"Write/Read/Erase" with Laser Irradiation of Dicyanoargentate(I) Doped and Pure Crystals

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Laser irradiation of single crystals of doped $Ag(CN)_2^-$/KCl and pure $KAg(CN)_2$ at 77 K results in dramatic changes in their emission spectra. Higher-energy bands that were either absent or weak start appearing concomitant with a quenching of the original major lower-energy bands as samples are exposed to 266 nm laser light. These changes are progressive with increased irradiation time and they are also reversible. Thus, when a given crystal is heated from 77 K to ambient temperature and then re-cooled to 77 K, hysteresis occurs as the original luminescence spectra before irradiation are obtained. Two doped $Ag(CN)_2^-$/KCl single crystals with Ag content of 1.21 and 2.23% (wt) as well as pure single crystals of $KAg(CN)_2$ show this "write/read/erase" effect to various extents. By analyzing the luminescence profile versus exposure time to 266 nm laser irradiation at cryogenic temperatures, it was possible to calculate the rate constants for the forward (k_1) and reverse (k_2) reactions of the writing process. The fastest changes are for the 1.21% doped crystals ($k_1 = 0.04493$ min^{-1}), followed by the 2.23% doped crystals ($k_1 = 0.01245$ min^{-1}) while the slowest changes were for pure $KAg(CN)_2$ ($k_1 = 0.00178$ min^{-1}). The results were explained in terms of a change in the distribution of $*[Ag(CN)_2^-]_n$ excitons with different geometries following laser irradiation.

Introduction

Photophysical studies of d^{10} Ag(I) complexes have been receiving increasing attention over the past fifteen years.[1−10] The luminescence bands for these complexes in the near-UV and visible regions are usually related to the association of individual complexes into dimers, clusters, and infinite chains or layers. In many of these compounds, the closed-shell Ag^I−Ag^I interaction (argentophilic bonding) is assisted by the presence of bridging or capping ligands. Only a few examples of ligand-unsupported argentophilic bonding have been reported.[11−15] Among these was our report of ligand-unsupported argentophilic bonding based on crystal structure, electronic structure, and temperature-dependent Raman studies of Tl[Ag(CN)$_2$].[11]

The molecular structure of dicyanoargentate(I) compounds, M[Ag(CN)$_2$], consists of layers of Ag(CN)$_2^-$ ions alternating with layers of the M counterions.[11,16,17] In these compounds, metal ions bond directly to the cyanide ligands and/or to water molecules in hydrated compounds. We have demonstrated that the luminescence in various single and doped crystals as well as solutions of the dicyanoargentates(I) are related to Ag−Ag bonded excimers and exciplexes.[5−7,18−21] Among this group, single crystals doped in alkali halide hosts exhibit multiple luminescence bands that can be resolved by site-selective excitation, resulting in *exciplex tuning* of the emission energies over a wide range of >18 000 cm^{-1} across the near-UV and visible regions.[6,21] The distribution of the relative band intensities can be controlled by varying the dopant concentration (Ag content),[7,18] host lattice (e.g., from KCl to NaCl),[19] and temperature (resulting in luminescence thermochromism).[18,19]

In this paper we show that exciplex tuning of Ag(CN)$_2^-$ doped and pure crystals can also be achieved by laser irradiation, which results in a reversible "write/read/erase effect". Reversible optical or electrochemical changes on molecular materials may render such materials potentially useful for data storage applications, as has been suggested recently for organic films that exhibit "write/read/erase" properties by redox switching[22] and for transition-metal cluster complexes whose magnetic moments reverse sign by only slight changes in the applied field strength.[23] The results here, however, are more closely related to the "optical memory" phenomenon reported by Zink and co-workers for Cu$^+$- and Cu$^+$/Ag$^+$-doped β-alumina in which the crystal "remembers" which part of it had been irradiated.[24−26] The changes in the luminescence spectra upon laser irradiation are related to reversible photophysical processes in both the systems described here and those described by Zink. This is in contrast to two related studies for Pb[Au(CN)$_2$]$_2$ and TlAg(CN)$_2$ in which irradiation led to reversible photochemical and redox changes.[27,28] Here we describe the effect of laser irradiation and temperature on the luminescence properties of three dicyanoargentate(I) doped and pure crystals and the results are analyzed to show the effect of varying the Ag content on the rate of the "write/read/erase" process.

Experimental Section

The synthesis of doped Ag(CN)$_2^-$/KCl and pure KAg(CN)$_2$ single crystals has been reported earlier.[18] The silver content in the doped crystals was determined by atomic absorption spectroscopy using a Model 857-Smith-Hieftje 11/12 spectrophotometer. Thus, analysis results for the Ag(CN)$_2^-$/KCl doped single crystals referred to as "batch 1" and "batch 2" gave a Ag content (wt) of 1.21% and 2.23%, respectively. Infrared and

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Raman spectra of all crystals (probed for intact single crystals) confirmed the persistence of the structure of the $Ag(CN)_2^-$ complex within the doped crystals as reported in refs 7 and 18.

Luminescence emission and excitation spectra were collected using a Photon Technology International Model QuantaMaster-1046 spectrophotometer. This instrument is equipped with a 75 W xenon lamp, two excitation monochromators, an emission monochromator, and a photomultiplier tube detector. Emission and excitation spectra were recorded at different temperatures using a Model LT-3-110 Heli-Tran cryostat from Air Products equipped with a temperature controller. Liquid nitrogen and liquid helium were used as the coolants. All excitation spectra were corrected for the wavelength-dependent output of the xenon lamp intensity using the quantum counter rhodamine B.

Irradiation experiments were carried out for doped $Ag(CN)_2^-$/KCl and pure $KAg(CN)_2$ single crystals by means of a Uniphase NanoUV-266 solid-state laser with 1 mW average output, 800 ps pulse width and a repetition rate of 8 kHz. Initially, a single crystal was mounted on a copper holder and cooled to 77 K. To allow thermal equilibrium to take place, emission and excitation spectra were recorded several times over a period of 30 min and it was ensured that no change in the luminescence intensity was obtained. The spectra obtained after 30 min are considered henceforth as the $t = 0$ spectra. The crystal was then irradiated with the 266 nm light of the solid-state laser for 5 min, after which the emission and excitation spectra were recorded. Laser exposure and spectral acquisition were repeated every 5 min for 1.5 h. After that, the crystal was warmed to room temperature for 2 h and then re-cooled to 77 K. As the recovery step, emission and excitation spectra were recorded after 30 min of its equilibrium at 77 K. Extreme care was taken that the sample remained stationary throughout all stages of the irradiation experiment. Control experiments were performed to ensure that no changes in the emission spectra were seen after irradiation had stopped (vide infra).

Results

We have reported earlier that single crystals of both doped crystals showed three major luminescence bands at 77 K with maxima at 296, 338, and 415 nm, henceforth referred to as bands A, B, and C, respectively.[18] Each emission band becomes dominant with a characteristic excitation wavelength while certain wavelengths can be used to generate more than one emission band. A tentative assignment of the emission bands, based on extensive previous studies of $[Ag(CN)_2^-]$ species,[5-7,18-21] relates band A to a $*[Ag(CN)_2^-]_2$ excimer, band B to a bent $*[Ag(CN)_2^-]_3$ exciplex, and band C to a linear $*[Ag(CN)_2^-]_3$ exciplex. We shall follow this assignment throughout this paper. At 77 K, single crystals of batches 1 and 2 of $[Ag(CN)_2^-]$/KCl show two emission bands at 338 (B), and 415 (C) nm while a single crystal of pure $KAg(CN)_2$ showed only one emission band at 415 nm (C). The relative intensities of these bands are temperature-dependent. Therefore, an illustration of the temperature-dependent emission spectra is given before proceeding to describe the irradiation experiments for the three samples.

Figure 1 shows the emission spectra of a single crystal of $[Ag(CN)_2^-]$/KCl batch 1 as a function of temperature upon excitation at 265 nm. As the temperature increases, the luminescence intensity for band B decreases while that for band C increases. This temperature-dependent behavior is an energy transfer process from band B excitons to the lower-energy excitons characteristic of band C. The activation energy for such a process can be readily obtained by Arrhenius treatment of the relative intensities for bands B and C. Thus, the data plotted
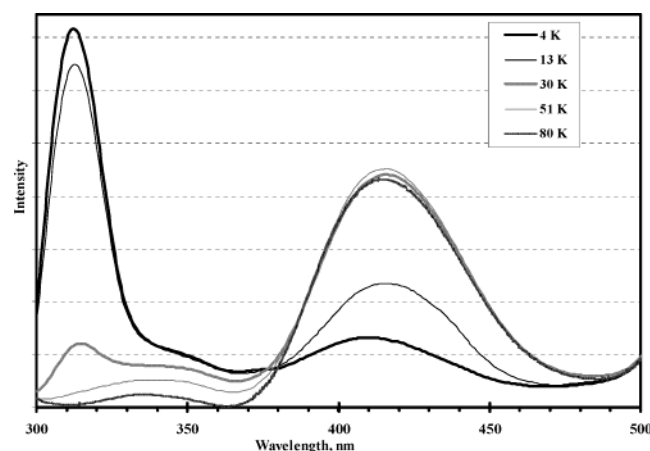

Figure 1. Emission spectra versus temperature for batch 1 of $[Ag(CN)_2^-]$/KCl crystals. All spectra were scanned with 265 nm excitation. Note the progressive increase in the relative intensity of the longer-wavelength band upon heating.
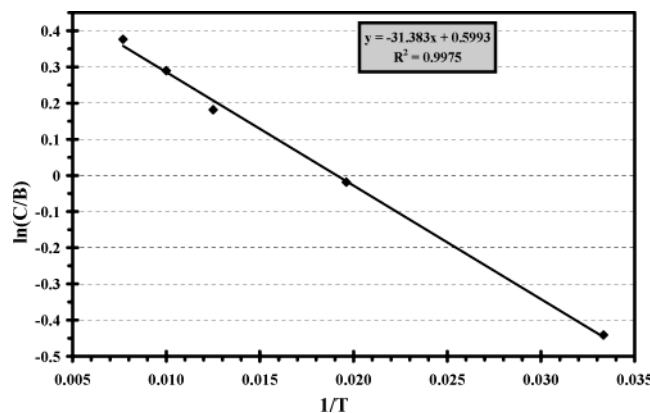

Figure 2. Arrhenius plot of the natural logarithm of the intensity ratio of bands C/B versus $1/T$ for batch 1 of $[Ag(CN)_2^-]$/KCl crystals. The slope value gives rise to an activation energy of 260.79 ± 0.04 J/mol.

in Figure 2 for batch 1 give an activation energy of 260.79 ± 0.04 J/mol. A similar treatment for batch 2 gives $E_a = 1437.55 \pm 0.01$ J/mol. Pure $KAg(CN)_2$ has not been considered in the study of energy transfer because at most temperatures (above $\sim$20 K) the compound exhibits only the luminescence band C. The smaller calculated E_a value for batch 1 than the corresponding value for batch 2 suggests a faster energy transfer from band B excitons to band C excitons for batch 1 compared to batch 2.

Figures 3, 4, and 5 show the luminescence spectra at 77 K versus irradiation time with 266 nm laser light for single crystals of pure $KAg(CN)_2$, batch 1, and batch 2 of the doped $[Ag(CN)_2^-]$/KCl crystals, respectively. It is noted that for all three crystals, exposure to 266 nm laser at 77 K leads to an increase in the intensity of the HE band along with a decrease in the intensity of the LE band. After warming up the crystal to room temperature and cooling to 77 K, the intensities of both bands return to essentially their original values before irradiation. In the case of pure crystals of $KAg(CN)_2$, only the LE band existed at 77 K before irradiation but upon exposure to 266 nm laser, the HE band appeared and started growing (Figure 3). In the case of the two doped crystals, both the HE and LE bands existed at 77 K before irradiation but upon exposure to 266 nm laser, the HE/LE intensity ratio started to increase with a more pronounced change for batch 1 (Figure 4) than for batch 2 (Figure 5). Thus, laser irradiation amounts to "writing" of data, as "read" by the luminescence spectra that show the enhancement in the HE band, and the data can be "erased" by heating
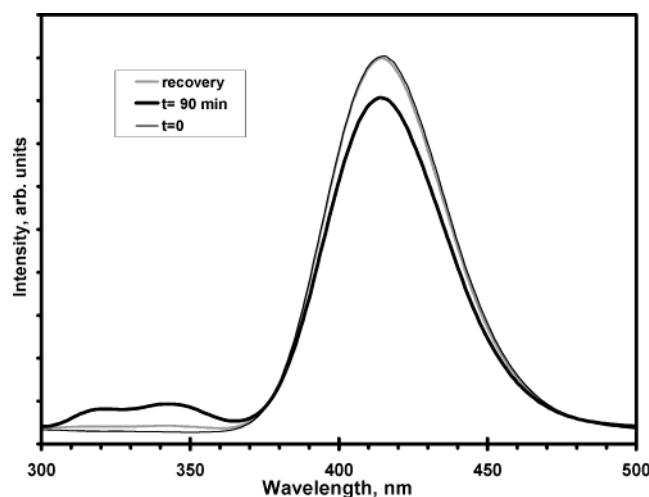
"Write/Read/Erase" with Laser Irradiation of $Ag(CN)_2^-$

Figure 3. Emission spectra versus 266 nm laser irradiation time at 77 K for pure $KAg(CN)_2$ crystals. All spectra were scanned with 275 nm excitation. Note the appearance of the short-wavelength bands following irradiation at 77 K and their quenching in the recovery step after the sample is heated to ambient temperature and then cooled again to 77 K.
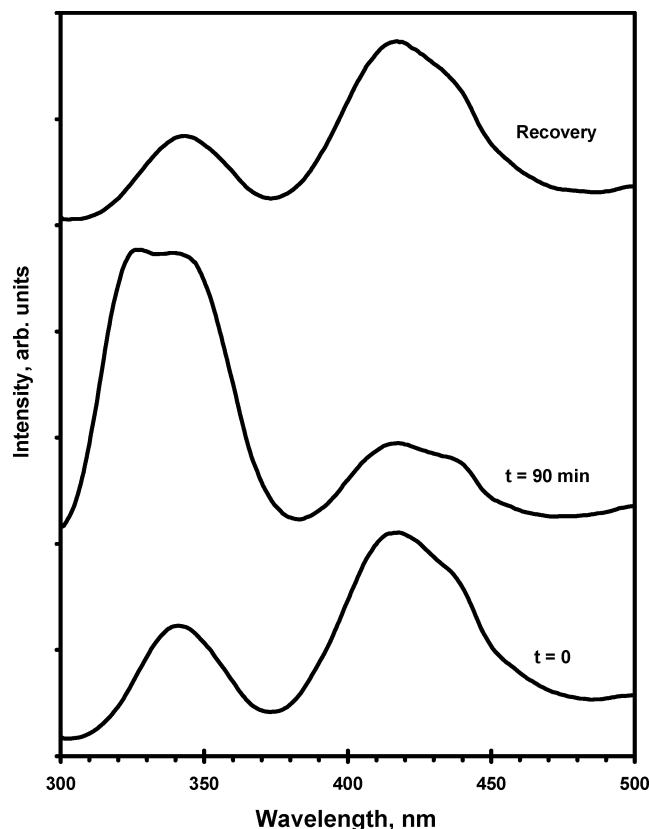

Figure 4. Emission spectra versus 266 nm laser irradiation time at 77 K for batch 1 of $[Ag(CN)_2^-]$/KCl crystals. All spectra were scanned with 275 nm excitation. Note the dominance of the short-wavelength bands following irradiation at 77 K and the regeneration of the original spectrum in the recovery step.
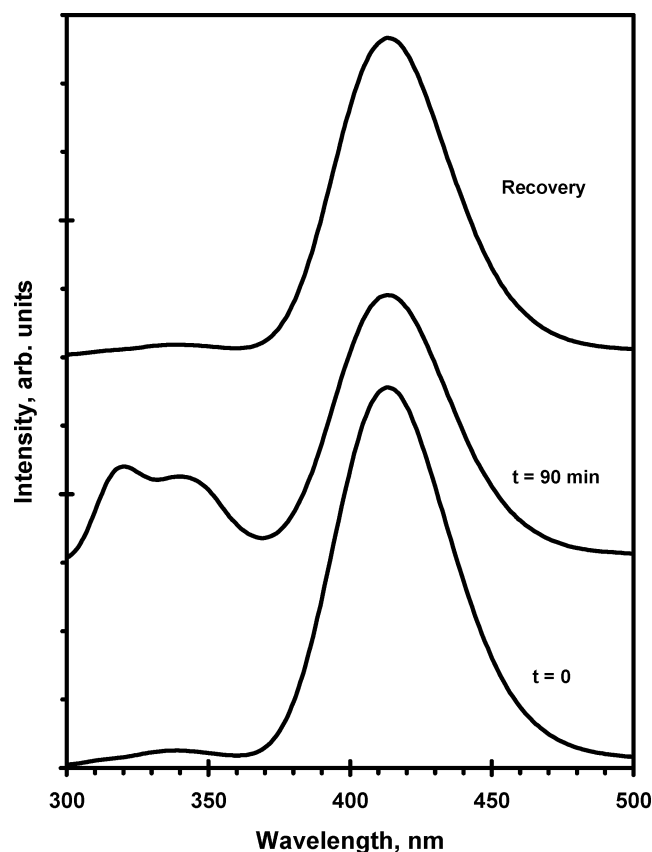

Figure 5. Emission spectra versus 266 nm laser irradiation time at 77 K for batch 2 of $[Ag(CN)_2^-]$/KCl crystals. All spectra were scanned with 275 nm excitation. Note the increased intensity of the short-wavelength bands following irradiation at 77 K, albeit to a lesser extent than in Figure 4, and the regeneration of the original spectrum in the recovery step.

170 the samples to ambient temperature, as "read" again by recording
171 the spectra when the samples are cooled back to 77 K and show
172 essentially the same luminescence spectra as those obtained
173 before irradiation. The percent recovery, calculated as the
174 integrated intensity of the spectrum generated after one cycle
175 of irradiation at 77 K, heating to ambient temperature, and
176 cooling again to 77 K, relative to the original integrated intensity
177 at 77 K before irradiation, was 98%, 76%, and 90% for batch

178 1, batch 2, and pure $KAg(CN)_2$, respectively. The irradiation
179 experiments for each sample were repeated three times (three
180 cycles). The high percent recovery for batch 1 was maintained
181 even after the second and third cycles yielding 97% and 95%,
182 respectively.
183   We have gathered data to quantitatively evaluate the time
184 evolution of the "write/read/erase" data storage behavior for each
185 of the three samples studied here. As shown in Figure 6, with
186 exposure to a 266 nm laser, the increase in the intensity of the
187 HE band concomitant with the decrease in the intensity of the
188 LE band occurs progressively with time for all three crystals.
189 For batch 1, a plateau occurs after 50 min for both bands (trace
190 a). A similar trend was observed for batch 2 (trace b) and pure
191 $KAg(CN)_2$ (trace c), but the change in the HE/LE intensity ratio
192 decreases on going from batch 1 → batch 2 → pure $KAg(CN)_2$.
193 In an attempt to quantify the difference in the behavior of the
194 three types of crystals studied via a kinetic parameter, irradiation
195 experiments were carried out at 77 K. Irradiation experiments
196 above 77 K did not lead to detectable changes in the relative
197 intensity of the HE and LE bands. The mechanism involved in
198 the writing process can be expressed as a reversible first-order
199 transformation of linear trimer excitons (*C) to bent trimer
200 excitons (*B) with the rate constants of the forward and reverse
201 processes designated as k_1 and k_2, respectively. Thus, the rate
202 expression can be represented as shown in eq 1:

$$\frac{d[*B]}{dt} = k_1[*C] - k_2[*B] \tag{1}$$

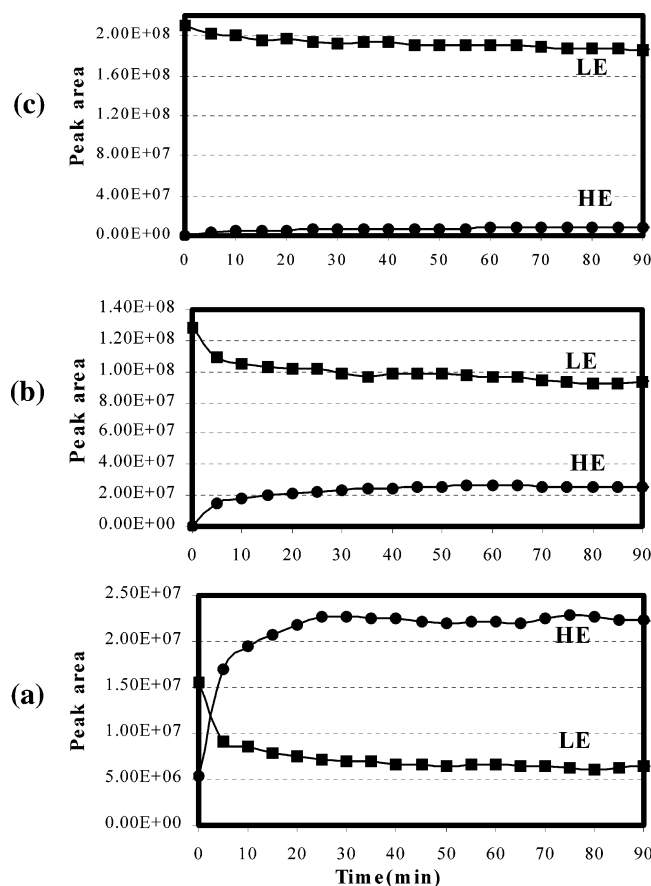203 while the mass balance is given by eq 2:

Figure 6. Variation of the peak areas of the HE and LE bands with exposure time to 266 nm laser light at 77 K in batch 1 (bottom), batch 2 (middle), and pure $KAg(CN)_2$ (top).

$$[*B]_0 + [*C]_0 = [*B]_t + [*C]_t = [*B]_e + [*C]_e \quad (2)$$

Subscripts "0", "t", and "e" in eq 2 refer to times 0, t, and equilibrium, respectively. At equilibrium,

$$\frac{d[*B]}{dt} = 0 = k_1[*C]_e - k_2[*B]_e \quad (3)$$

Equations 1−3 can be rearranged to obtain eq 4:

$$\frac{d[*B]}{dt} = (k_1 + k_2)\,([*B]_e - [*B]_t) \quad (4)$$

which can be rearranged and integrated over the limits $[*B]_t = [*B]_0$ to $[*B]_t$ and $t = 0$ to t to obtain eq 5:

$$\ln([*B]_e - [*B]_t) = -(k_1 + k_2)t + \ln([*B]_e - [*B]_0) \quad (5)$$

The concentration of a reactant or product is directly proportional to a physical property of a reactant or product. The physical property was taken as the integrated peak area of luminescence band B. As shown in Figure 7, plotting $\ln([B]_e - [B]_t)$ versus t for batch 1 at 77 K yields a straight line with a good fit ($R^2 = 0.9924$). From the slope, the $(k_1 + k_2)$ value was calculated as 0.057 min^{-1}. Similar data were obtained for batch 2 and pure $KAg(CN)_2$, for which linear plots were also obtained (Supporting Information). The equilibrium constant, k_1/k_2, can be calculated from the ratio of peak areas for the HE/LE band when they reach a steady state after 90 min of irradiation time. Solving the two simultaneous equations with two variables, we calculate the values of k_1 and k_2 as shown in
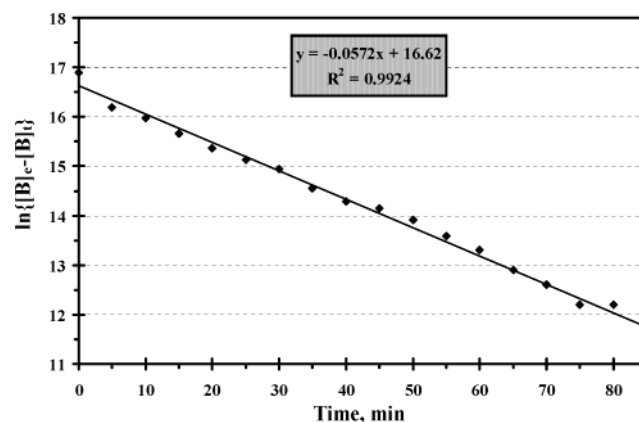

Figure 7. A plot of the natural logarithm of $\{[B]_e - [B]_t\}$ of [Ag-(CN)$_2^-$]/KCl batch 1 with increasing exposure time at 77 K.

TABLE 1: Calculated k_1 and k_2 Values at 77 K for the Three Crystals Studied

sample	$k_1 + k_2$	k_1/k_2	k_2, min^{-1}	k_1, min^{-1}
batch 1	0.0570	3.72	0.0121	0.04493
batch 2	0.0567	0.281	0.0443	0.01245
pure $KAg(CN)_2$	0.0409	0.0456	0.0391	0.00178

Table 1 for the 77 K data. The k_1 values in Table 1 suggest the memory writing process (k_1) in batch 1 is 3.6 times faster than in batch 2 and more than 25 times faster than in pure $KAg(CN)_2$, thus providing a quantitative parameter for the spectral data shown in Figures 3−6.

To verify the accuracy of the kinetic rate constant values, the following experiments were performed: (1) A fresh crystal that was never irradiated with laser light did not show changes in its luminescence spectra at 77 K with time in the absence of laser irradiation; (2) A crystal that was irradiated at 77 K, warmed to room temperature, and then cooled again to 77 K did not show changes in its luminescence spectra at 77 K with time during this recovery step in the absence of laser irradiation; (3) A crystal irradiated for X minutes at 77 K, which exhibits a different emission spectrum from the $t = 0$ spectrum, was kept in the dark at 77 K without further irradiation. The luminescence spectra versus time for this crystal were all the same as the $t = X$ spectrum.

Discussion

Previous work by our group[5−7,11,18−21,27−29,30] and others[12−15,31−34] has demonstrated the propensity of Ag(I) species to aggregate either as pure complexes or as doped impurities in a host lattice despite the inherent weakness of the ground-state Ag(I)−Ag(I) interactions. We have shown that the argentophilic bonding in $Ag(CN)_2^-$ species is a cooperative process.[35] Hence, the distribution of Ag(I) centers in a host lattice is not governed simply by statistical distribution analysis[6,7] as thermodynamic factors dictate the clustering of silver species together. Hence, emission characteristic of associated Ag(I) oligomers was detected in crystals doped with very small amounts of silver, and structural evidence indicating this association—including EXAFS and FTIR for the doped solids—reinforced the emission data.[7,29] We also have shown that all emissions observed in Ag(I)-doped materials were due to associated Ag(I) species and no emissions assigned to monomers were detected.[5−7] When the $Ag(CN)_2^-$ ions in the KCl lattice are excited with UV light, neighboring complexes bond with one another to form Ag−Ag bonded luminescent $*[Ag(CN)_2^-]_n$ excitons with different "n" and geometries, leading to a distribution

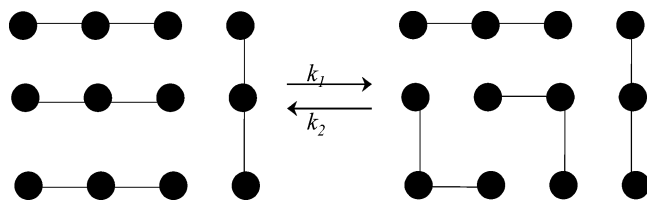"Write/Read/Erase" with Laser Irradiation of Ag(CN)$_2$$^-$ | *J. Phys. Chem. B* **E**

Figure 8. An illustration of the suggested change in the distribution of Ag−Ag bonded *[Ag(CN)$_2$$^-$]$_n$ excitons upon laser irradiation. The increased number of bent trimer excitons concomitant with a decrease in the number of linear trimer excitons in the forward reaction (the writing process) should lead to a higher HE/LE intensity ratio, as observed experimentally.

of these species such that each exciton can be selectively excited with a characteristic wavelength. Among *[Ag(CN)$_2$$^-$]$_3$ trimer exciplexes, the linear isomers are slightly lower in energy than the bent isomers. Although bands characteristic of both isomers are observed, the LE band (C) characteristic of the linear isomer is stronger than the HE band (B) at 77 K (Figure 1), suggesting that the C excitons outnumber the B excitons at that temperature. We suggest that laser irradiation compensates for the slightly higher energy of the bent trimer exciton and, hence, leads to conversion of some of the linear trimer exciplexes to bent ones, leading to the spectral changes at 77 K shown in Figures 3−5 that give rise to the "writing" process.

Because the LE and HE bands were tentatively assigned, respectively, to linear and bent *[Ag(CN)$_2$$^-$]$_3$ (vide supra) and because irradiation leads to the enhancement of the HE emission intensity, we propose that irradiation leads to a change in the distribution of *[Ag(CN)$_2$$^-$]$_n$ excitons with the two different geometries following laser irradiation. The distribution of the excitons is governed by both statistical and, more importantly, thermodynamic factors.[6,7] While a given distribution that favors the LE excitons may exist at a certain temperature (e.g., 77 K), irradiation with 266 nm laser light is proposed to provide the energy difference between that distribution and an alternative distribution that favors the HE excitons. This leads to the writing process. Figure 8 illustrates this hypothesis. The rearrangement proposed here occurs between bound excitons corresponding to Ag−Ag bonded trimer exciplexes while the corresponding ground-state oligomers are virtually unbound. This excited-state transformation can be trapped and detected at cryogenic temperatures. It is important to note that these are photophysical changes that persist only in the excited state, as opposed to permanent photochemical changes. Hence, warming the crystals back to room temperature in the dark (without the laser light) provides the energy that leads to restoring the ground-state geometry of the complexes to be again bound by the weak ground-state Ag(I)−Ag(I) interactions, thus "erasing" the temporary photophysical changes that were trapped at 77 K. When the crystals are cooled again to 77 K, they act as if they had not been irradiated and the original spectra showing greater intensities for the LE bands are regenerated because the crystals do not "memorize" the previous irradiation. The mobility of these excitons in the single crystal decreases upon increasing the strain in the crystal (ionic radii of K$^+$ and Ag$^+$ are 1.33 and 1.26 Å, respectively).[36] An increase in the strain upon increasing the Ag content should lead to slower optical changes.

Conclusions

Laser irradiation of single crystals of doped Ag(CN)$_2$$^-$/KCl and pure KAg(CN)$_2$ results in dramatic changes in their emission spectra. These changes are sensitive to temperature, silver content, and irradiation time. At 77 K, higher-energy (HE) bands that were either absent or weak start appearing concomitant with a quenching of the original major lower-energy (LE) bands as samples are exposed to 266 nm laser light. These changes are progressive with increased irradiation time, and they are also reversible. The fastest changes at 77 K are for doped crystals with low Ag content. The changes are due to changes in the distribution of Ag−Ag bonded *[Ag(CN)$_2$$^-$]$_n$ excitons with different geometries following laser irradiation. The increased number of bent trimer excitons concomitant with a decrease in the number of linear trimer excitons in the forward reaction (the writing process) leads to a higher HE/LE intensity ratio. The work is being expanded to study the effect of the host lattice in doped crystals and counterions in pure crystals on the writing process.

Supporting Information Available: Further spectral data for batch 2 of [Ag(CN)$_2$$^-$]/KCl and pure KAg(CN)$_2$ (pdf). This material is available free of charge via the Internet at http://pubs.acs.org.

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