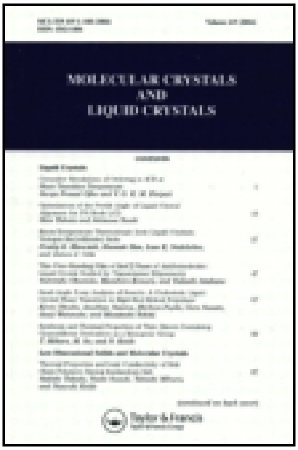

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High Temperature Pshb Materials: Molecular Doped Xerogels and The Problem of Spectral Diffusion

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HIGH TEMPERATURE PSHB MATERIALS: MOLECULAR DOPED XEROGELS AND THE PROBLEM OF SPECTRAL DIFFUSION

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Abstract Organic-inorganic hybrid solids have been prepared using sol-gel process. The sol-gel technique offers a room temperature attractive approach for introducing molecules into amorphous inorganic materials. Molecular doped inorganic or hybrid (organic-inorganic) xerogels are revealed to be suitable for high temperature PSHB. With molecules covalently grafted or chemically bonded to the inorganic network, a maximum temperature of 120 K has been achieved. Temperature cycling experiments reveals the importance of spectral diffusion in these systems. Spectral diffusion appears to be the most important difficulty to overcome.

INTRODUCTION

Since the discovery in 1974 of Persistent Spectral Hole-Burning (PSHB), considerable work has been done on molecular doped organic materials, being perfectly ordered (as in crystals) or highly disordered (as in glassy or in polymeric states). Until now, only a few studies have been done for molecular doped inorganic or hybrid (organic-inorganic) hosts. The sol-gel process is known as a synthetic route for the preparation of molecule and cluster doped xerogels in any desired shape, including thin films. Numerous materials have been processed for different applications such as catalysts, sensors, information recording, non-linear optics, solid state dye-lasers [1-3].

In this paper, we have selected some of our results obtained on porphyrin and quinizarin doped inorganic or hybrid (organic-inorganic) xerogels and we report on the promising behaviour of such systems at high temperatures (> 100 K).

IN SEARCH FOR HIGH TEMPERATURE HOLE-BURNING

Several conditions have to be fulfilled in order to burn persistent spectral holes at high temperature (> 100 K). Among these conditions, the more important are:

1. A physically stable host and/or dopant, not volatile of course and still remaining solid at room temperature!
2. A stable and efficient photochemical or non-photochemical burning process, not reversible at high temperature.
3. A weak linear electron-phonon coupling, with a low temperature dependence.
4. No spectral diffusion.

The first condition excludes hosts like most organic glasses which become liquid at room temperature, ice or hyper-quenched water, but also surfaces with physi-sorbed molecules. The second condition implies that the microscopic photoinduced process responsible for the hole appearance has to give rise to a stable photoproduct. This is mainly determined by the height of the product-photoproduct barrier which should be high enough to eliminate any possibility of back-conversion. It excludes subtle photochemical transformations like proton tautomerization in porphyrins and most proton transfer mechanisms. Highly stable reactions like a photoelectron detachment followed by the trapping of the ejected electron on a deep defect appears much more suitable. The third point is very interesting to discuss. It means that the changes of the hole width and the hole shape with increasing the temperature have to be minimised. A burnt hole reflects two contributions: one is the zero-phonon hole, the second is the phonon side band hole whose relative importance determines the Debye-Waller factor α_D, and then the linear electron-phonon coupling. In a simple model, the following temperature dependence for α_D is predicted:

$$\alpha_D(T) = \exp\left[-S \cdot \coth\left(\frac{\Omega_m}{2kT}\right)\right]$$

where Ω_m is the energy difference between the maximum of the phonon side band and the zero phonon line and S, the Huang-Rhys factor, measures the electron-phonon coupling strength. The decrease of α_D when increasing temperature will be minimum if S is small and Ω_m large. The value of Ω_m is related with the most probable energy of the phonon distribution. Stiff lattices with no soft modes at energies lower than 20 cm^{-1} will be favourable. Finally, the fourth point is concerned with all the processes responsible for energy migration through the inhomogeneous band among non-resonant species: fluctuations of low-energy modes specific to disordered media (TLS), structural relaxations and configuration changes, energy transfer mechanism. All these processes are known under the generic expression of spectral diffusion. The importance of their contribution depends on the system and on the temperature.

Two main points should be fulfilled: host cages with high frequency acoustic modes like those reported for water (50 and 180 cm^{-1}) [4] and low values of the Huang-Rhys coefficient like in systems with adsorbed molecules on surfaces [5]. The idea then is to look for quite rigid and stiff hosts (cross-linked polymers, glassy silicates), but to try to control the way a guest molecule is attached to the host as for physi-sorbed or chemi-sorbed species on surfaces. In the way to make concrete this idea, interesting hosts appears with inorganic or hybrid (organic-inorganic) xerogels because these systems form 3-D cross-linked networks in which guest molecules can be permanently trapped in pores.

SOL-GEL PROCESS AND XEROGEL MATERIALS

The sol-gel process is an inorganic polymerisation based on the property of some liquid compounds (the precursors) to react at ambient temperature and to form a 3-D macroscopic network. All samples studied in this work have been prepared using a slow hydrolysis reaction with the use of a 1:4 mixture of zircon and silicon alkoxide precursors(*) , followed by their polycondensation and drying under ambient atmosphere. After drying the gel for about one month, a transparent dense solid with a glassy aspect and called xerogel, is obtained. Typical densities are around 1.8 $g.cm^{-3}$. However, depending on the way the solvent is removed from the gel, solids with a large spectrum of densities and porosities can be synthesised. For instance, extracting the solvent under hypercritical conditions, the breakdown of the gel structure will be avoided and very light solids, with large pore sizes and called aerogels are produced.

The properties of the xerogels have been largely improved in the last few years by modifying the synthetic procedure and by using organofunctional silicon alkoxides. Owing to the improvement of mechanical properties, the dense xerogels can be polished and the optical transmission be perfect (92% at 633 nm for a cylindrical sample of 1 cm in thickness). Modified alkoxide precursors $R\text{-}Si(OEt)_3$ where R is a non-hydrolysed hydrophobic group, lead to organic-inorganic matrices. The permanent organic group decreases the mechanical tensions during the drying process. Because the sol-gel process evolves at room or moderate temperatures, organic guest molecules are easily introduced in the liquid solution at the initial stage of the preparation. After drying, they will be permanently trapped in pores of nanometric size (1-2 nm typically) through the inorganic network (Figure 1a).

In present work, different molecules have been embedded in dense gels with a closed porosity. Four silicon alkoxides have been used : the well known tetraethoxysilane ($Si(OEt)_4$ or TEOS) and three systems having permanent organic groups : methyl-triethoxysilane (CH_3-, MTEOS), vinyl-triethoxysilane ($CH_2{=}CH$-, VTEOS) and amyl-triethoxysilane (C_5H_{11}-, ATEOS) in order to prepare organic-inorganic hybrid matrices.

(*) The prefix Zr is added to the name of the host to state explicitely the use of the zirconium alkoxide precursor.

Also a mixed system prepared from an aluminosilicate precursor $(BuO)_2$-Al-O-Si-$(OEt)_3$ and hereafter noted AlOSi has been studied. With the modification of the permanent organic group in hybrid xerogels, the chemical composition of the "organic carpet" present at the surface of the pores will be changed (Figure 1b) and then the nature of the interaction between the guest molecule and the host can be, in some way, controlled.

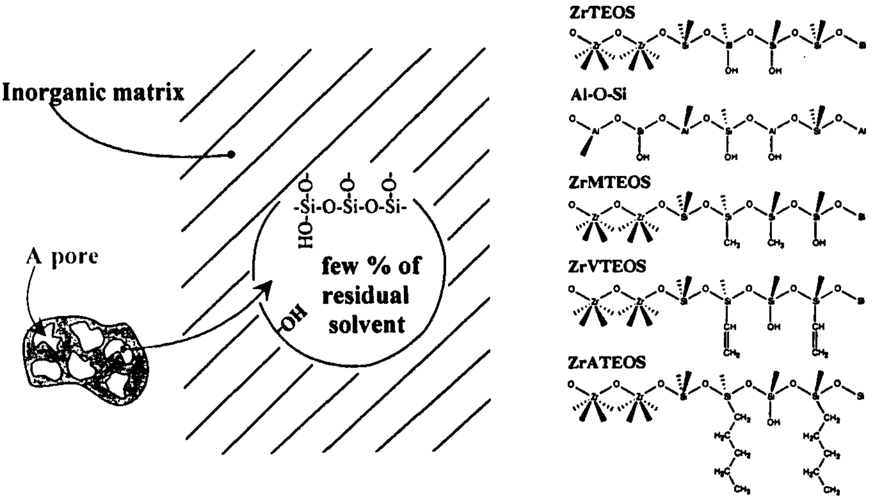

FIGURE 1 a) Schematic of a xerogel b) Chemical composition of the different gels synthesised.

SELECTED RESULTS

Porphyrins doped xerogels

The major differences between purely inorganic samples and hybrid organic-inorganic samples concern the local environment of the inserted chromophore. In inorganic hosts, 4-5 % of the silicon atoms are not fully reticulated and the remaining -OH groups can interact strongly with the guest. In the case of normal tetra-phenyl porphyrin (TPP), this interaction results in acid-base reactions and in the formation of dication $TPPH^{2+}$ species. In the case of fluorinated derivatives like tetra-(pentafluorophenyl) porphyrin (TPFP), the presence of fluor atoms on the phenyl groups avoids the protonation of the porphyrin ring [6]. In organic-inorganic hosts, the inner surface of the pores is mainly covered with methyl, vinyl or amyl groups. This "organic carpet" has a screening effect on the acidic properties of the hydroxyl groups and helps in the preservation of the chemical identity of the dopant. Also, a monotone decrease of the phonon side band is observed from ZrMTEOS, ZrVTEOS to ZrATEOS host [7,8], which means that, bigger is the organic group, less is the linear electron-phonon interaction between the guest and the silicate network. However, at the same time, severe steric effects can be applied on the guest. The comparison between the three hybrid organic-inorganic systems gives the following image: guest molecules are surrounded and partially hindered by the organic groups, main contributions to the phonon side band are due to local phonons and more probably to librations of the guest molecule: increasing the size of the side group will obstruct the librations and libration frequencies will increase. These views are supported by measurements of the photo-induced reorientation of triphenylmethanes in these xerogels at room temperature [9]: the recovery time after a pulse of polarised light increases in the following order: ZrTEOS, ZrMTEOS, ZrVTEOS, which is interpreted as an increase of the local viscosity. For the porphyrin derivative dispersed in various xerogel hosts, the measured values for Ω_m are about 15 cm^{-1}, like reported for polymers. The resulting temperature behaviour of burnt holes is also not different and the highest temperature until PSHB was still observed in such systems was not greater than 40-50 K. Now, if the guest molecules are grafted to the host by covalent bonds, librations will be strongly hindered and an increase of phonon energies is expected. We did this in two ways: through complexation or through covalent bonding.

Quinizarins doped xerogels

We compare the behaviour of simple quinizarin (1,4-di-hydroxy-anthraquinone, noted QS) with a modified one by grafting of a long aliphatic chain (-$C_{22}H_{45}$, noted QC). When quinizarin (QS or QC) is included in an AlOSi xerogel, drastic changes of the absorption spectrum are observed [8]. Similar changes were reported for quinizarin deposited on γ-alumina surfaces [10].

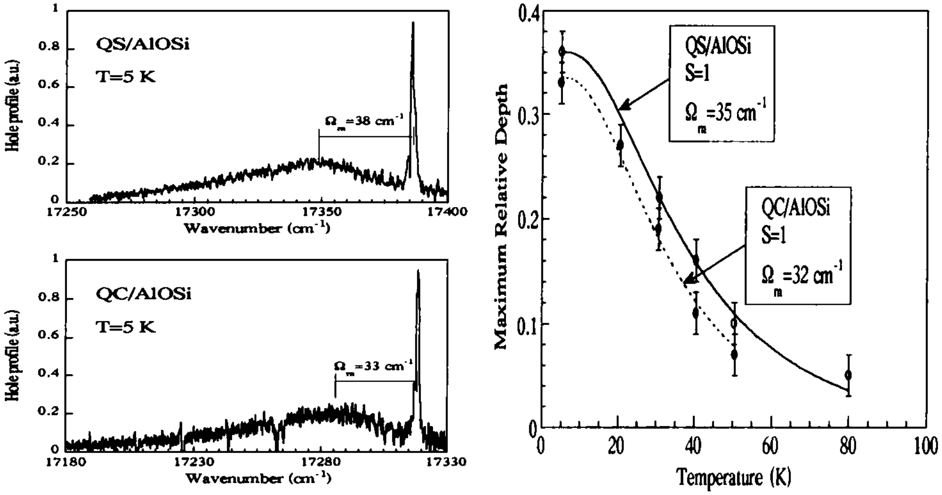

FIGURE 2 a) Hole profiles with Ω_m values $P_b = 0.6$ mW.cm^{-2}, $t_b = 300$ s b) Maximum relative hole depth versus temperature

These strong spectral disturbances result from the complexation of quinizarin with Al atoms. The same spectral changes are also observed in ZrTEOS or ZrMTEOS hosts due to complexation with Zr atoms. This means that quinizarin molecules are preferentially located in zirconate islands. There is no complexation with silicium observed when quinizarin is included in silicates synthesised without the addition of zirconium alkoxide. The fluorescence lifetime is much longer for complexed quinizarin than for the normal one. Also, it is shorter when quinizarin is complexed with aluminium than with zirconium. The following values have been measured and presented in table I [8]:

TABLE I: Fluorescence lifetime of quinizarin in different dense xerogels

QS/ AlOSi	QC/ AlOSi	QC/Zr TEOS	QC/Zr MTEOS	QC/Zr VTEOS	QS/ TEOS	QS/ VTEOS	QC/ TEOS	QC/ MTEOS	QC/ VTEOS
11 ns	8 ns	10.7 ns	14.7 ns	16.2 ns	1.8 ns	2.4 ns	1.6 ns	2.7 ns	2.4 ns

The hole-burning efficiency is much higher in the silicate glasses when quinizarin is complexed with zirconium than in the aluminosilicate xerogel. However, the highest temperature for PSHB has been achieved in AlOSi. In an AlOSi:quinizarin sample, the value of Ω_m is about 35-38 cm^{-1} for QS and around 30-33 cm^{-1} for QC (Figure 2a). In such system, holes could be burnt until 80 K. In Figure 2b, we plot the maximum relative depth of holes burnt just at the saturation limit. The temperature dependence is controlled by Ω_m. Despite the inaccuracy of these measurements, a satisfactory agreement is found between the experimental data and the fitting curve [11]:

$$\text{Depth} = \exp(-S.(1+2.\bar{n}(\Omega_m))$$

with S=1 and the value for Ω_m deduced from the experimental data of Figure 2a.

Grafted Porphyrin into a xerogel

We also prepared new precursors in which porphyrin type molecules are double covalently attached on a sol-gel precursor by using amidation of protoporphyrin-IX (PP-IX) with aminopropyl-triethoxysilane [12] (Figure 3a). Doped xerogels were then elaborated by using copolymerisation of the porphyrin attached alkoxysilane with usual sol-gel precursors (TEOS, MTEOS or VTEOS). This led to the first preparation of doped xerogels in which porphyrin molecules are grafted to the gel network via flexible organic spacers. Advantages are the following: limitation of the phase separation between organic molecules and the inorganic network and increase of the long term chemical stability, also, a possible increase of the dopant concentration at a maximum of one dopant molecule per silicon atom!

A sample of ZrVTEOS with protoporphyrin-IX grafted by two covalent bonds to the silicate network has been prepared (doping concentration of about 10^{-3} M). Several holes were burnt at 5 K using different burning times. Previously burnt holes are not erased when a new hole is burnt on their "blue" or "red" side. Also, no phonon side bands in the hole burnt spectra could be recorded which means that the Debye-Waller factor α_D should be quite large in these systems approaching the value one. The hole-burning quantum efficiency is calculated from our experimental data. A quite high value of about $1.2\text{x}10^{-2}$ is evaluated in the case of ZrVTEOS samples at 5 K [12]. In this system, the tautomerization due to the interchange of the inner protons of the free-base porphyrin is the photochemical mechanism for hole-burning. Holes are easily burnt (in 1 s with $P_b \approx 0.2$ mW.cm^{-2}) and they remain quite narrow (less than 2 cm^{-1}) even at temperatures as high as 20 K. Increasing the temperature makes the holes broaden rapidly. Still detectable holes could be burnt with moderate fluences (2 to 5 mW.cm^{-2} during 5 mn) at 120 K. However, at this temperature, the hole is quite broad (FWHM = 120 to 130 cm^{-1}, only 32 cm^{-1} at 80 K) and it disappears when T > 150 K. This limitation should be easily overcome using others photochemical mechanisms.

The temperature dependence of $\Gamma(T) = ½\Gamma_{\text{hole}}$ is given in Figure 3b. The data are fitted with the following equation [11]:

$$\Gamma(T) = \Gamma_0 + a.T^n + \sum_i b_i.(\exp(\frac{W_i}{kT}) - 1)^{-1}$$

where $\Gamma_0 = (2\pi T_1)^{-1}$, the second term represents the electron-TLS contribution and the third term is for the phonon contribution. The value of Γ_0 is 12 MHz determined by the measurement of the fluorescence lifetime at room temperature (12.7 ns for PP-IX grafted in ZrVTEOS, 13.1 ns in ZrMTEOS [8]).

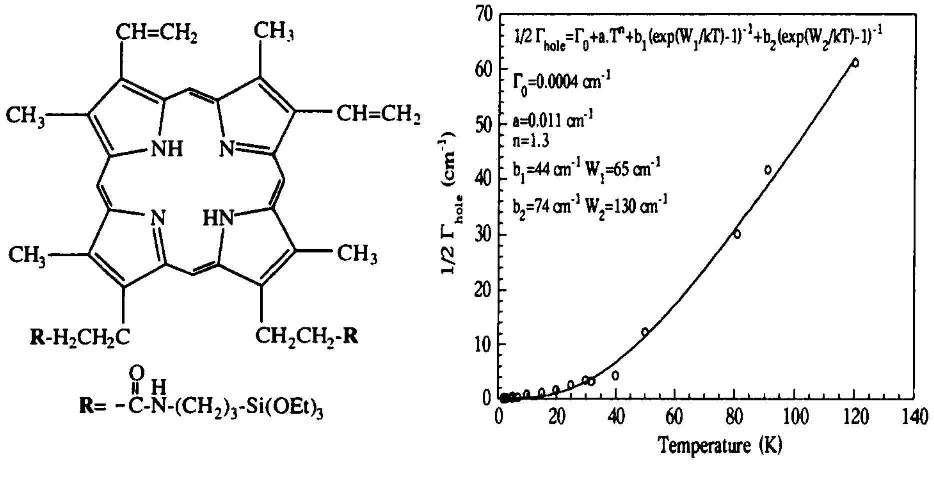

FIGURE 3 a) The modified precursor with the PP-IX attached alkoxysilane b) Hole width dependence versus temperature

In the low temperature regime, below 30-40 K, the system obeys a $T^{1.3}$ law. Above 40 K, thermally activated processes prevail. According to Raman and neutron scattering data for dense xerogels [13] and silicate glasses [14], there is a broad distribution of phonon modes in the low frequency range (< 200 cm^{-1}) with two maxima, one around 65 cm^{-1} and another around 130 cm^{-1}. It is quite satisfactory to find that our data can be fitted by fixing the W_i to the values deduced from Raman data.

Porphyrin doped aerogels

We have studied such an aerogel with a density of about 0.1 $g.cm^{-3}$ and doped with a fluorophenylporphyrin derivative. Its fractal dimension measured by neutron scattering was 2.1 and its spectral dimension 1.3. Such systems are characterised by a different Raman spectrum than for dense xerogels and the presence of acoustic modes at quite low frequencies. The density of low frequency TLS is also expected to be high. The consequence is a fast increase of the hole width when the temperature is raised. Results are shown in Figure 4b with also the drawing of a saturated burnt hole (Figure 4a). In such system, unsaturated holes are hard to burn. Even at low fluence, a pseudo phonon side band is always visible, which means a high linear electron-phonon coupling.

In low density aerogels (< 0.2 $g.cm^{-3}$) prepared without catalyser (neutral aerogel), Raman data [15] shows that the maximum of the distribution of bulk phonons is around or lower than 30 cm^{-1}. Again, a satisfactory agreement is obtained between our data and the fitting curve.

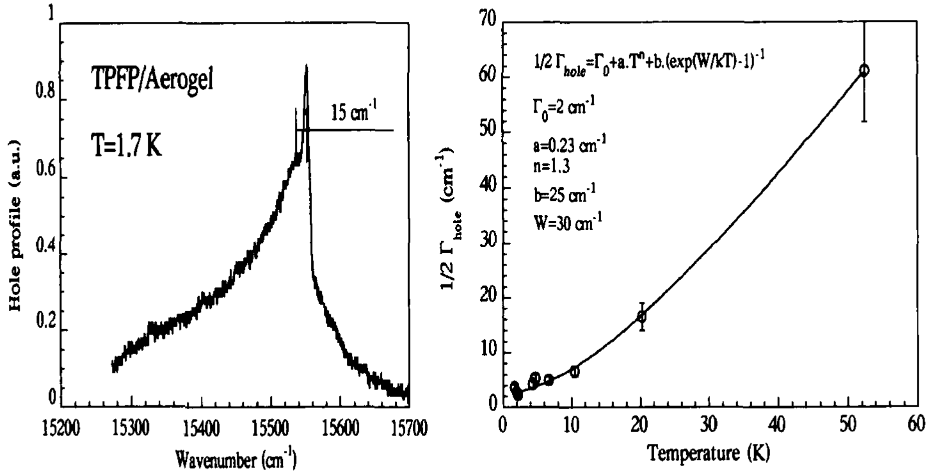

FIGURE 4 a) Hole profile of a saturated hole $P_b = 1$ $mW.cm^{-2}$, $t_b = 1800$ s b) Hole width dependence versus temperature

TEMPERATURE CYCLING AND SPECTRAL DIFFUSION

A persistent burnt hole can probe the changes with time occurring in the local environment around burnt molecules. In standard TLS theory, local environment changes are described as flip-flop of groups of atoms between the two wells of a local double-well potential. According to the distribution of the double-well parameters, fast and slow TLS can be distinguished. Fast TLS contribute to the homogeneous width, slow TLS are responsible for the increase with time of the hole width (spectral diffusion). A simple way to show evidences of the role played by slow TLS in a specific host is to perform a thermal cycling PSHB experiment. The experimental procedure is as follows: a hole is burnt at a low temperature T_1 and its width is measured Γ_{h1}, then the temperature is raised to $T_2 > T_1$ and the sample is kept at this temperature for a time τ, finally, the temperature is decreased to T_1 and the hole width is measured again Γ_{h2}. If there is no spectral diffusion, the thermal cycle should be reversible and $\Gamma_{h1} = \Gamma_{h2}$ is expected. In case of spectral diffusion, irreversible changes have occurred during the thermal cycle and $\Gamma_{h2} > \Gamma_{h1}$.

In AlOSi:quinizarin, we observed strong evidence for spectral diffusion. The hole width of a hole burnt or warmed up at a higher temperature does not decrease nearly when the sample is cooled down (Figure 5a). In the ZrVTEOS:PP-IX grafted sample, we burnt holes at high temperature and we measured their hole width. Then, the temperature was lowered and the hole width measured again. We find this intriguing result that no narrowing of the burnt hole is observed when the temperature is lowered (Figure 5b).

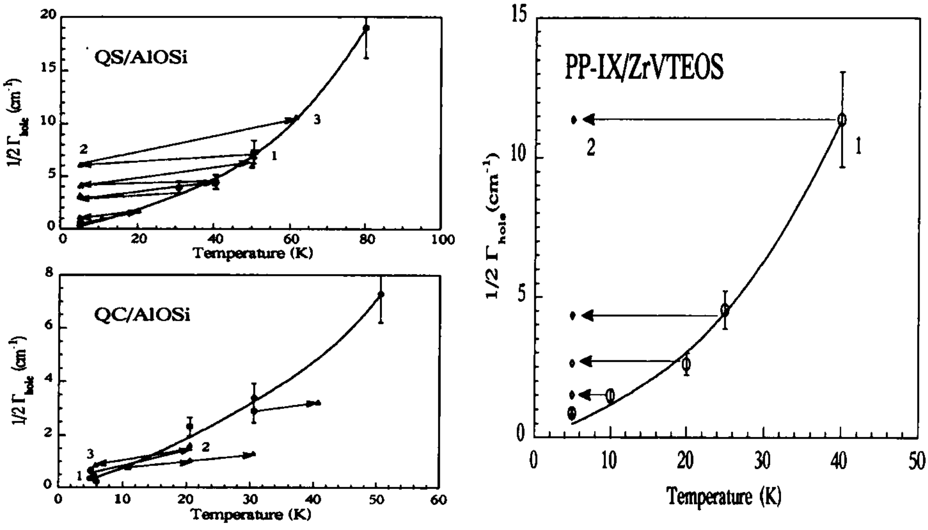

FIGURE 5 a) In AlOSi:quinizarin: temperature cycling experiments b) In ZrVTEOS:PP-IX: holes are burnt at high temperature and read at 5 K

These facts appear as a strong evidence that the main contribution to the hole width is due to spectral diffusion, which appears as a negative consequence of the grafting.

When a hole is burnt in such system, strong disturbances are induced around burnt molecules in the TLS bath which needs time to be thermalised.

CONCLUSION

Grafting the guest to the host

To increase the rigidity of the host as well as to limit the degrees of freedom of the active molecule in order to reduce the contributions of librational movements to the hole width, the dopant is grafted to the host. We did it in two ways: through complexation or covalent bonding. An important remark concerns the fact that the grafting does not increase the linear electron-phonon coupling. We believe the reason is the blocking of local low frequency modes, especially translational modes and partly of librational modes of the guest. This fact has a good consequence for the high temperature PSHB behaviour.

Spectral diffusion

The negative consequence in a naive view is the fact that the sensitivity of the guest to environmental changes increases strongly. Especially at elevated temperature, local rearrangements will induce frequency shifts which cannot disappear when the temperature is lowered.

Comparison with other data

The data are reported for the maximum temperature achieved. From table II, the high temperature PSHB performances of aluminium phthalocyanine tetrasulfonate (APT) in buffered hyperquenched glassy water (HGW) appears quite remarkable. However, sol-gel hosts with grafted molecules look promising and more intense research is needed.

TABLE II Comparative data on PSHB performances for organic molecules in inorganic hosts:

T (K)	Host	Guest	Γ_{inh} (cm^{-1})	Γ_{hole} (cm^{-1})	P_b (mW/cm^2)	t_b (s)	λ_b (nm)	[ref.]
77	buffered HGW	APT	400	6.4	0.03	60	668	[16]
77	on γAl_2O_3	quinizarin DAQ	1000	15	12	500	570	[5]
80	sol-gel AlOSi	quinizarin DAQ	200	38	20	600	575	[8]
80	zeolite $AlPO_4$-5	ZnPhthalo-cyanine	450	19	13	100	655	[17]
90	on γAl_2O_3	OctaEthyl-Porphin	280	54	3.7	900	612.8	[18]
120	sol-gel ZrVTEOS	PP-IX grafted	440	124	4.5	300	629	[12]
140	semi-cond. TiO_2	ZnTTBP	390	≈200	3.8	1200	627.8	[19]

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