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DYNAMICS OF GLASSES DOPED WITH RARE EARTH IONS: A STUDY BY PERMANENT AND TRANSIENT HOLE-BURNING

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The homogeneous linewidths of the electronic transitions ${}^1D_2 \leftrightarrow {}^3H_4$ of Pr^{3+} and ${}^5D_0 \leftrightarrow {}^7F_0$ of Eu^{3+} in silicate glass as a function of temperature have been obtained by means of hole-burning between 0.4 and 12 K, and 0.4 and 3.3 K, respectively. It was found that $\Gamma_{hom} \propto T^{1.0}$ for both inorganic glassy systems at low temperatures. The influence of the experimental time scale on the holewidth has been studied. No effect was observed for Eu^{3+} between 200 ms and 120 s. While permanent (hours) and short lived holes (minutes to seconds) were observed for Pr^{3+}, only the latter are clearly observed for Eu^{3+}. The hole recovery time was measured as a function of temperature.

1. Introduction

Many optical dephasing studies on organic and inorganic glasses doped with impurities have been reported in the last decade [1]. The aim was to get a better understanding of the dynamics and local structure of amorphous materials. In the first experiment of this sort, performed on Eu^{3+} in silicate glass by means of fluorescence line-narrowing (FLN) between 8 and 90 K, the homogeneous linewidth, Γ_{hom}, was found to be more than an order of magnitude larger than in crystals at low temperatures [2]. Furthermore, Γ_{hom} followed a quadratic temperature dependence which was much weaker than the exponential or T^7-dependence typical for crystals. From a subsequent hole-burning experiment on the same system at 1.6 K it was concluded that the T^2-dependence seems to extend down to low temperatures [3].

Other FLN experiments on various rare earth ions in inorganic glasses between ≈ 10 K and 800 K yielded a similar T^2-dependence of Γ_{hom} [4,5]. Most of the theories developed to interpret these results have been based on a coupling of the optical transition to two-level systems (TLS, or low-frequency modes of the glass) which interact with either phonons or 'fractons' of the bath [6].

In contrast to the large number of dephasing measurements on inorganic glasses at high temperature, very few data exist below 10 K. It has been found that Pr^{3+} in silicate glass follows $\Gamma_{hom} \propto T^{1.0 \pm 0.2}$ between 1.6 and 20 K. The results were identical when measured by hole-burning and accumulated photon echoes [3]. The other system studied was Nd^{3+} in fused silica in which two-pulse nanosecond photon echo experiments showed that Γ_{hom} is proportional to $T^{1.3}$ between 0.1 and 1 K [7].

Since hole-burning experiments on many organic glasses and an inorganic porous glass doped with organic molecules yielded a $T^{1.3}$-dependence of Γ_{hom} between 0.3 K and 20 K [8–11], it is of interest to determine whether such a power law is universally valid for glasses at low temperature, or whether it is restricted to organic guest molecules in amorphous hosts. We have investigated the homogeneous linewidth as a function of temperature for two inorganic amorphous systems, Pr^{3+} and Eu^{3+} in silicate glass, by means of permanent (PHB) and transient (THB) hole-burning between 0.4 and 12 K, and 0.4 and 3.3 K, respectively. We have further studied the influence on the holewidth of the experimental time scale from 120 s down to 200 ms, and have determined the hole recovery rate as a function of temperature.

2. Results and discussion

2.1. Pr^{3+}: silicate glass

The absorption band of the ${}^1D_2 \leftarrow {}^3H_4$ transition of Pr^{3+} (0.1%) in silicate glass at low temperatures extends from ≈ 570 nm to ≈ 610 nm [3]. Its large width is due to an overlap of five crystal-field components, of which only the lowest one decays radiatively. Fast radiationless relaxation occurs from higher crystal-field levels, which is supported by the fact that it was not possible to burn holes at wavelengths smaller than 597.5 nm.

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Narrow holes of about 100 MHz width could be burnt between 606.5 nm and 597.5 nm at 1.2 K. In contrast to the results found in ref. [3], the holes did not become broader as the wavelength decreased to 597.5 nm, indicating that the holewidth, Γ_{hole}, is not affected by different local environments. This result was found to be independent of temperature. Furthermore, the holewidths at 606.0 nm were a factor of 2 smaller than previously reported [3], probably due to the order of magnitude lower burning fluences used by us.

Fig. 1 shows the homogeneous linewidth, $\Gamma_{\text{hom}} = \frac{1}{2}\Gamma_{\text{hole}}$ at zero burning fluence, as a function of temperature between 0.4 and 12 K, which follows $\Gamma_{\text{hom}} \propto T^{1.00 \pm 0.02}$. These experiment which have been extended down to 0.4 K here, confirm the linear T-dependence reported in ref. [3]. Notice that when $T \to 0$ Γ_{hom} extrapolates to zero, which is to be expected on a MHz-scale, since $\Gamma_0 = (2\pi T_1)^{-1}$ is less than a kHz. The measurements were made on a time scale of ~ 100 s. We have not only observed long-lived holes for Pr^{3+} (of about hours) [3] at $T > 1.2$ K, but also short lived holes between 0.4 and 1.2 K which were not previously reported for this system.

The short lived holes burnt in Pr^{3+} : silicate glass have a lifetime τ of about 460 *s* at 0.4 K, which decreases to ≈ 140 s at 1.2 K (see fig. 2). The value of τ is independent of wavelength. The temperature dependence of τ^{-1} was found to be linear: $\tau^{-1} = (6.0 \pm 0.1) \times 10^{-3}\, T^{1.0 \pm 0.1}$, between 0.4 and 1.2 K.

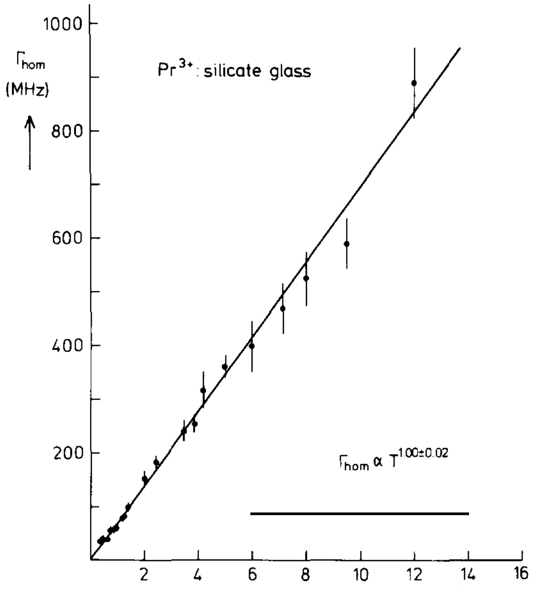

Fig. 1. Temperature dependence of the homogeneous linewidth, Γ_{hom}, of the $^1D_2 \leftarrow {}^3H_4$ transition of Pr^{3+} : silicate glass. The holes were burnt at 606.0 nm. Notice that $\Gamma_{\text{hom}} \propto T^{1.00 \pm 0.02}$.

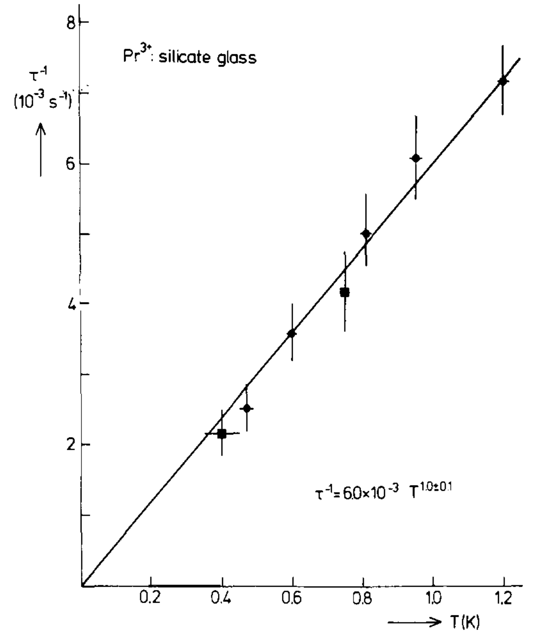

Fig. 2. Inverse of the hole-lifetime. τ^{-1}, as a function of temperature. Holes were burnt at 600.5 nm (circles) and 606.0 nm (squares). The data follow $\tau^{-1} = (6.0 \pm 0.1) \times 10^{-3}\, T^{1.0 \pm 0.1}$.

2.2. Eu^{3+}: silicate glass

The absorption band of the $^5D_0 \leftarrow {}^7F_0$ transition of Eu^{3+} (0.25%) in silicate glass at ≈ 580 nm has a large inhomogeneous width, $\Gamma_{\text{inh}} \simeq 100$ cm^{-1}, due to a wide range of static environments [4].

In contrast to Pr^{3+} : silicate glass, we have only observed short-lived holes. The mechanism here is assumed to be population redistribution of the nuclear ground state quadrupole levels [3]. The lifetime of a hole for Eu^{3+} is $\tau = 160$ s at 0.75 K.

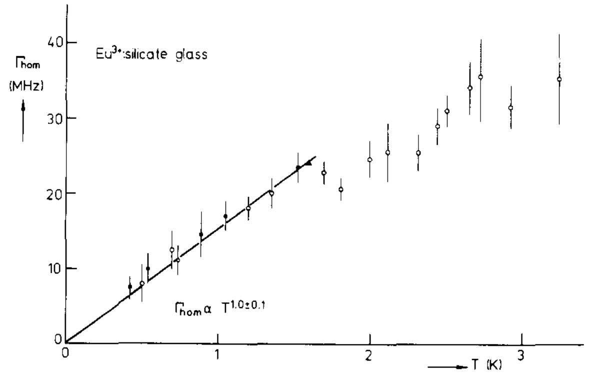

Fig. 3. Temperature dependence of the homogeneous linewidth, Γ_{hom}, of the $^5D_0 \leftarrow {}^7F_0$ transition of Eu^{3+} : silicate glass. The holes were burnt at 580 nm. The experimental time scale was > 100 s (closed circles) and < 5 s (open circles). Notice that $\Gamma_{\text{hom}} \propto T^{1.0 \pm 0.1}$ for $T < 1.6$ K.

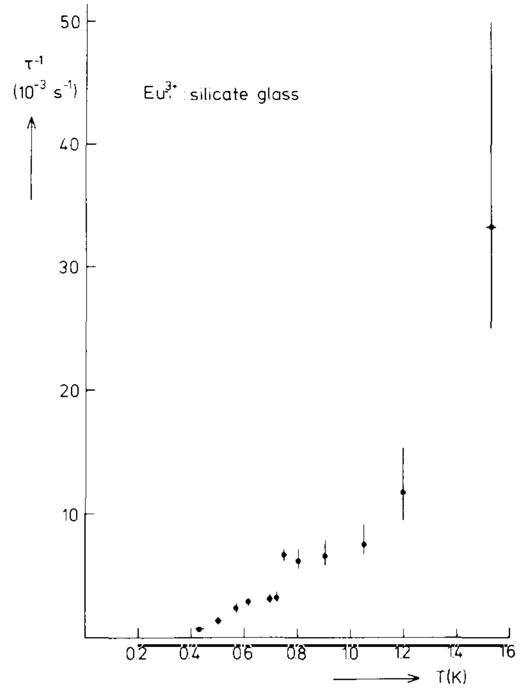

Fig. 4. Inverse of the hole-lifetime (SLR-time), τ^{-1}, as a function of temperature, τ^{-1} is not linearly dependent on T.

The temperature dependence of Γ_{hom} is shown on fig. 3 between 0.4 and 3.3 K. The data follow a linear dependence from 0.4 to 1.6 K and extrapolate to $\Gamma_{\text{hom}} = 0$ MHz for $T \to 0$. At $T > 1.6$ K, however, the values of Γ_{hom} deviate from this line and bend towards smaller values. We expect a crossover to the previously reported T^2-dependence at higher temperatures [1,2,12]. If, on the other hand, a line were traced through all the data points from 0.4 up to 3.3 K, a residual linewidth of $\Gamma_0 \simeq 5$ MHz would remain which is much larger than the fluorescence-lifetime limited value, $\Gamma_0 = (2\pi T_1)^{-1}$ of less than a kHz.

In fig. 4 the inverse of the hole-lifetime or average spin–lattice relaxation rate, τ^{-1}, as a function of temperature between 0.4 and 1.6 K is plotted. The data do not follow a linear dependence on T. There seems to be a discontinuity in the value of τ^{-1} at (0.74 ± 0.01) K, which invites further investigation.

Finally, we should mention that the holewidths for Eu^{3+} are not influenced by reducing the experimental time scale from 120 s to 200 ms, at 1.2 K. This result is consistent with time-resolved FLN experiments with a spectral resolution of about 1 GHz on Eu^{3+} in inorganic glasses at $T > 10$ K [2,12].

3. Conclusions

We have found that the temperature dependence of the homogeneous linewidth, Γ_{hom}, is linear at low temperatures for both Pr^{3+} ($0.4 \text{ K} < T < 12$ K) and Eu^{3+} ($0.4 \text{ K} < T < 1.6$ K) in silicate glass. We have not observed a crossover to the expected T^2-dependence at higher temperatures yet. The $T^{1.0}$ dependence may be explained by some of the theoretical models reported in the literature [2,6], if one assumes a dipole–dipole coupling between the TLS and the rare earth ion, and a constant density of TLS-states. In addition, a direct process involving rapidly relaxing nearby crystal field levels would give a linear T-dependence of Γ_{hom} [13].

Whereas two hole-burning mechanisms (permanent and short-lived) seem to be active for Pr^{3+}, only short-lived holes are dominant for Eu^{3+} in silicate glass [3]. The lifetime of the latter is determined by spin–lattice relaxation (SLR) between nuclear hyperfine levels. The hole recovery rate for Pr^{3+} was found to depend linearly on temperature. The time scale of the experiment does not influence the value of Γ_{hom} for Eu^{3+} in silicate glass between 200 ms and 100 s. Hole-burning experiments on a ms-time scale are in progress.

Acknowledgements

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