to a practical storage system. One of the biggest problems is the low temperature at which the PHB phenomena occurs. The scientific approach to solve this problem includes the investigation on the temperature dependence of homogeneous width and the thermal stability of the system. These aspects also have been attracting scientific interest from the viewpoints of the elucidation of dephasing process, Debye-Waller factor, structural relaxation, backward reaction of photoproducts, and so on. High-temperature PHB is discussed in Section 5. Another big problem is the destructive reading of data bits caused by the irradiation of reading light. Generally, the extent of a photochemical process depends linearly on the irradiation energy in the short irradiation time. This linear dependence causes another hole burning around the previous holes leading to the destruction of data bits during the irradiation of reading light. For the suppression of this destruction of data bits, the threshold or non-linear dependence of the burning process on the irradiation energy should be needed. The non-linear dependence of hole burning process is realized by two-photon photochemistry, and this performance is attained by two-color photochemistry. This hole burning mechanism is called the photon-gated PHB$^{13,14}$ and is discussed in Section 6.

2. Hole formation and photochemical reactions for PHB

The phenomena of PHB occur as mentioned following. When dye molecules/matrix system is cooled down to very low temperatures absorption lines of each dye molecule become very sharp. The spectral width of this line is called the homogeneous width, $\Delta\omega_h$. But when the dye molecules exist in a real matrix, they lie in slightly different microenvironment and then the frequencies of their absorption lines slightly differ from each other due to the inhomogeneity of microenvironment around them, resulting in a absorption spectrum similar to that at room temperature or in solution. This spectral width is called inhomogeneous width, $\Delta\omega_{ih}$. Thus the absorption band is supposed to consist of very sharp homogeneous lines.

When a narrow band laser is irradiated at a dye/matrix system, this laser light is absorbed only by the dye molecules whose frequency of homogeneous absorption is at laser frequency. If these dye molecules or their microenvironments change persistently with the shift of absorption frequency, the persistent decrease of absorption becomes a hole. When the shift of absorption frequency occurs via photochemical change of dye molecules, this phenomenon is called photochemical hole burning (PHB). When the shift occurs through rearrangement of microenvironment around the dye molecules without those chemical change of the dye molecules, this phenomenon is called non-photochemical hole burning (NPHB) or photophysical hole burning.

A homogeneous width mentioned above becomes narrow at low temperatures. Generally this type of absorption line is a zero-phonon line. A zero-phonon line originates from an electronic transition without phonon creation or emission. The sharpness of a zero-phonon line is due to the long lifetime for zero-phonon transition compared with phonon-assisted transition. The phonon-assisted transition leads to a phonon side band. For the PHB phenomenon, the existence of zero-phonon lines is essential and therefore the large Debye-Waller factor is very important, which represents a fraction of a zero-phonon line in the integrated molecular absorption. Small stokes shift between peaks of absorption and fluorescence spectra is also important for the existence of sharp zero-phonon lines.

The width of a zero-phonon line or a homogeneous width, $\Delta\omega_h$, becomes wider as the temperature rises. The relation between the $\Delta\omega_h$ and the lifetimes of an electronic transition is expressed as following,$^3,4$ $^\text{ }\text{ }$

$$\Delta\omega_h = 1/T_1 + 1/2T_2^* = 1/T_2$$

where $T_1$ is population lifetime or so-called lifetime of an upper level, $T_2^*$ is pure dephasing time or phase relaxation time, and $T_2$ is the lifetime which is determined by the inverse of homogeneous width. The pure dephasing time, $T_2^*$, is a kind of lifetime which is determined by the extent of interaction between electronic levels and phonon or other excitation. In this interaction, the energy of the system is conserved and only the phase of wave function is shifted. In other words, the dephasing time is the lifetime of correlation among the phases of wave function for each electronic level. The photon echo technique can directly measure $T_2$ via measurement of the decay of echo signal, which is pointed out to have the relation of Fourier transform with a hole profile.$^{15}$

The photochemical change leading to hole formation is attained by various processes, e.g., proton tautomerization in a porphyrin ring,$^{16}$ rearrangement of hydrogen bonding between dihydroxyanthraquinone (DAQ) and host matrix,$^{17}$ photo-induced electron transfer in color centers.$^{18}$ The materials and reactions for PHB are summarized in Fig. 1.

The porphyrin system is one of the most investigated system for PHB reaction from the early stage of PHB investigation. The proton tautomerization in a free-base porphyrin ring resulting in the change in its microenvironment is thought to be the PHB reaction of porphyrin system.$^{16}$ Since the potential barrier in the ground states between two tautomers is
enough high for the elimination of thermally activated crossing between them below 100 K, the hole is imagined to be thermally stable below 100 K. But other hole filling processes, e.g., structural relaxation of matrix, exist and therefore all holes is not thermally stable below 100 K. The thermal stability and ability of high-temperature PHB in porphyrin system is discussed in detail in Section 5.

Quantum efficiency of hole formation, $\Phi$, is calculated by using the following equation:

$$\Phi = \frac{[\frac{d(A/A_0)}{dt}]_{t=0} A_0 \Delta \omega_b}{10^3 I_0 (1 - 10^{-\epsilon}) \epsilon}$$

(2)

where $A$ is time-varying absorbance, $A_0$ is the absorbance before irradiation, $[\frac{d(A/A_0)}{dt}]_{t=0}$ is the initial slope of the irradiation time dependence of hole depth, $I_0$ is the incident laser intensity given in einstein/cm$^2$sec, $\epsilon$ is the molar extinction coefficient for inhomogeneous line profile at the hole burning wavelength and temperature. The homogeneous line width, $\Delta \omega_b$, is estimated from the initial hole width at each temperature. In this calculation, site-selectivity is taken into account.

The efficiency of hole formation, $\Phi$, strongly depends on the type of reactions inducing PHB phenomena. The value of $\Phi$ for tautomerization of free-base tetraphenylporphin (TPP) is about $1 \times 10^{-3}$ at 4 K irrespective of the nature of matrix polymers. The influence of the substituents in meso-phenyl groups of TPP on the quantum efficiency of hole formation at 20 K is shown in Fig. 2.

There seems no substantial relationship between $\Phi$ and the Hammett $\sigma$ values of the substituents. The results are consistent with a NMR measurement showing a constant rate of proton tautomerization for various meso-substituted TPP.

Dihydroxyanthraquinone (DAQ) is another well
investigated PHB system. In this case, rearrangement of hydrogen bonding between a DAQ molecule and host matrix occurs leading to the shift of resonant frequency of a DAQ molecule. Since the active part of a DAQ molecule for PHB reaction is outside of a molecule, a hole burnt in this system might be thermally less stable than porphyrin systems which have a PHB-active part inside of a dye molecule, because the thermal fluctuation of the matrix directly interacts with the PHB-active part of DAQ.

Site-selective electron transfer and elimination of backward reaction is investigated for PHB reaction. A hole is created for the lack of electron for the absorption in irradiation frequency. In rare-earth ion systems, photo-ionization and trapping of ejected electron is reported to be able to cause the PHB phenomena. Organic donor-acceptor systems are also reported to show such electron-transfer-type PHB phenomena. These PHB systems are also expected as photon-gated PHB systems as mentioned in Section 6.

The photodecompositions of dimethyl-s-tetrazine, anthracene-tetracene adduct, and dihydrophenazine are known to cause the PHB phenomena. The hole of dihydrophenazine burnt at 4 K in fluorene molecular crystal can be recovered again at 4 K after temperature cycle up to room temperature. A combination of a photosensitizer with photoreactive polymers also gives a possibility of hole formation. Recently two-color photosensitization of zinc-porphin derivative-glycidylazidopolymer system was found out to be a new type photon-gated PHB system.

3. Cycle annealing experiments and thermal stability of holes

A hole profile inevitably includes the information on microenvironment around guest molecules. A hole can be used as a spectral probe for the dynamics of the host matrices. Cycle annealing experiments have been carried out for studying the temperature dependence of the extent of structural relaxation around the guest molecules. A cycle annealing experiment is performed as follows. First a hole is burnt at low temperature and measured on the profile, and then temperature of the system is elevated and annealed. Next the system is cooled down to the previous temperature, and a hole profile is measured. This temperature cycle is repeated several times with raising the elevated temperature. From this cycle annealing experiment, two types of information are obtained. One is the extent of spectral diffusion caused by the structural relaxation around guest molecules. The extent of the spectral diffusion can be estimated from the change in hole width after the temperature cycle. The structural relaxation during the temperature cycle is interpreted with the two-level-system (TLS) model. In this interpretation, the structural relaxation is represented by the tunneling between the two levels in low temperature range and by the activation process crossing two levels in high temperature range. Another information is the extent of thermally activated backward reaction of photoproducts. The extent of the backward reaction can be estimated from the change in hole area after the temperature cycle. Hole area reflects the number of reacted molecules when it is measured at the same temperature. Therefore the change in hole area after the temperature cycle reflects the change in the number of reacted molecules and the extent of the thermally activated backward reaction. In the case of porphin derivatives, however, the influence of thermal backward reaction can be neglected at temperatures below 100 K from the NMR measurements. Figure 3 shows the typical result of the cycle annealing experiment for freebase tetraphenylporphin (TPP)/phenoxy resin (PhR). A hole becomes small at elevated temperatures due to the reversible change in the Debye-Waller factor and the irreversible change caused by spectral diffusion, and is restored partially after cooling down.

One of the typical results for the cycle annealing experiments is shown in Fig. 4. This figure shows the irreversible broadening of the hole, \( \Delta \omega_r \), and constancy of relative hole area during the temperature cycle for tertiary-butylphthalocyanine/3-methylpentane glass. In this system, hole area does not change and it corresponds to the lack of thermally activated backward reaction. The change in \( \Delta \omega_p \) is explained by a one-phonon tunneling process and an activated process, but their physics is not clear.

![Fig. 3. A typical result of cycle annealing experiment for TPP/PhR.](Image)
Thermal stability of a hole burnt at low temperatures has been studied with the cycle annealing experiments for various systems and the results have given much information on the thermal stability of the systems especially on that around guest molecules. The example of the systems studied with the cycle annealing experiments and their results are listed in Table 1. Thermal stability of the system is probed by PHB measurements from the two viewpoints as mentioned above, i.e., spectral diffusion and thermally activated backward reaction. Recently excellent thermal stability of a hole has been reported for molecular crystal and neutron-irradiated sapphire systems in addition to BaClF ion crystal. In these systems, holes can be observed again at 4K after the annealing up to room temperature. These systems are thought to have much high barrier between ground state and photoproduct state and have excellent thermal stability of the matrices.

4. Low energy excitation modes in amorphous polymers

Thermal properties of amorphous materials, e.g., heat capacity, are quite different from those of crystalline materials due to the existence of non-thermally-equivalent states. For example, amorphous polymers have exceed heat capacity compared with those of crystalline states. The excess heat capacity is caused by the existence of low energy excitation modes which are originated from the non-thermally-equivalent states in amorphous polymers. The low energy excitation modes are extramodes compared with the Debye modes in crystal. These modes in polymers have been studied and elucidated with heat capacity measurements and neutron inelastic scattering measurements. Recently, these modes also have been estimated with PHB measurements.

A hole consists of three parts. Schematic representation for these three parts is shown in Fig. 5. First part is a zero-phonon hole which has been discussed as a "hole" above in this article. A zero-phonon hole is a sharp hole and exists at the irradiation laser frequency, and consists of a photoreactive guest molecules whose zero-phonon line exists at the laser frequency. Second part is a phonon side hole. A phonon side hole is a broad hole at the higher energy side of a zero-phonon hole, and consists of phonon side bands of the same guest molecules as for zero-phonon hole. Third part is a pseudo-phonon side hole at the lower energy side of a zero-phonon hole. A pseudo-phonon side hole consists of zero-phonon lines whose phonon side bands exist at the laser frequency. When interaction between guest molecules and matrix is weak, a phonon side band absorption is weak and then the Debye-Waller factor is close to unity especially at low temperature. In such system, a phonon side hole is quite small but a pseudo-phonon side hole is rela-

Table 1. Examples of the systems studied with cycle annealing experiments and their results.

<table>
<thead>
<tr>
<th>Systems</th>
<th>Maximum annealing temperature</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPP/phenoxy resin</td>
<td>120 K</td>
<td>36</td>
</tr>
<tr>
<td>TPP/poly(methyl methacrylate)</td>
<td>100 K</td>
<td>12</td>
</tr>
<tr>
<td>TPP/aromatic polyimide</td>
<td>130 K</td>
<td>12</td>
</tr>
<tr>
<td>TPPS/poly(vinyl alcohol)</td>
<td>150 K</td>
<td></td>
</tr>
<tr>
<td>DAQ/amorphous silica</td>
<td>65 K</td>
<td>27</td>
</tr>
<tr>
<td>5,10-dihydrophenazine</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[in fluorene single crystal]</td>
<td>room temperature</td>
<td>31</td>
</tr>
<tr>
<td>neutron-irradiated sapphire</td>
<td>room temperature</td>
<td>37</td>
</tr>
<tr>
<td>BaClF:Sm²⁺</td>
<td>room temperature</td>
<td>14</td>
</tr>
</tbody>
</table>
The energy difference between a zero-phonon hole and a pseudo-phonon side hole reflects the energy of a phonon mode in polymer systems coupling with the guest molecules.6) The phonon modes estimated with the method mentioned above are reported to be independent of guest molecules and to be an inherent parameter for the characterization of amorphous polymers.6,40) Moreover these phonon modes were compared with the low energy excitation modes estimated with heat capacity measurements and neutron inelastic measurements, and agree well with each other.6,22) The

Table 2. The energies of low energy excitation modes determined by PHB, $E_s$, heat capacity, $E_c$, neutron inelastic scattering, $E_l$, and photon echo, $E_p$, measurements.

<table>
<thead>
<tr>
<th>chromophore/amorphous polymer matrix</th>
<th>$E_s$ ($\text{cm}^{-1}$)</th>
<th>$E_c$ ($\text{cm}^{-1}$)</th>
<th>$E_l$ ($\text{cm}^{-1}$)</th>
<th>$E_p$ ($\text{cm}^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPPS/PVA</td>
<td>23.5$^6$, 25$^{40}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DAQ/PVA</td>
<td>23.0$^6$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>rhodamine-540/PVA</td>
<td>25$^{40}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TPPC/PVA</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TPP/PDMA</td>
<td>12.1$^6$, 12$^{40}$</td>
<td>12$^{38}$</td>
<td></td>
<td>12$^{45}$</td>
</tr>
<tr>
<td>DAQ/PDMA</td>
<td>13.6$^6$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TTPC/PDMA</td>
<td>6.4$^{28}$</td>
<td>5.2$^{38}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TTPC/Dextran</td>
<td>13$^{58}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>rhodamine-B/PDMA</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ODRB/PDMA</td>
<td>18$^{52}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TPP/PDMA</td>
<td>13$^{40}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TPP/PDMA</td>
<td>16$^{40}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TPP/PLMA</td>
<td>16$^{40}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TTPC/PHEMA</td>
<td>23$^{40}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TTPC/Dextran</td>
<td>30$^{40}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>bacteriochlorophyll a</td>
<td>30$^{63}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TPP/Phenoxy resin</td>
<td>15.1$^{21}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TPP/Epoxy resin (EDA)</td>
<td>14.6$^{53}$</td>
<td></td>
<td></td>
<td>15$^{59}$</td>
</tr>
<tr>
<td>TPP/Epoxy resin (MDA)</td>
<td>17.1$^{43}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TPP/Polyimide</td>
<td>13.3$^{52}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TPP/LCP</td>
<td>12.6$^{60}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TPP/PET (undrawn)</td>
<td>10.9$^{41}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TPP/PET (5-times drawn)</td>
<td>11.8$^{51}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TPP/Polystyrene</td>
<td>10.1$^{5}, 14^{40}$</td>
<td>9.1$^{38}$</td>
<td></td>
<td>12$^{29}$</td>
</tr>
<tr>
<td>TPP/Polyisilane</td>
<td>9.8$^{61}$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

phonon modes coupled with guests molecules estimated from PHB measurements, $E_a$, and low energy excitation modes estimated from heat capacity measurements, $E_c$, and neutron inelastic measurements, $E_L$, are listed in Table 2, as well as those evaluated from photon echo measurements, $E_p$. The phonon modes in a polymer coupled with guest molecules is supposed to be low energy excitation modes which contribute the excess heat capacity of amorphous polymer.

Low energy excitation modes estimated from PHB measurements are reported to reflect the microscopic ordered structure of polymer matrices. Drawn and undrawn poly (ethylene terephthalate) (PET) systems have different phonon-mode frequencies as shown in Table 2. The PET system is known to have more ordered structure by drawing. The phonon-mode frequency of PET systems is supposed to increase with the increase in the orderliness of matrices. This tendency is also observed in drawn and undrawn polyimide systems. Phonon mode frequencies coupled with guest molecules of epoxy resin system is reported to change with the change in curing agents. From Table 2, hydrogen bond formation in PVA, PHEMA and dextran as well as an ordered structure in protein is also reflected by the high phonon frequency estimated from PHB measurements.

Temperature dependence of the Debye-Waller factor is estimated from PHB measurements. The Debye-Waller factor, $DW(T)$, is defined by the following equation:

$$DW(T) = S_0(T) / [S_0(T) + S_p(T)]$$  \( (3) \)

where $S_0(T)$ is integrated intensity of a zero-phonon line and $S_p(T)$ is integrated intensity of a phonon side band. The $DW(T)$ represents a fraction of a zero-phonon line in the absorption of a dye molecule. If the oscillator strength of a dye molecule does not depend on temperature and then $S_0(T)$ is conserved for the change in temperature, $T$, the temperature dependence of $DW(T)$ can be estimated from the temperature dependence of $S_0(T)$. The temperature dependence of $S_0(T)$ is measured from the temperature dependence of the area of a zero-phonon hole. Since the interaction between a dye molecule and matrix polymers is weak at 4 K, the $DW(4)$ for polymer matrix systems is close to unity ($DW(4) \approx 0.9$ for TPP/PMMA). Therefore, $S_0(T)/S_0(4)$ roughly corresponds to the $DW(T)$. Figure 6 shows the temperature dependence of $DW(T)$ estimated from $S_0(T)/S_0(4)$ for various systems. In this measurement, a hole is burnt at higher temperatures first and then cooled down to 4 K for the suppression of thermally activated backward reaction of photoproducts. These results agree well with the results obtained by photon echo technique. From the comparison between Table 2 and Fig. 6, it is seen that the TPPS/PVA has the large $E_a$ value and shows small temperature dependence of $DW(T)$. It is consistent with the theory.

The temperature dependence of $DW(T)$ is given by:

$$DW(T) = \exp[-C \int \coth(h\omega/2k_BT) P(\omega)g(\omega)d\omega]$$  \( (4) \)

where $C$ is a constant, $k_B$ is Boltzmann’s constant, $1/2 \coth(h\omega/2k_BT)$ is the average number of phonons in the lattice mode $h\omega$ at temperature $T$, $P(\omega)$ is the Stoke’s shift, and $g(\omega)$ is the density of states which have an energy $h\omega$. When the dominant lattice mode $h\omega$ contributing $g(\omega)$ has a large energy, the $DW(T)$ shows a small temperature dependence. The similar $E_a$-value dependence of the $DW(T)$ is also reported for TPP/epoxy resin systems and it is also consistent with the theory.

5. High temperature hole formation in polymer systems

The study on high temperature PHB gives much information on the temperature dependence of homogeneous width and the laser-induced hole filling. Moreover high temperature PHB is very important for the application of PHB to a practical frequency-domain optical storage system. Hole formation above liquid nitrogen temperature (77 K) has been reported for some systems, but the mechanism for them is not clear yet. Recently, the kinetics for the high-temperature PHB in polymer systems has been elucidated with taking account to the nature of laser-induced hole filling.

Temperature dependence of homogeneous width for amorphous host systems is reported to follow the low-power-law relation on $T$ ($T \propto a^{-2}$). The homogeneous width of polymer systems at 80 K estimated from extrapolation from low temperature is enough sharp to create a hole even at 80 K. But hole formation at 80 K in polymer systems is reported for only a few systems, i.e., tetraphenylporphin (TPP)/phenoxy resin (PhR), TPP/epoxy resin (EpR), and sulfonated TPP (TPPS)/poly (vinyl alcohol) (PVA). Other TPP/polymer systems are not
reported to have the capability of hole formation at 80 K. These facts suggest the existence of factors other than a homogeneous width for the hole formation at 80 K. Typical hole profiles burnt at 4.2–80 K for TPP/PhR are shown in Fig. 7. The good thermal stability of porphins could be attributed to the internal proton tautomerization mechanism for hole formation,\(^{16}\) because the internal protons in the porphin ring is thought to interact weakly with host matrices compared with other photoreactive guest molecules leading to the suppression of interaction between PHB-active part and matrices. Very recently non-photochemical hole burning of Cr\(^{3+}\) ion in PVA at 80 K has been reported, but the hole area decreased remarkably with time and it became half in an hour.\(^{51}\) Spontaneous hole filling of a non-photochemically burnt hole has been reported previously.\(^{52}\) Figure 8 shows the temperature dependence of hole formation efficiency, \(\Phi\), calculated by using Eq. (2) for TPP in various polymers. The temperature dependences of the Debye-Waller factor estimated from the PHB measurements as mentioned above are also shown in Fig. 8 by dashed lines. The temperature dependence of \(\Phi\) almost agrees with that of the Debye-Waller factor up to around 30–50 K for each system, but deviates considerably at 80 K. It indicates that the temperature dependence of hole formation efficiency is determined not only by the temperature dependence of the Debye-Waller factor, but also by the temperature dependence of the structural relaxation of the matrix polymers.

In order to go insight into the structural relaxation processes, i.e., irreversible spectral diffusion and hole filling processes, the annealing temperature dependence of hole area during the cycle annealing experiments was studied (Fig. 9).\(^{53}\) In these experiments, a hole burnt at 4.2 K by 0.75 mW/cm\(^2\) laser irradiation for 1–5 min was annealed at 30, 50, and 80 K for 30 min and measured at 4.2 K successively. As can be seen from Fig. 9, the hole areas scarcely changed up to 80 K-annealing and more than 80 percents of initial area was conserved for all the systems. It means that the thermally activated backward reaction hardly occurs and that spectral diffusion leading to irreversible broadening of hole width without change in hole area is the dominant process in this temperature region. The slight decrease in hole area after the temperature cycle of 80 K could be interpreted by the contribution of the non-photochemically burnt hole.

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**Fig. 7.** Typical hole profiles burnt at 4.2–80 K for TPP/PhR.\(^{21}\)

**Fig. 8.** Temperature dependence of hole formation efficiency, \(\Phi\), for TPP/PhR (△), TPP/EpR (○), TPP/PMMA (□) and TPP/PS (○). Temperature dependence of Debye-Waller factor for TPP/matrix systems estimated from \(S_0(T)/S_0(4)\) is represented by the dashed line.\(^{46}\)

**Fig. 9.** Annealing temperature dependence of hole area measured at 4.2 K during the cycle annealing experiments for the TPP/PhR (△), TTPS/PVA (○), TPP/PMMA (□), TPP/PET (△), TPP/PI (○), and TPP/PSi (□).
As to the irreversible change in hole width, $\Delta \omega_r$, during cycle annealing experiments, almost all the systems except for the TPP/poly(phenylmethylsilane) showed the same annealing temperature dependence of $\Delta \omega_r$ irrespective of the capability of hole formation at 80 K. Thus, the extents of the spectral diffusion for these systems were pointed out to be almost the same in this temperature region, suggesting that the spectral diffusion process hardly affects the capability of hole formation at 80 K.

Next, laser irradiation was performed during the cycle annealing experiments for obtaining information on the laser-induced hole filling. Figure 10 shows the annealing temperature dependence of hole area with and without the laser irradiation at elevated temperatures for the TPPS/PVA, TPP/EpR, and TPP/PI. The irradiation condition was 0.75 mW/cm$^2$ for 1 or 10 min at 30, 50, and 80 K and the energy separation between the frequency of an initial hole burnt at 4.2 K and that of laser irradiations at elevated temperatures was 50–100 cm$^{-1}$. The irradiations were carried out on the lower energy side of the initial hole. In Fig. 10 hole area decreases considerably with the irradiation at each temperature for the TPP/PI but no decrease for TPPS/PVA and TPP/EpR. The systems which have the capability of hole formation at 80 K show small decrease in hole area with the irradiation at elevated temperatures compared to the systems which do not have the capability of hole formation at 80 K.

The irreversible change in hole width, $\Delta \omega_{ir}$, for the TPP/PI during the cycle annealing experiments with and without the irradiation showed no difference, indicating the absence of the change in hole width during the laser-induced hole filling. The photo-induced structural relaxation leading to hole filling makes the system approach thermal equilibrium and therefore it does not change the width nor the frequency of an initial hole. This laser-induced hole filling might originate from the deactivation process of chromophores which lead to the structural relaxation of spatially neighboring but energetically separating sites in the system.

Thus, the systems which have the capability of hole formation at 80 K have small rate of laser-induced hole filling at 80 K. Hole formation at 80 K is observed mainly in hydrogen bonding matrix systems such as TPP/PhR, TPP/EpR, and TPPS/PVA. So the small rate of the laser-induced hole filling at 80 K would be due to the existence of hydrogen bonding in the matrix polymers.

6. Photon-gated PHB

For a practical application of PHB for frequency-domain optical memory system, a threshold for data writing should be needed for non-destructive reading. Since the rate of one-photon photochemistry is linear for the amount of absorbed photon in the early stage, hole burning leading to the destruction of data bits inevitably occurs during the laser irradiation for reading. There could be some techniques for making a threshold for burning a hole or gating for a hole burning photochemistry with external field (e.g., additional laser irradiation, electrical field or magnetic field). In this section, one of these techniques, photon-gated PHB, is presented.

Photon-gated PHB is the hole burning phenomenon which occurs via two-photon photochemistry with two colors. In this technique, one photon, $\lambda_1$, excites the electronic state in the burning frequency and another photon, $\lambda_2$, gives rise to photochemistry leading to hole creation. The frequency range of $\lambda_1$ and $\lambda_2$ should not be overlapped. When only the $\lambda_1$ is irradiated for detection of a hole, no hole is created due to the absence of the $\lambda_2$ and it enables one to make non-destructive reading. This mechanism can be said to be photon-controlled photochemistry. One of the example for the mechanism of photon-gated PHB in a rare-earth ion system is shown in Fig. 11.

The systems for photon-gated PHB are listed in Table 3. There are three types of major photon-gat-
ed PHB reactions. One is the two-photon (two-color) oxidation of rare-earth ion\textsuperscript{14,54,55} via its metastable electronic state as shown in Fig. 11. Ejected electrons are thought to be trapped by trapping states which are presumably defects and impurities.

The second mechanism is two-photon photo-electron transfer from a donor molecule to an acceptor molecule via triplet state of the donor molecule.\textsuperscript{13,28} In such systems, a donor molecule is excited to \textit{S}$_1$ state with absorption of \( \lambda_1 \) and then it converts to the lowest triplet state (\textit{T}$_1$). When the \( \lambda_2 \) is absent, it deactivates to the ground state (\textit{S}$_0$) and the system does not change without the creation of holes. When the \( \lambda_2 \) is present, the donor molecule is activated to upper triplet state (\textit{T}$_n$). The frequency of \( \lambda_2 \) is fitted to the frequency of triplet-to-triplet absorption. If the \textit{T}$_n$ state is preferable to the electron transfer to the acceptor, the depletion of the electron in the ground state of the donor molecule causes a hole at the frequency of \( \lambda_1 \). For the persistency of a hole, the transferred electron should not go back to the donor. Generally it is accomplished by the decomposition of acceptor molecules.

Moreover, the photon-gated PHB is expected to be useful probe for the investigation on electron transfer phenomena. The photon-gated PHB through \textit{T}$_n$ state could be very sensitive probe for the electron transfer phenomena from \textit{T}$_n$ state, because the electron transfer phenomena from other levels, i.e., \textit{S}$_1$ or \textit{T}$_1$, does not need to be considered when acceptor level is selected properly. Recently donor-acceptor electron transfer systems are investigated by using photon-gated PHB.\textsuperscript{56,57}

The third and very recently observed mechanism is the two-color sensitization of a guest molecule followed by the triplet excitation energy transfer to the matrix photoreactive polymer.\textsuperscript{33} In Zn-tetrabenzoporphin (ZnTBP)–glycidylazidopolymer system, two-color sensitized photoreaction of azido-groups (\( \lambda_1 = 635 \text{ nm, } 38 \mu \text{W/cm}^2; \lambda_2 = 488 \text{ and } 514 \text{ nm, } 8 \text{ mW/cm}^2 \) for 1 min at 20 K) drastically changed the microenvironment of guest ZnTBP molecules leading to an effective hole formation, while no hole was observed without gating laser irradiation.

### 7. Conclusion

The important factors for the applicability of PHB to ultra-high density optical storage are supposed to be:

1. high efficiency of hole formation,
2. elevation of operating temperature and thermal stabilization of holes,
3. non-destructive reading of holes,
4. high speed writing and reading of holes.

The elucidation of the effects of molecular structures of both guest molecules and host matrices on hole formation efficiency and its temperature dependence is essential to the first and second items. PHB itself gives important information as a new method of spectroscopy on the electron-phonon interaction and low-energy excitation modes of amorphous matrices. The recent advance in photon-gated PHB is also reviewed, which is a promising technique for realizing the third and fourth items.

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### References

Photochemical Hole Burning in Optical Materials

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