Picosecond luminescence and competing nonradiative processes in As_2S_3 glass

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Photoluminescence (PL) in As_2S_3 glass was measured with ~7-psec resolution using a streak camera. We find that the Stokes shift occurs in <20 psec, and that the *maximum radiative* rate is $\nu_1 = (4 \pm 1) \times 10^8$ Hz. Nonradiative decay dominates at high T, but persists at low T, probably due to tunneling. For $T > 100$ K the observed decay time varies as $\exp(-T/T_0)$ like the cw PL efficiency, indicating that similar nonradiative mechanisms may apply for slow and fast PL. We suggest that transient absorption and PL probe different carrier subsets. A localized exciton model is discussed in relation to the fastest PL processes.

Current understanding of electronic phenomena involving localized states in amorphous (a) semiconductors has been strongly influenced by studies of subbandgap photoluminescence (PL).[1-4] For the prototype chalcogenide glass a-As_2S_3 previous experiments have found that the PL is characterized by a wide distribution of monomolecular (i.e., independent of excitation intensity) decay times ranging from less than 10 nsec to several milliseconds.[1,3] It is thought that different geminate (because of the monomolecular decay) recombination processes account for the slow (S) PL decaying in $10^{-6} - 10^{-3}$ sec and the fast (F) PL decaying in $< 10^{-6}$ sec.[2,4] The time-resolved PL spectrum[5] is a broad subbandgap peak [~0.5 eV full width at half maximum (FWHM)] whose center shifts to lower energy (through the range ~1.6 → 1.1 eV) with increasing delay time. Band-tail or higher energies (> 2.0 eV) are required for photoexcitation[1,3]; in addition for FPL (but not for SPL) the emission shifts to higher energy with increasing excitation energy.[2-4] A substantial part of the energy difference between emission and excitation has been attributed to a Stokes shift accompanying localization at defect sites[1,3,6] or small polaron formation.[7]

The maximum radiative rate ν_1 has not been measured directly for any amorphous semiconductor. This is because the largest decay rates, even at low temperature, are considerably beyond the temporal resolution (> 10 nsec) of the fastest experiments reported.[2-4] In the present work this limit is decreased to ~7 psec. Consequently, for the first time we are able to isolate the most rapid radiative processes and thereby determine ν_1. We also determine the temperature (T) dependence (8 – 204 K) of the effective nonradiative rate $\bar{\nu}_n(T)$ in competition with ν_1. In addition the spectral dependence of the picosecond buildup and decay kinetics is investigated for emission energies between 2.1 and 1.5 eV. Recently picosecond recombination processes in arsenic chalcogenide glasses have also been studied by monitoring the decay of photoinduced absorption (PA).[8,9] The relationship between the PA and the present PL results is discussed.

The experiments employed an active-passive mode-locked Nd^{3+}:yttrium aluminum garnet (YAG) oscillator.[10] Single pulses (30 psec FWHM, $\lambda = 1064$ nm) were extracted using a double Pockels cell scheme, amplified, and split into two beams. The first beam was frequency doubled (2.33 eV) in KD*P, filtered, and weakly focused (0.5 mm) on the sample housed in a variable-temperature helium refrigerator. The intensity was 0.2 GW/cm^2, below both the damage threshold and the two-photon absorption region in a-As_2S_3.[8] The excitation density was ~10^{17} photons/cm^3, corresponding to α (2.33 eV) ≈ 20 cm^{-1} (within the Urbach edge) for $T < 200$ K.[11] The second beam was directed upon a GaAs photoconductive high-voltage switch used to provide the deflection voltage ramp for a streak tube (S-20 response). This synchronized the streak tube sweep to within 2 psec with the excitation pulse, allowing accurate averaging of picosecond optical information from successive laser shots.[12] Front surface PL was measured. Data from up to 300 laser shots were averaged to obtain the results. The As_2S_3 glass was high-quality optical window material from Servo. It was carefully cleaned and vacuum degassed at 100 °C. The visible and infrared absorption, and the cw luminescence spectra agreed with previous work, showing no anomalies due to impurities.[1,3,11]

Figure 1 displays the instantaneous PL intensity $I(t)$ measured at 8 and 154 K from 0 to 300 psec; $I(t)$ corresponds to the total intensity in the bandwidth 2.1 – 1.5 eV. By virtue of these time and energy constraints our experiments probe only the most

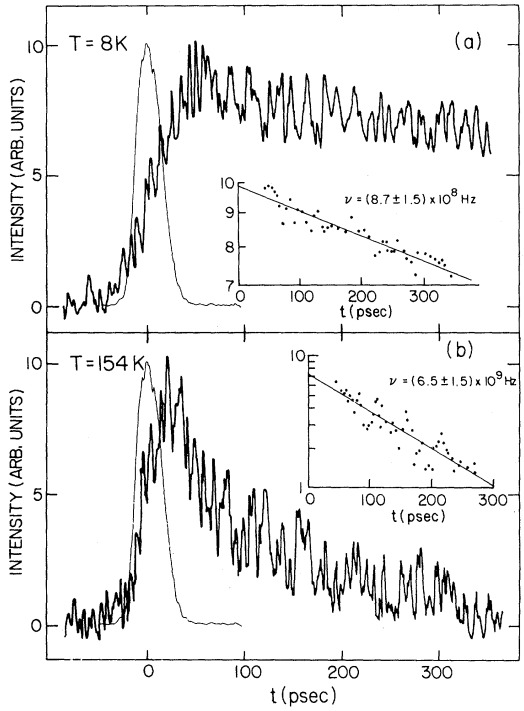

FIG. 1. Measured buildup and decay of PL (1.5 − 2.1 eV) in a-As_2S_3. Insets show least-squares fit assuming an exponential decay. The laser excitation pulse is also displayed. 200 shots were averaged in (a) and 300 were averaged in (b).

rapid FPL processes.[2,4] Using different high-energy cutoff filters (2.1, 1.9, and 1.7 eV) we studied the dependence of both the buildup and decay times on PL energy at 8 and 154 K. Within experimental accuracy *no* variation in these times was found, although the integrated intensity decreased for the lower-energy cutoffs. These results are consistent with a single process contributing to PL in our energy and time regimes. Whether picosecond processes extend to still lower energy with any intensity awaits future measurements with an S-1 response streak tube.

In all our measurements the PL buildup time was observed to follow an instantaneous response to the laser pulse. Considering our signal-to-noise ratios we find that the deconvoluted buildup time is ≤ 10 psec except for the lowest-temperature data illustrated by the 8-K results shown in Fig. 1. In that case a slightly longer buildup time (≤ 20 psec) is found which we are presently investigating in greater detail. Consequently we can set an upper limit of ~ 20 psec on the time for photoexcited carriers to relax into emitting states, regardless of the energy of those states (within 2.1 − 1.5 eV) or the temperature. Since several tenths of an electronvolt are lost during this relaxation period, our PL observations support a strong-coupling rapid process requiring only a *few steps*. The Stokes shift mechanisms which have been proposed, involving bond switching or breaking at defect sites,[1,3,6] or small polaron formation,[7] fit this criterion. However, it is doubtful that more than a small fraction of the energy lost in the first 20 psec could be accounted for by *multistep* relaxation through the band tails to lower energy states. We expect that such a process should be slower because of the decreasing density and increasing localization of successive states. On the other hand we do not rule out an important role for multistep band-tail processes in the relaxation accompanying SPL.[1,13]

In Fig. 1 the insets show the best fit of an exponential decay to our data for $t > 30$ psec (i.e., after the laser pulse). Typical uncertainties in the decay rates are (15 − 20)%. At 8 K the observed rate is 8.7×10^8 Hz but by 204 K it has increased to 2.2×10^{10} Hz. Above this temperature we were unable to measure the PL decay rate due to deterioration of the signal-to-noise ratio. The detailed temperature dependence of the observed decay rate $\nu(T)$ is shown in Fig. 2. We also attempted to fit the PL decay by a power law $t^{-m(T)}$ and by the product $t^{-T/T'}\exp(-\nu' t)$ with constant T' and ν' to test whether the empirical behavior discovered in Ref. 3 for $t > 100$ nsec (mostly SPL) could be extended to our case. Invariably the fits were inferior because a power-law dependence varies either too rapidly at small t or too slowly at large t. Furthermore temperature-independent values of T' and ν' could not be found which provided reasonable fits over the entire range 8 − 204 K. We concluded that neither expression could be justified compared to a simple exponential decay.

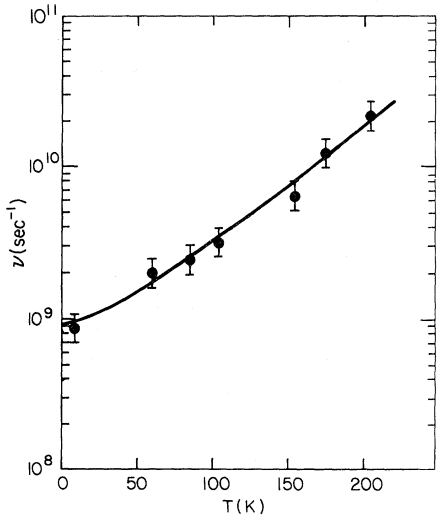

FIG. 2. Temperature dependence of the observed PL decay rate in a-As_2S_3. At high T the decay rate is determined primarily by nonradiative processes; the dependence is similar to that for η_{cw}^{-1} (see text). The solid line representing $\nu_1 + \bar{\nu}_n(0)\exp(T/T_0)$ fits all the data quite closely.

In Fig. 2 the data were fitted to the equation $\nu(T) = \nu_1 + \bar{\nu}_n(0)\exp(T/T_0)$. Here it is assumed that the observed decay rate has a temperature-independent radiative component ν_1 describing the fastest PL processes in a-As_2S_3, and a temperature-dependent nonradiative component $\bar{\nu}_n(T)$ which competes with ν_1. Our three-parameter least-squares fit (solid curve in Fig. 2) yields $\nu_1 = (4 \pm 1) \times 10^8$ Hz, $\bar{\nu}_n(0) = (4 \pm 1) \times 10^8$ Hz, and $T_0 = 53 \pm 5$ K. This functional form for $\bar{\nu}_n(T)$ was chosen *both* because of the good fit it gives to the data and because of its connection to the well-known[1] T^2 activated behavior exhibited by the cw quantum efficiency η_{cw} over 10 – 230 K. The latter connection becomes more transparent when we consider the effective quantum efficiency $\eta_1 = \nu_1/\nu(T)$ due to nonradiative competition with ν_1. Our data show that for $T > 100$ K, $\eta_1 \propto \exp(-T/T_0)$ similar to η_{cw} except that $T_0 \approx 26$ K[1] in the cw case. (We regard the factor-of-2 difference in T_0 as significant because our fit was sensitive to this parameter.) Since η_{cw} is dominated by SPL[5] while η_1 corresponds to the *maximum* rate ν_1, the observed similarity in functional dependence on T is surprising. It suggests that similar mechanisms could account for the *nonradiative* decay of SPL and FPL in a-As_2S_3.

Several possibilities have been proposed for the operative nonradiative mechanism, including spatial tunneling,[1] a distribution of activation energies,[3] and phonon-carrier collisions.[6] At present there is no clear consensus, and a detailed discussion is beyond the scope of this Communication. However, we note one point on the basis of our results. At low T nonradiative competition with ν_1 is still appreciable, because $\bar{\nu}_n(0) \sim \nu_1$. Therefore, it is likely that tunneling of some type, which does not vanish as $T \rightarrow 0$ K,[14] makes a significant contribution to the nonradiative decay of (at least) the fastest emission processes.

Recent picosecond PA studies[8,9] in chalcogenide glasses have shown that the decay of absorption due to photoexcited carriers is quite different from that reported here for picosecond PL. For a-$As_2S_{2.25}Se_{0.75}$ excited at the same position on the band tail as in our experiments (i.e., at the same absorption coefficient) PA decays in ~3 psec at 85 K increasing to 12 psec at 300 K. In contrast we observe that the PL decays in 410 psec at 85 K decreasing to < 10 psec at 300 K. We do not find these differences inconsistent but rather complementary — indicating that the subsets of carriers contributing to PA and PL are separate. During or just after thermalization a fraction $\sim \eta_{cw}$ (0 K) = (10–20)% of the carriers are trapped at luminescence centers in states with a low absorption cross section; the remainder contribute to PA. We suggest that a portion of the *initial* rapid decay of PA observed in Ref. 9 may derive from carrier capture at PL centers. This would place the onset time for PL between 0.1–1 psec. The main channel for the decay of (band-tail excited) PA has been attributed to geminate nonradiative recombination.[9] Our experimental results (and those of Ref. 9) show that this channel proceeds ~100 times faster at 85 K than the nonradiative channel competing with ν_1, implying that the respective decay mechanisms are different.

Because of the disorder inherent in an amorphous solid we expect that after thermalization there will be a broad distribution of electron-hole separations r. We can conceive of two qualitatively different situations — either the electron and hole are spatially separated, or their wave functions overlap sufficiently to form a localized exciton. In the separated case emission is thought to proceed via radiative tunneling[1] with the rate $\nu_T \exp(-2\alpha r)$, where α^{-1} is the wave-function extent; whereas for the localized excitonic picture it is more appropriate to use the expression $\nu_d = \sqrt{\epsilon}4/3(e^2/\hbar c)\omega^3/c^2|\langle r_d \rangle|^2$ for the emission of a dipole er_d imbedded in a dielectric ($\epsilon = 5.9$ for a-As_2S_3). Although the tunneling expression has been more commonly applied,[1,3] recently a localized exciton model with strong lattice coupling was invoked for FPL (~10-nsec decay) in a-As_2S_3.[2] We favor the localized exciton picture here for ν_1, because it is plausible that the *maximum* radiative rate $\nu_1 = 4 \times 10^8$ Hz corresponds to recombination of photoexcited pairs with the *minimum* electron-hole separation. On the other hand for longer-lived processes we expect that tunneling should be the dominant decay mode.

The question we wish to explore here is to what extent does the observed kinetics allow the two radiative processes to coexist? In considering the two pictures one expects the tunneling-rate expression to break down, and the exciton model to apply, when r approaches α^{-1}. Estimates of α^{-1} from PL[1,3] and PA[9] results range between 2 and 7 Å, a reasonable range for localized states in chalcogenides.[15] Using the dipole expression in the exciton case we find $\nu_d = \nu_1$ for $r_d = 2.9$ Å, within the range of α^{-1}. It would seem then that the localized exciton picture provides a consistent short-time limit to the slower tunneling recombination involving distant pairs. In further support of this consistency we note that estimates[1,3] for the limiting rate ν_T based on a radiative tunneling description of the temporal shift of the PL peak for $t > 10$ nsec are comparable to our measured value of ν_1.

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