PHYSICAL REVIEW B, VOLUME 65, 245404

Photostimulated luminescence and dynamics of AgI and Ag nanoclusters in zeolites

Wei Chen,[1] Alan G. Joly,[2] and Joel Roark[1]
[1]*Nomadics, Inc., 1024 South Innovation Way, Stillwater, Oklahoma 74074*
[2]*Pacific Northwest National Laboratory, P.O. Box 999, Richland, Washington 99352*

(Received 2 January 2002; revised manuscript received 15 March 2002; published 28 May 2002)

The photoluminescence and photostimulated luminescence of Ag and AgI nanoclusters formed in zeolite-Y are studied using fluorescence spectroscopy. The photoluminescence spectra of AgI nanoclusters show emission from both AgI as well as Ag nanoclusters which are present in small amounts in the AgI nanoclusters, while in the photostimulated luminescence, only the emission of Ag clusters is observed. While the photoluminescence from both Ag and AgI particles displays subnanosecond and microsecond lifetimes, the emission from photostimulated luminescence shows very short, picosecond lifetimes. A model which ascribes the photostimulated luminescence to recombination of electrons trapped in the zeolite with Ag in close proximity to the trap site is proposed. The appearance of strong photostimulated luminescence with short decays in these systems demonstrates that nanoparticles have potential for digital storage and medical radiology applications.

DOI: 10.1103/PhysRevB.65.245404 PACS number(s): 78.55.−m, 73.22.−f

I. INTRODUCTION

Silver and silver halide (AgX) clusters have been well studied due to their applications in photography where the absorption of light results in the formation of small Ag clusters at the surface of the halide microcrystal. These clusters then catalyze the reduction of the entire AgX microcrystal during the development process. In addition, silver and silver complexes encapsulated in zeolites may be used as photocatalysts for a variety of reactions[1] and as a medium for optical storage.[2] Thus small clusters of these materials such as nanoparticles may offer unique advantages for photosensitive applications. Recently, both Ag and AgI nanoparticles encapsulated within zeolite-Y were shown to exhibit strong photostimulated luminescence.[3,4]

Photostimulated luminescence (PSL) is a process in which trapped charges are released by photons to produce luminescence through recombination with other defect centers. This approach has been used extensively in x-ray radiology.[5,6] The use of BaFBr:Eu^{2+} phosphors, which display the PSL effect, for x-ray storage and imaging, has proved to be one of the most successful detectors in digital radiography.[6] The photostimulated luminescence mechanism of BaFBr:Eu^{2+} involving x-ray irradiation proposed by Takahashi *et al.* assumes that during x-ray irradiation, the Eu^{2+} ions are partly ionized into their trivalent charge state (Eu^{3+}) and the liberated electrons drift via the conduction band to form *F* centers.[5] Upon subsequent photostimulation, the electrons are released from the *F* centers into the conduction band and recombine with Eu^{3+} ions to produce the photostimulated luminescence of Eu^{2+} at 390 nm. More recent results, however, have attributed photostimulated luminescence in this system to the formation of a PSL complex where the charge transfer occurs via a tunneling mechanism.[7,8]

One of the applications of PSL phosphors is medical imaging storage.[5,6] Such phosphors must posses the properties of high density, high brightness, short decay lifetimes, suitable emission and stimulation energies, and low light scattering.[9] The energy gap between the trap states and the conduction band (trap depth) of the phosphors is critical to the effective operation of the detector. The trap depth to the conduction band must be small enough so that stimulation with laser light is possible, yet sufficiently large to prevent random thermal release of the electrons from their traps. Generally, the trap depth should be larger than 0.5 eV to prevent thermal release or fading at room temperature. In addition, the wavelength separation between the stimulation light for reading (corresponding to the color center absorption band) and the emitted light for monitoring must be sufficiently large so that noise signals due to scattered reading light are easily avoided. Ideally, the phosphors should have only one type of trap to reduce signal loss due to electron migration among different traps.[10] To data, there is no PSL phosphor that meets all these requirements. The PSL phosphor used in commercial x-ray imaging systems is BaFBr:Eu^{2+}. However, the BaFBr:Eu^{2+} phosphor suffers from poor readout temporal resolution due to the long decay lifetime of Eu^{2+} emission [0.8 μs (Ref. 6)] as well as scattering of the stimulating laser light from the platelike polycrystals. In addition, the hygroscopic nature of this phosphor limits the stability of the system. Thus a new type of PSL phosphor with improved characteristics is desirable and the subject of extensive investigation.[11–19]

Due to quantum-size confinement, the luminescence efficiency in nanophase materials may be enhanced relative to bulk materials.[20,21] In addition, the luminescence wavelength is tunable with size.[22] Light scattering is significantly reduced in nanoparticles compared with micron-sized particles, since the light scattering intensity is proportional to the decrease of the particle size.[23] Therefore, nanophase materials may represent an efficient PSL phosphor for x-ray storage. The phenomenon of photostimulated luminescence from nanoparticles has recently been reported by several groups.[3,4,15,24] In this article, photostimulated luminescence dynamics from both Ag and AgI nanoparticles encapsulated in zeolite-Y are reported. In principal, the photophysics from these two nanoparticles could be markedly different for AgI is a semiconductor while Ag is metallic. Due to the propensity of silver halides to form small silver clusters on their

0163-1829/2002/65(24)/245404(8)/$20.00

surfaces, studying both types of species together may facilitate better understanding of the mechanisms responsible for the PSL observed in both systems. The photophysics observed in this study from both particles are indeed similar. The results show a significant reduction in the lifetime of the PSL relative to the normal photoluminescence (PL) in both particles. A model that attributes this result to the formation of a zeolite-Ag complex is proposed.

II. PREPARATION AND CHARACTERIZATION

The preparation of Ag and AgI clusters in zeolite-Y (henceforth Ag/Y and AgI/Y) has been reported elsewhere.[3,4] Briefly, Ag^+ ions were first exchanged into the cages of the zeolite. The zeolite powder was slurried in de-ionized water with the acidity adjusted to pH 6 with nitric acid. Silver nitrate was added and the mixture was stirred at room temperature for 2 h. The Ag^+-ion-exchanged zeolite was collected by filtration and then washed with de-ionized water until no Ag^+ was detected in the filtrate. Ag clusters were formed in the zeolite cavities by vacuum heat treatment at 250 °C in the dark. To prepare AgI clusters, the resulting Ag^+-ion-exchanged zeolite powder was slurried in a sodium iodide solution by stirring at 100 °C for 2 h, after which the materials were collected by filtration and washed extensively with deionized water and finally dried and calcined at 250 °C in dark and in vacuum for 2 h. Previous work has shown that these particles are between 1 and 2 nm in size, which corresponds well with the size of the sodalite cages of the zeolite.[4]

The photoluminescence and photostimulated luminescence spectra were recorded on a SPEX FLUOROLOG 3 fluorescence spectrophotometer. A pulsed nanosecond optical parametric oscillator/amplifier (OPO) (Spectra-Physics MOPO-730) operating at a 10-Hz repetition rate was used to collect the PL lifetime data. The output of the OPO was frequency doubled in KDP to produce the PL excitation light. The excitation light was directed onto the particles, and emission was collected at right angles to the excitation and focused into a 1/8-m monochromator equipped with a standard photomultiplier tube. The photomultiplier tube output was directed into a digital oscilloscope to record the emission decays. The response time of the system was measured to be about 15 ns full width at half maximum (FWHM).

The PSL lifetimes were too short to be measured with the nanosecond OPO system. In this case, excitation was provided by the output of a femtosecond regeneratively amplified titanium:sapphire laser system operating at 1 kHz. The 150-fs pulses of this laser at 800 nm and 200 mJ were directed onto the particles, and the emission was collected at right angles and focused onto a streak camera (Hamamatsu C5680). Suitable bandpass and cutoff filters were used to collect the luminescence at different wavelengths. The time resolution was determined to be about 14 ps FWHM using a standard scattering material.

III. RESULTS

A. Photoluminescence and photostimulated luminescence spectra of AgI nanoclusters in zeolite-Y

AgI nanoclusters encapsulated in zeolite-Y show strong luminescence and photostimulated luminescence at room temperature. Figure 1 displays the excitation spectra of AgI/Y particles when monitoring an emission wavelength corresponding to the emission maximum of Ag particles (~510 nm). The excitation peak at 265 nm is due to AgI nanoclusters, while the excitation peak at 305 nm results from Ag nanoclusters.[4] Under UV irradiation at 254 nm, the intensity of the AgI peak decreases, while the intensity of the Ag peak increases. The AgI/Y emission intensity recovers under subsequent illumination using a visible source. Since silver halides are known to produce metallic Ag clusters upon irradiation,[4,25–27] it is not surprising to find significant Ag particle luminescence from the AgI/Y particles. In addition, Ag is known to coexist with AgI in zeolite-Y.[4] Therefore, photoluminescence from Ag clusters is observed in AgI/Y particles even in non-UV-irradiated samples.

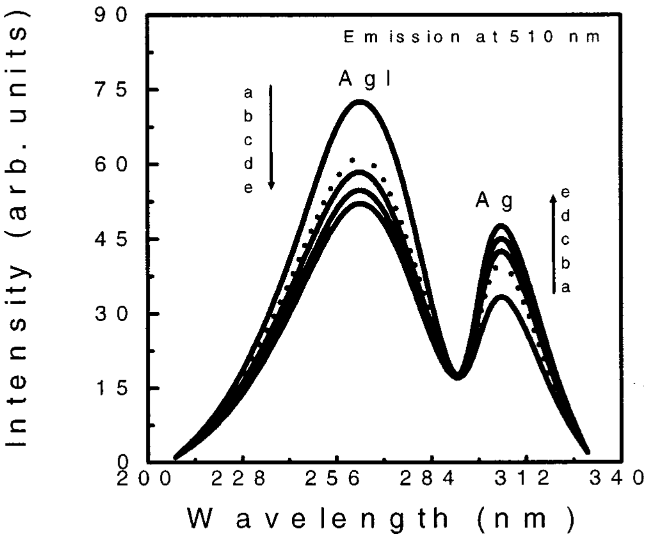

FIG. 1. Fluorescence excitation spectra of AgI/Y before (a) and after UV irradiation at 254 nm for 5 (b), 8 (c), 11 (d), and 15 (e) min, respectively.

Figure 2 shows the PL spectra of AgI/Y following excitation at 305 nm (the peak of the Ag nanocluster absorption). The broad emission band actually consists of two subbands. The first band results from AgI nanoparticle emission peaking at 474 nm and appears as a small, but discernable shoulder on the blue energy edge of the broad emission peak in Fig. 2. The second band results from Ag nanocluster emission centered at 510 nm.[4] The luminescence decreases in intensity when the sample is irradiated by ultraviolet light at 254 nm. This decrease can be partially recovered by exposing the sample to visible light. When AgI/Y particles are excited at 275 nm (near the peak of the AgI absorption), there is a noticeable redshift in the PL spectrum[4] relative to excitation at 305 nm.

After UV irradiation for a few minutes, strong PSL can be detected from AgI nanoparticles in zeolite-Y as shown in Fig. 3. PSL excitation is easily stimulated using near-infrared wavelengths.[4] Figure 3 shows that the emission consists almost exclusively of Ag nanoclusters resulting in a narrower band than the PL emission band, and the PSL emission band is redshifted from the PL emission band.

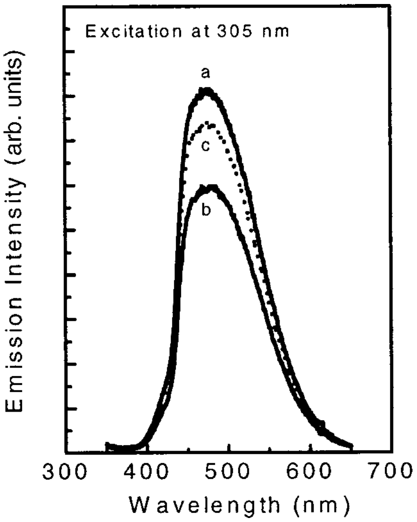

FIG. 2. Photoluminescence spectra of AgI/Y before (a) and after (b) UV irradiation at 254 nm for 5 min. After exposure to a visible lamp for 5 min (c).

Additionally, after UV irradiation, an electron spin resonance signal is detected (Fig. 4). The *g* value (2.002) of this signal is close to that of the *F* center (2.0023), indicating that the signal is from electron centers[28] created either in the zeolite matrix or else in the nanoparticles themselves. These color centers could be the source of the electrons released during the PSL process.

The PSL longevity of AgI/Y nanoparticles was measured by noting the change of PSL intensity with time. At room temperature, the PSL signal loses ~25% of its intensity in 2 h and 50% in 5 h. This degradation is faster than that of BaFBr:Eu^{2+} bulk PSL phosphors, whose decay is only 25% in 8 h.[6] The loss of PSL intensity is related to the trap depth and the sample temperature. Shallower traps and/or higher temperatures reduce the storage time by allowing thermally activated electrons released from the traps to migrate via the conduction band. Those electrons that do not retrap ultimately lead to decreased PSL intensity. In this case, the *F*-center trap depth is likely less than in BaFBr:Eu^{2+}, leading to shorter storage times. Although the storage longevity of AgI nanoparticles is less than BaFBr:Eu^{2+}, nonetheless, viable optical storage is possible with nanoparticle-based systems.

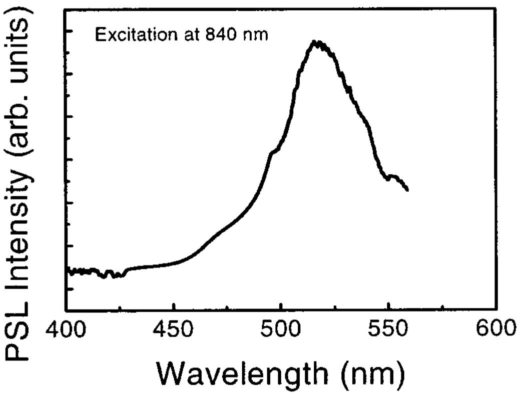

FIG. 3. PSL spectra of AgI/Y after UV irradiation at 254 nm for 10 min. Excitation at 840 nm.

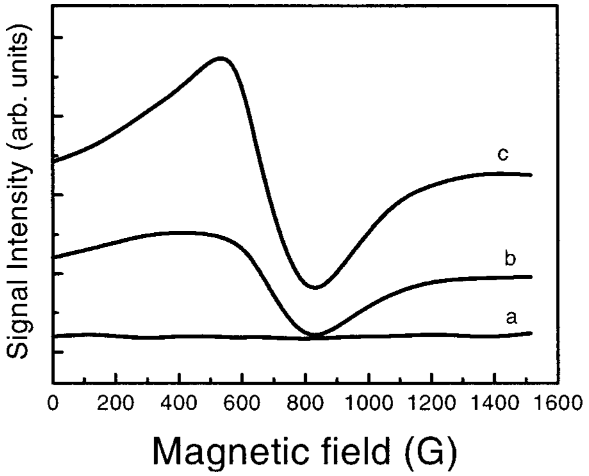

FIG. 4. Electron spin resonance of AgI/Y before (a) and after UV irradiation at 254 nm for 8 min (b) and 15 min (c), respectively.

B. Photoluminescence and photostimulated luminescence spectra of Ag nanoclusters in zeolite-Y

Similarly, Ag nanoclusters in zeolite-Y are photosensitive and exhibit strong photostimulated luminescence. Figure 5 shows the emission spectra of Ag/Y particles following excitation at 310 nm. After UV irradiation at 254 nm for 10 min, the luminescence intensity decreases significantly [Fig. 5(b)]. The luminescence increases in intensity slightly when the sample is then irradiated at 840 nm [Fig. 5(c)]. The luminescence increases further by exposure to a 650 nm light for 10 min [Fig. 5(d)]. The luminescence is almost back to its

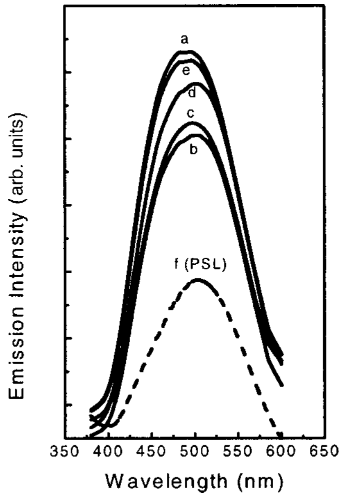

FIG. 5. The 310-nm excited photoluminescence spectra of Ag/Y before (a) and after UV irradiation at 254 nm for 10 min (b), then exposure to 840-nm photons for 10 min (c), then 650-nm photons for 10 min (d), and then to a visible lamp for 10 min (e). Trace (f) is the photostimulated luminescence spectrum stimulated at 840 nm.

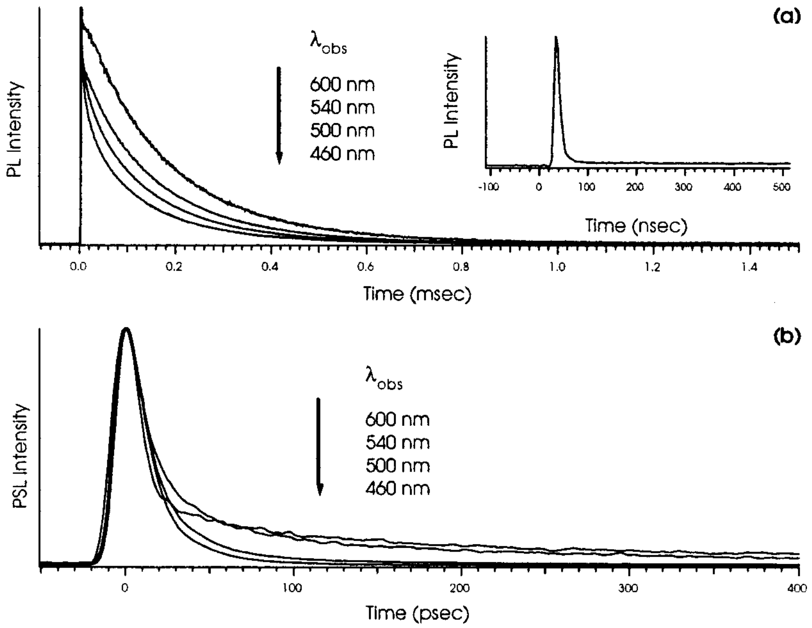

FIG. 6. Lifetime decays of (a) photoluminescence (excitation at 305 nm) and (b) photostimulated luminescence (excitation at 800 nm) in AgI/Y nanoparticles. The inset in (a) displays the PL lifetime at higher time resolution showing the fast (<15 ns) time component.

original intensity after exposing to a visible lamp for an additional 20 min [Fig. 5(e)]. After UV irradiation, strong photostimulated luminescence is observed from Ag nanoclusters, which is shown in Fig. 5(f). As in AgI/Y particles, the PSL spectrum is slightly shifted to a longer wavelength from the photoluminescence spectrum of the clusters. Similar to AgI/Y, Ag/Y particles show a marked decrease in PL after UV irradiation. This decrease is almost completely reversible following irradiation by photons between 650 and 900 nm. Thus both materials may be considered for use as reusable image or digital storage media.

C. Photoluminescence and photostimulated luminescence lifetimes

The photoluminescence and photostimulated luminescence decay lifetimes of AgI/Y are shown in Figs. 6(a) and 6(b). PL and PSL luminescence lifetimes from Ag/Y particles are shown in Figs. 7(a) and 7(b) for comparison. The insets show PL spectra taken with higher time resolution and show the existence of two time regimes. The first is very fast, less than the instrument response of 15 ns. The second regime is on the order of microseconds. Both the fast- and slow-lifetime components are observed at all emission wavelengths.

The microsecond PL and subnanosecond PSL lifetime regimes from both particles show multiexponential behavior at all combinations of emission and excitation wavelengths used in this study. This multiexponential behavior does not allow exact determination of all lifetimes and amplitudes: however, there are some very clear trends which are summarized below and in Table I.

(i) PL from both Ag/Y and AgI/Y show both fast (<15 ns) and slow (microsecond) components at all emission wave-

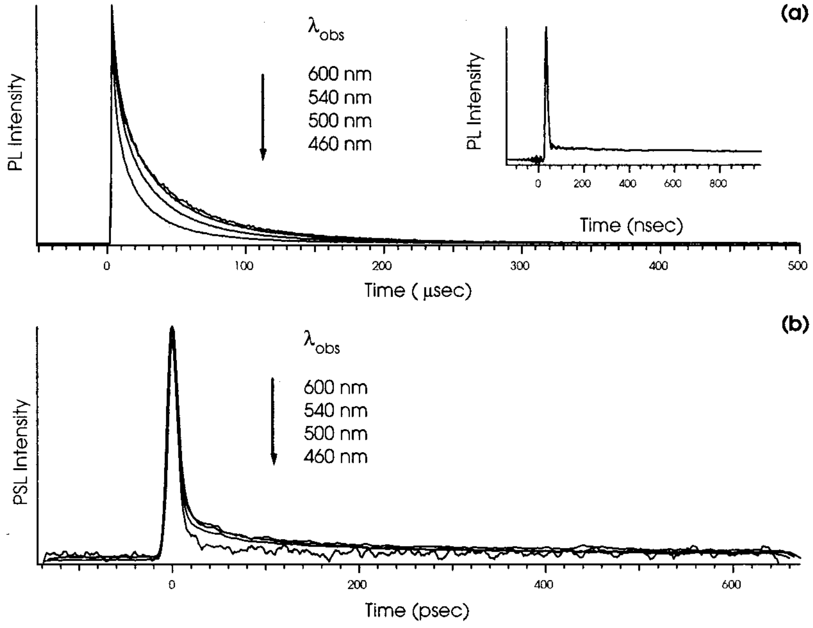

FIG. 7. Lifetime decays of (a) photoluminescence (excitation at 305 nm) and (b) photostimulated luminescence (excitation at 800 nm) in Ag/Y nanoparticles. The inset in (a) displays the PL lifetime at higher time resolution showing the fast (<15 ns) time component.

TABLE I. PL and PSL lifetimes of Ag/Y and AgI/Y nanoparticles. Values shown are the longest decay components of a multi-exponential fit. Errors ± 10%.

	Ag/Y particles		AgI/Y particles	
Emission (nm)	PL lifetime[a] (μs)	PSL lifetime[b] (ps)	PL lifetime[c] (μs)	PSL lifetime[b] (ps)
460	50	160	175	90
500	65	320	185	125
540	67	670	191	170
600	80	830	208	190

[a] Excitation at 350 nm.
[b] Excitation at 800 nm.
[c] Excitation at 275 nm.

lengths following excitation at either 275 or 305 nm. The photoluminescence decay curves obtained at the different excitation wavelengths show a small, but noticeable difference. Due to the multiexponential nature of the lifetimes, it is difficult to ascertain whether this difference is attributable to slight differences in decay times, different relative amplitudes of the decay components, or a combination of both factors.

(ii) For both Ag/Y and AgI/Y particles, the longest PL lifetimes (of the multiexponential decay) are noticeably shorter at blue emission wavelengths than for red emission following excitation at either wavelength. In addition, the longest PL lifetime from Ag/Y particles is about 3 times shorter than that from AgI/Y particles. The longest time component ranges from about 50 to 80 μs in Ag/Y particles, while in AgI/Y nanoclusters, the lifetime ranges from 175 to about 200 μs, depending on monitored emission wavelength.

(iii) The PSL lifetimes from both Ag and AgI show only fast components. The PSL lifetimes are fit with a biexponential decay function convoluted with the instrument response function. The results show that the PSL lifetimes are shorter for red emission wavelengths relative to the blue emission wavelengths for both Ag and AgI particles. There is an instrument limited component at zero time which may be due to extremely fast trapping of the excited electron as has been observed in colloidal AgI nanoparticles.[29] PSL lifetimes for Ag/Y particles are longer than the corresponding lifetimes for AgI/Y particles. For Ag/Y particles the longest component of the biexponential fit varies from 160 ps at 460 nm to 830 ps at 600 nm. In AgI/Y particles, this component ranges between 90 ps at 460 nm to about 190 ps at 600 nm.

IV. DISCUSSION

Any model proposed to explain these results must at a minimum explain the following observations: (1) Photoluminescence from Ag particles is observed following excitation at the absorption maximum of AgI in AgI/Y particles, (2) the observed photostimulated luminescence spectrum from AgI/Y particles is composed almost entirely of luminescence from Ag particles, (3) despite the fact that Ag is a metal and AgI a semiconductor, the PL and PSL lifetimes from both particles are remarkably similar, and (4) in the PL lifetime data of both particles, there are two distinct time regimes, while in the PSL lifetime data, there is only a fast component. Shortened PSL lifetimes relative to PL lifetimes have been observed previously.[12,19] In CaS:Eu, Sm phosphors, the PSL decay time of Eu^{2+} is less than 14 ps,[19] which is much shorter than the spontaneous emission lifetime of Eu^{2+}. Similar results have been observed in $SrAl_2O_4:Eu^{2+}$, Dy^{3+}, where a factor of 3 shortening of the PSL versus the PL lifetimes has been observed.[12] In the above cases this lifetime shortening has been explained as resulting from fast retrapping or lattice relaxation[12] or by resonant energy transfer or rearrangement of the Eu^{2+} levels.[19]

Ag photoluminescence from AgI/Y particles has been observed previously.[4] An ‘‘autoreduction’’ mechanism has been invoked to explain the appearance of Ag along with AgI in these nanoclusters.[4] That is, the zeolite acts to reduce silver cations incorporated in the zeolite cages during the nanoparticle fabrication process, to Ag particles. In addition, irradiation of AgI is known to produce small Ag clusters on the surface[4,25–27] and the PL results on AgI/Y indicate that UV irradiation produces an increase in Ag luminescence concurrent with a decrease in the AgI luminescence. Therefore, it is reasonable to conclude that there are small Ag clusters likely on the surface of the AgI particles. The fact that excitation of AgI results in luminescence from Ag particles reveals that energy transfer takes place between the two species as has been observed previously.[4] The close proximity of the two moieties would facilitate such transfer. Similar results have been reported for nanoscale silver oxide.[30]

Figure 3 demonstrates that PSL from AgI/Y particles is dominated by the luminescence from Ag particles. In addition, both systems show extremely fast PSL decay times. Although these decay times differ by about a factor of 3, they do not show the large differences that might be expected given that Ag is a metal while AgI is a direct-band-gap semiconductor. The differences in PL and PSL lifetimes may well reflect the different energetics between the two, but these differences are not extremely pronounced. In addition, both particles show identical PL and PSL lifetime behaviors i.e., both fast and slow components in the PL versus only a fast component in the PSL. These observations lead to the conclusion that the PSL photophysics within AgI/Y particles is primarily determined by Ag clusters on the surface of the AgI nanoclusters.

The PL lifetimes from both particles show multiexponential behavior with two very distinct time regimes: a fast ($<$15 ns) and a slow (50–100 ms) time scales. Two distinct subsets either of Ag or AgI particles or environments within the zeolite sample would produce such results. There are many possible explanations for the existence of these two time regimes. (i) The fast decay may be a result of differences in the strength of the transition moment of some species relative to others. This could be the result of stronger interaction with the zeolite. (ii) One subset may be from clusters within the sodalite cages, while the other is from clusters within the supercages of the zeolite. Interactions between the Ag or AgI moiety and the different cage types of the zeolite could result in two distinct subsets. (iii) There could be two different sizes or conformations of clusters within the cages: for instance, one with a smaller number of atoms (molecules) and one with a larger number. (iv) One subset may have an extremely efficient nonradiative decay pathway available relative to the other species. Coupling to trap states in the zeolite or trapping of the excitations within the nanoparticle could account for the fast decay. The slower decay would then be from a subset of particles which have either different configurations or environments such that efficient trapping does not occur.

To sort out these possibilities, it is important to note that the size of the particles is consistent with formation only within the smaller sodalite cages: no evidence of larger nanoclusters residing in the supercages is present. Therefore, it is unlikely (ii) is correct. Matrix isolated Ag clusters are known to have different absorption and emission spectra depending on size[31–37] and conformation.[37] If different sizes or conformations produced the two distinct subsets, some PL emission wavelengths should have all or mostly the fast-decay component and other wavelengths mostly the slow component. Both components are observed at all emission wavelengths, indicating that selective emission based on cluster size or conformation is unlikely to be the cause of the two time regimes. This casts doubt on explanation (iii). Previous optical measurements of Ag clusters in zeolites have noted that the spectra are similar to Ag clusters in rare-gas matrices.[38] These interactions are considered weak,[39] and therefore it is unlikely that such interactions would lead to a drastic change in the electronic transition moment. Therefore, explanation (i) may be ruled out. The conclusion that the fast-time decay arises from a subset of species that couple to efficient trap sites either within the nanocluster themselves or within the zeolite framework, provides a plausible explanation for the observed results. Short excited-state lifetimes have been observed in AgI colloidal nanoparticles by femtosecond transient absorption.[29] These short lifetimes have been related to trapping and nonradiative electron-hole recombination within the nanoparticles.[29] Trapping to states within the zeolite would also serve to shorten the observed lifetimes. Efficient electron trapping in the zeolite must occur in order to observe the photostimulated luminescence. In addition, trapping may occur at other sites both within the zeolite or the nanoclusters. The slower, microsecond luminescence then originates from species that are not efficiently coupled to the trap states.

Figure 8 displays an energy level schematic that explains the photophysics in these nanoparticles and the nature of the trap sites. In order to understand the observed results, the likely geometrical and chemical distribution of both Ag and AgI clusters within the zeolite must be considered. After ion exchange, Ag^+ cations are encapsulated into the zeolite cages. In the formation of AgI nanoclusters, reaction with I^- anions produces AgI nanoclusters in the zeolite cages, while there are still some Ag^+ ions that coexist along with the AgI clusters.[4] In either case, the Ag^+ ions are "autoreduced" to Ag^0 when the samples are heated in vacuum according to the following reaction:[40]

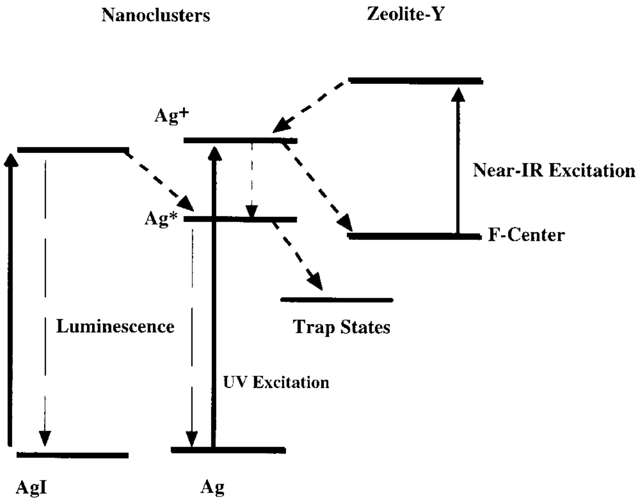

FIG. 8. Energy level schematic depicting the various photophysical processes in Ag/Y and AgI/Y nanoparticles. Solid lines represent photon excitation, dashed lines represent luminescence, and dotted lines represent energy transfer between levels.

$$2Ag^+ + ZO^{2-} \rightarrow 1/2O_2 + 2Ag^0 + Z,$$

where ZO^{2-} represents a zeolite framework, and Z represents a zeolite framework with a missing oxygen link (oxygen vacancy), i.e., with a Lewis acid site. The autoreduced Ag is most likely in close proximity and coupled to the Lewis acid site forming an Ag-Z complex at the interface. Because this complex is at the interface of the particle and the zeolite, it will have additional trap sites (represented as trap states in Fig. 8), such as surface states, available as well.

Excitation of AgI particles results in PL from either AgI or else Ag via efficient energy transfer (Fig. 8). This leads to the slower, microsecond luminescence if the particle is not efficiently coupled to the trap sites in the zeolite or nanocluster. The near-UV photons used in these experiments are not capable of generating free electrons and holes in the zeolite framework. Hence Ag^0 is likely ionized to Ag^+ by UV irradiation ($Ag^0 \rightarrow Ag^+$) leading to both a source of electrons, and a luminescent center, Ag^+. The ionized electron may be captured in the Lewis acid sites (oxygen vacancies) that are the acceptors of electrons and/or in trap states of AgI or Ag nanoclusters. These electron centers are likely responsible for the electron spin resonance (ESR) signal. The trapped electrons in the zeolite Lewis acid sites produce the F-center near-infrared absorption required to stimulate PSL. Upon further irradiation with low energy photons, these electrons are released and may recombine with the Ag^+ centers through either tunneling or through the conduction band, both scenarios have been invoked to explain PSL.[5,7,8,13,18] The photoreleased electron may recombine with Ag^+ to give the emission of Ag^0 as follows:

$$e + Ag^+ \rightarrow Ag^{0*} \rightarrow Ag^0 + h\lambda,$$

where e represents electrons released from the color center, Ag^{0*} is the excited state of the Ag cluster, and Ag^0 is the ground electronic state after emitting the photons ($h\lambda$). As a result, in either AgI/Y or Ag/Y particles, only PSL from Ag particles is observed. The PSL emission displays only the fast decay due to the proximity of the nanoparticles with trap sites either within the zeolite or at the surface and interface of the complex. Thus the PSL originates from the Ag-*Z* complex at the interface of the nanoparticles and the zeolite. Likewise, recent results of PSL from BaFBr:Eu^{2+} phosphors postulate that the PSL originates at interfaces defined by grain boundaries and dislocations.[8] The subnanosecond PL lifetime component also likely originates from this complex.

Not all Ag clusters will reside near a Lewis acid site in the zeolite however. Nor is it likely that all AgI/Y particles have Ag clusters associated with them. Those clusters that do not have access to efficient trap states will, upon irradiation, display the longer (microsecond) lifetime decays similar to that reported for AgBr nanoparticles.[41] However, those clusters of either Ag or AgI particles that have an Ag particle in close association with a Lewis acid site will have an extremely short lifetime and become the luminescent center upon photostimulation. In addition, there may be other trap sites within the zeolite and migration may occur between them as has been postulated previously.[10] The existence of additional trap sites and transfer between them only serves to shorten the lifetime further. This mechanism is similar to one proposed to explain PSL in a number of x-ray storage materials.[7,8,13,18] In this case, PSL complexes are formed which have the active luminescent center and electron trap in close proximity. Tunneling serves to connect the two species. In the present case, the Ag^{+}-*Z* site serves as a PSL complex where excitation of the electron from its trap within the zeolite results in transfer to the Ag^{+} center.

In addition to the fast and slow regimes evident in the lifetime data, there is significant lifetime decay dispersion with respect to emission wavelength in both the PL and PSL. In both cases, red emission wavelengths have slower lifetime decays than the blue wavelengths. This can be explained by noting that small Ag clusters have different absorption and emission wavelengths depending on size[31–37] and geometry.[37] Sodalite cages in zeolite-Y are on the order of 1.3 nm: therefore, only small Ag and AgI clusters may fit inside. It is likely therefore that there exists a distribution of small cluster sizes or conformations within the cages. This inhomogeneity could result in multiexponential decay lifetimes as well as the dispersion of the lifetimes with wavelength. Thus red emission wavelengths may probe different sizes or conformations of the clusters relative to others. The fact that the PSL spectra from both particles is redshifted from the PL may be a result of certain cluster sizes or conformations being more efficiently coupled to the zeolite oxygen vacancies. The slight differences observed in the PL decay curves depending on the excitation wavelength are also likely due to these different sizes or conformations. Different excitation wavelengths may allow partial photoselection of the size, conformation, or environment (proximity and/or coupling to the zeolite) of the clusters.

Finally, PSL observed from AgI/Y particles is qualitatively stronger than PSL from the Ag/Y particles. The PSL lifetimes are also shorter in AgI/Y compared to Ag/Y. It is unclear from the data whether these differences reflect the different energetics between the two particles or are a result of other factors. Therefore, AgI/Y may be a better material for x-ray storage relative to Ag/Y. However, these short lifetimes and strong PSL make both of these materials good candidates for new phosphor screens because of the significantly enhanced readout rates possible. These materials may also be useful for digital storage applications.

V. CONCLUSION

In summary, strong photoluminescence and photostimulated luminescence are observed from Ag and AgI nanoclusters formed in zeolite-Y. The PL lifetimes demonstrate the existence of two subsets of nanoparticles: one with a long (microsecond) lifetime and the other with a much shorter, subnanosecond lifetime. In contrast, PSL lifetimes show only a fast, picosecond lifetime. The origin of the photostimulated luminescence is ascribed to the formation of a PSL complex between interfacial Ag^{+} and Lewis acid sites in the zeolite in close proximity, while the PL originates from both the PSL complex and from nanoparticles which are not strongly coupled to the zeolite oxygen vacancies. The strong photostimulated luminescence with short decay lifetime demonstrates that nanoparticles have promising application in digital storage and medical radiology.

ACKNOWLEDGMENTS

Two of the authors (W.C. and J.R.) would like to thank Nomadics, Inc., the National Science Foundation (NSF), and the National Institute of Health (NIH) for financial support. The authors are grateful to W. Hess for valuable discussions and useful comments on the manuscript. Part of the research described in this paper was performed at the W. R. Wiley Environmental Molecular Sciences Laboratory, a national scientific user facility sponsored by the Department of Energy's Office of Biological and Environmental Research and located at the Pacific Northwest National Laboratory (PNNL). PNNL is operated by Battelle for the U.S. Department of Energy under Contract No. DE-AC06-76RLO1830.

---

[1] T. Sun and K. Seff, Chem. Rev. **94**, 857 (1994), and references therein.

[2] Yokono *et al.*, Japanese patent SHO-61-61894.

[3] W. Chen, Z. Wang, L. Lin, J. Lin, and M. Su, Phys. Lett. A **232**, 391 (1997).

[4] W. Chen, Z. Wang, Z. Lin, L. Lin, K. Fang, Y. Xu, M. Su, and J. Lin, J. Appl. Phys. **83**, 3811 (1998).

[5] K. Takahashi, K. Kohda, J. Miyahara, Y. Kanemitsu, K. Amitani, and S. Shionoya, J. Lumin. **31–32**, 266 (1984).

[6] M. Sonda, M. Takano, J. Miyahara, and H. Kato, Radiology **148**, 833 (1983).

[7] H. von Seggern, T. Voigt, W. Knupfer, and G. Lange, J. Appl.

Phys. **64**, 1405 (1988).

[8] A. M. Gurvich, R. S. Mil'shtejn, M. G. Myakhkova, S. I. Golovkova, J. Ruediger, and V. P. Kavtorova, Radiat. Prot. Dosim. **34**, 265 (1990).

[9] M. K. Crawford and L. H. Brixner, J. Lumin. **48–49**, 37 (1991).

[10] W. Chen, Q. Song, and M. Su, J. Appl. Phys. **81**, 3170 (1997).

[11] P. K. Bandyopadhyay, G. W. Russell, and K. Chakrabarti, Radiat. Meas. **30**, 51 (1999).

[12] W. Jia, H. Yuan, S. Holmstrom, H. Liu, and W. M. Yen, J. Lumin. **83–84**, 465 (1999).

[13] H. von Seggern, A. Meijerink, T. Voigt, and A. Winnacker, J. Appl. Phys. **66**, 4418 (1989).

[14] J. Gasiot, P. Braunlich, and J. P. Fillard, Appl. Phys. Lett. **40**, 376 (1982).

[15] Y. Masumoto and S. Ogasawara, J. Lumin. **87–89**, 360 (2000).

[16] K. Chakrabarti, V. K. Mathur, L. A. Thomas, and R. J. Abbundi, J. Appl. Phys. **65**, 2021 (1989).

[17] W. Jia, H. Yuan, L. Lu, H. Liu, and W. M. Yen, J. Lumin. **76–77**, 424 (1998).

[18] A. Meijerink and G. Blasse, J. Phys. D **24**, 626 (1991).

[19] W. Fan, Y. Wang, X. Hou, L. Du, W. Zhao, B. Yang, and L. Niu, J. Appl. Phys. **85**, 451 (1999).

[20] W. Chen, R. Sammynaiken, and Y. Huang, J. Appl. Phys. **88**, 1424 (2000).

[21] J. Yu, H. Liu, Y. Wang, F. E. Fernandez, and W. Jia, J. Lumin. **76–77**, 252 (1998).

[22] Vol. 4 of *Handbook of Nanostructured Materials and Nanotechnology, Optical Properties*, edited by Hari Singh Halwa (Academic, San Diego, 2000).

[23] M. Kaszuba, J. Nanopart. Res. **1**, 405 (1999).

[24] Y. Masumoto and S. Ogasawara, Jpn. J. Appl. Phys., Part 2 **38**, L623 (1999).

[25] T. Tan and M. Murofushi, J. Imaging Sci. Technol. **38**, 1 (1994).

[26] J. F. Hamilton, Adv. Phys. **37**, 359 (1988).

[27] O. I. Micic, M. Meglic, D. Lawless, D. K. Sharma, and N. Serpone, Langmuir **6**, 487 (1990).

[28] J. R. Shulman and W. D. Compton, *Color Centers in Solids* (Pergamon, New York, 1962).

[29] M. C. Brelle and J. Z. Zhang, J. Chem. Phys. **108**, 3119 (1998).

[30] L. A. Peyser, A. E. Vinson, A. P. Bartko, and R. M. Dickson, Science **291**, 103 (2001).

[31] A. P. Marchetti, A. A. Muenter, R. C. Baetzold, and R. T. McCleary, J. Phys. Chem. B **102**, 5287 (1998).

[32] W. Harbich, S. Fedrigo, F. Meyer, D. M. Lindsay, J. Lignieres, J. C. Rivoal, and D. Kreisle, J. Chem. Phys. **93**, 8535 (1990).

[33] I. Rabin, W. Schulze, and G. Ertl, J. Chem. Phys. **108**, 5137 (1998).

[34] S. Fedrigo, W. Harbich, and J. Buttet, J. Chem. Phys. **99**, 5712 (1993).

[35] C. Felix, C. Sieber, W. Harbich, J. Buttet, I. Rabin, W. Schulze, and G. Ertl, Phys. Rev. Lett. **86**, 2992 (2001).

[36] C. Felix, C. Sieber, W. Harbich, J. Buttet, I. Rabin, W. Schulze, and G. Ertl, Chem. Phys. Lett. **313**, 105 (1999).

[37] I. Rabin, W. Shultze, G. Ertl, C. Felix, C. Sieber, W. Harbich, and J. Buttet, Chem. Phys. Lett. **320**, 59 (2000).

[38] R. Kellerman and J. Texter, J. Chem. Phys. **70**, 1562 (1979).

[39] G. A. Ozin, F. Hugues, and S. M. Mattar, J. Phys. Chem. **89**, 300 (1985).

[40] P. A. Jacobs, J. B. Uytterhoeven, and H. Beyer, J. Chem. Soc., Faraday Trans. 1 **75**, 56 (1979).

[41] M. I. Freedhoff, A. P. Marchetti, and G. L. McLendon, J. Lumin. **70**, 400 (1996).