

Experiments with Glow-in-the-Dark Toys: Kinetics of Doped ZnS Phosphorescence

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Many semiconductors exhibit the property of phosphorescence, the phenomenon whereby a material excited by visible or ultraviolet radiation glows (i.e., emits visible light) for a substantial time after the excitation source has been removed. Absorption of visible or ultraviolet radiation, from sunlight or room lights, causes excitation of electrons and produces nonequilibrium concentrations of electrons and holes in the solid. Light is emitted as the electrons recombine with the holes, a process that occurs at a rate dependent on the material and the temperature. One phosphorescent semiconductor commonly used in glow-in-the-dark toys and emergency signs is copper-doped zinc sulfide (ZnS:Cu), a material that produces a yellow-green glow. We have found the study of this light emission to be a suitable introduction to kinetics and to semiconductors.

Experimental Procedure

A Glow-Yo yo-yo (Duncan #3057NP) and an Amazing Glow Ball (Noteworthy #GB0565B Baseball) were obtained from Toys-R-Us. We also obtained copper-doped zinc sulfide Glow-in-the-Dark Phosphorescent Pigment (P-1000) and Glo-Vinyl Tape (such as used in theaters) from Hanovia Division of Conrad, 100 Chestnut St., Newark, NJ 07105.

Samples were placed in a Shimadzu RF-5000 Spectrofluorophotometer and excited with ambient light or a 120-W flood lamp. The sample compartment was then closed and either an emission spectrum was recorded or the kinetics were followed at 530 nm by recording the emission intensity every second for several minutes. A 3-nm slit width was used on the emission monochromator and the spectrometer was operated at low sensitivity. Data recording began when light emission was on scale.

For variable temperature experiments the sample was placed in a glass cell and the temperature controlled by circulating water over the sample from a GCA Precision R40 constant-temperature bath. A dark cloth was used to cover the glass cell in the instrument compartment in order to avoid the interference of outside light. For data taken below 25 °C, nitrogen gas was used to purge the sample compartment to avoid water condensation. The yo-yo was cut on a band saw to fit snugly in the glass cell. The Hanovia P-1000 pigment was well mixed with DER 324 resin and DEH 24 hardener (Dow Chemical Co.); the epoxy hardened into a pellet, which was anchored in the glass cell by the use of small weights.

Data were also recorded using a cadmium sulfide photocell (Radio Shack 276-196) connected to an ohm-

meter. The excited sample and photocell were placed in a dark box and the resistance was recorded as a function of time.

Samples of doped ZnS were prepared in an inert atmosphere at 950 °C according to the literature procedure (1) from phosphor grade ZnS (specify phosphor grade when ordering from Aldrich Chemical Co., Milwaukee, WI, or Prochem Inc., Rockford, IL). Different dopants produced different luminescent colors: Ag, light blue; Mn, light orange; Cu, yellow-green. All had considerably shorter phosphorescent lifetimes than the commercial P-1000 material.

Results and Discussion

ZnS is a semiconductor, a material with an electron-filled lower energy valence band and an empty upper conduction band (2). ZnS:Cu contains a copper dopant present as Cu^+ , presumably occupying a Zn^{2+} site. For every two Cu^+ ions that replace Zn^{2+} ions there would be one S^{2-} ion vacancy to compensate charge. [Charge balance schemes other than sulfur vacancies that have been used to prepare ZnS:Cu involve the simultaneous doping of Cu^+ for Zn^{2+} with either Al^{3+} for Zn^{2+} or Cl^- for S^{2-} (3).]

ZnS is known to have an energy gap between the two bands of about 350 kJ/mol (3.6 eV). Given the large band gap of ZnS, a very small concentration of mobile holes and electrons is expected from autoionization. In the case of ZnS:Cu-based, glow-in-the-dark materials, the electronic energy level of the doped copper site falls within the band gap (4). Illumination by ambient light excites electrons from intraband-gap-doped copper sites to the conduction band by several routes. (See Figure 1.)

When electrons from the conduction band recombine with holes in the copper level, light is given off. The wavelength of maximum emission intensity for the glow-in-the-dark samples corresponds to a photon energy of about 220 kJ/mol (540 nm). In the absence of illumination, the population of excited-state electrons decreases with time, the number of electrons returning to the copper-site holes decreases, and the amount of light given off decreases.

Figure 2 shows the emission spectrum for the Glow Ball recorded every 30 s. The emission intensity decreases with time and the maximum intensity wavelength changes minimally. All of the samples tested had a maximum wavelength between 520 and 540 nm. There may be a small variation in copper-site energy levels; if so the slight observed shift to longer phosphorescence wavelength with time is consistent with the higher en-

ergy transitions decaying at a slightly faster rate.

In studying the rate of phosphorescence, illumination produces a population of excited states. We take the emission intensity produced by the recombination of electrons and holes, having concentrations n and p , respectively, to be proportional to the excited-state population.

In zero-order kinetics the rate at which the phosphorescence intensity diminishes will be independent of the concentrations of electrons and holes. A plot of intensity versus time should be linear. This was not observed. [See Figure 3 (top).]

In first-order kinetics the rate would depend on either the concentration of electrons or of holes. Exponential or multiexponential phosphorescence decay might be expected for a semiconductor (5). Simple first order decay, where $[A]$ is the concentration of the excited state, yields

$$\text{rate} = \frac{-d[A]}{dt} = k[A]$$

Integrating with respect to time,

$$\int_0^t \frac{d[A]}{[A]} = -k \int_0^t dt$$

results in

$$\ln [A] - \ln [A]_0 = -kt$$

A plot of $\ln [A]$ versus time should be linear with a slope equal to minus the rate of the reaction. Our data did not fit simple exponential decay for any of our samples. (See Figure 3 [middle] for example.) Curve-fitting to multiexponentials was similarly poor. First-order kinetics might be expected for a doped semiconductor with $n \gg p$ or $p \gg n$, in which case the concentration of the particle in the minority (holes in an n-type semiconductor, electrons in a p-type semiconductor) will vary considerably during the return to the ground-state equilibrium and control the rate of light emission.

In second-order kinetics the rate of light emission would depend on the concentrations of both electrons and holes. Second-order decay, where the rate-determining step involves two equal concentrations, yields

$$\text{rate} = \frac{-d[A]}{dt} = k[A]^2$$

Integrating with respect to time,

$$\int_0^t \frac{d[A]}{[A]^2} = -k \int_0^t dt$$

results in

$$\frac{1}{[A]} - \frac{1}{[A]_0} = kt$$

A plot of $1/[A]$ versus time should be linear with a slope equal to the rate of the reaction. Data from our samples of Glo-Yo yo-yo, the Amazing Glow Ball, two samples of P-1000 pigment, and Glo-Vinyl Tape all fit this equation. [See Figure 3 (bottom) for example.] Second-order kinetics might be expected for a semiconductor with n equal or nearly equal to p .

A literature summary (5–8) indicates that an abrupt drop in brightness (probably exponential) followed by a slow power-law decay, $I = a/(t+t_0)^b$ with b in the range of

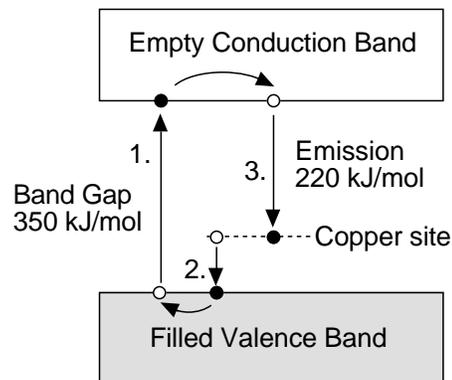


Figure 1. Energy diagram for ZnS:Cu phosphorescence. 1. An electron is excited from the filled valence band to the empty conduction band. 2. An electron from the copper site fills the valence band hole, $\text{Cu(I)} - e^- \rightarrow \text{Cu(II)}$. 3. Combination of a conduction band electron with a copper site hole, $\text{Cu(II)} + e^- \rightarrow \text{Cu(I)}$, produces light emission in a slow step. Excitation with less than band gap energy can also occur by the reverse of step 3.

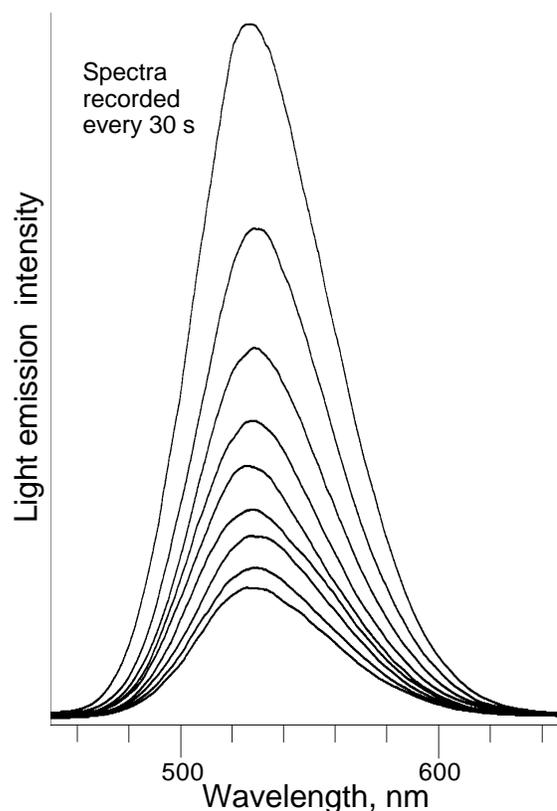


Figure 2. Emission spectra recorded every 30 s for a foam Glow-Ball after prior excitation with ambient light. Data were recorded using 3-s scans and a 3-nm slit width. The peak maximum occurs at about 525 nm and increases slightly in wavelength as the emission decays. Similar results were observed for all samples.

0.2 to 2, is generally observed for sulfide phosphors. Our data are consistent with these observations. The data in Figure 3 can be curve-fit (9) to $I = a/(t+t_0)^b$ yielding $a = 52428$, $t_0 = 54$, and $b = 0.986$ with a correlation coefficient of .9999. Use of this equation is problematic because intensity values depend strongly on t_0 , the time between infinite emission intensity and the start of data gathering. All samples tested for temperatures between 10 and 80 °C fit this equation with correlation coefficients of .9999 or better, with b ranging between 1 and 1.2. By using the normal second-order decay equation [the inverse of $I = a/(t+t_0)^b$, where $b = 1$, is $1/I = kt + \text{constant}$], comparison of rates is simplified. Evidence for a faster initial decay was observed by cooling the sample in a clear dewar flask containing liquid nitrogen. The complicated decay observed was much quicker than at room temperature and was curve-fit to a value of $b = 0.4$, suggesting that an initial fast process had been slowed enough to be observed.

We were also interested in whether a simple photocell could serve as a light-detection apparatus. Figure 4 was drawn from data obtained using a CdS photocell and gives similar results to those obtained in Figure 3. All that is required for students to obtain kinetic data is a photocell, ohmmeter, and a glow-in-the-dark sample. P-1000 suspended in epoxy in a test tube that fits a blocktronic provides a convenient device. Data taken every 10–15 s for 2 min are sufficient.

Two Glow-Yo yo-yos, one at room temperature and one in hot water, can be used to demonstrate the effect of temperature on reaction rate. Darkening the room starts the demonstration. The yo-yo at elevated temperature is brighter and returns more quickly to the ground state than the colder yo-yo. In order to quantitatively measure the activation energy for the phosphorescence of the glow-in-the-dark samples, emission intensity rate data were recorded at a series of different temperatures. Figure 5 (top) shows the plots of second-order decay versus time for temperatures between 10 and 80 °C for the Hanovia P-1000. The slope of the line increases with respect to temperature.

The Arrhenius equation is

$$\text{rate} = Ae^{(-E_a/RT)}$$

where E_a is the activation energy, R is the molar gas constant, T is the absolute temperature, and A is a constant. Taking the natural log of each side,

$$\ln(\text{rate}) = \ln(A) - E_a/(RT)$$

and further simplifying gives

$$\ln(\text{rate}) = \ln(A) - (E_a/R) \times (1/T)$$

A plot of $\ln(\text{rate})$ versus $1/T$ should be linear with a slope of $-E_a/R$.

The yo-yo had an activation energy of 9 kJ/mol. One batch of P-1000 pigment had an activation energy of 14 kJ/mol, while a second lot had an activation energy of 17 kJ/mol. [See Figure 5 (bottom).]

In general, reaction rates obtained from samples placed in the glass cell were slightly lower than rates obtained when the sample was placed in open air. This may be because the glass will absorb UV light and not excite electrons to higher energy levels in the sample.

In an attempt to further characterize the ZnS:Cu (10), we doped ZnS according to literature procedures. Different dopants produced different luminescent colors (see **Experimental Procedure**). Cu doping did produce the yellow-green luminescence observed for the glow-in-

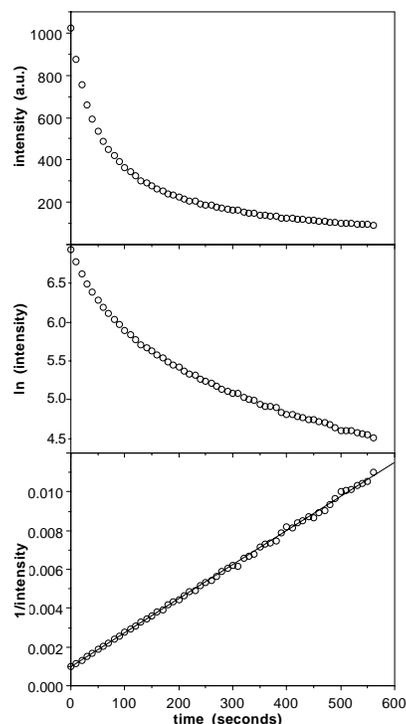


Figure 3. Top: Emission intensity (arbitrary units) for Hanovia P-1000 pigment after excitation with a 120-W flood lamp and recorded with a spectrofluorophotometer. Data in the figure are plotted for 10-s intervals. Similar results were observed for all samples. Middle: Natural log of the emission intensity as a function of time. A linear plot is expected for first-order decay. Bottom: Inverse emission intensity as a function of time. A linear plot is expected for a second-order reaction. The slope of this line is the rate of the decay.

the-dark toys. We found that doping “phosphor grade” ZnS was necessary to produce material exhibiting phosphorescence, albeit at greater expense and having much shorter lifetimes than for commercial P-1000. According to one supplier (Novak, R. Prochem Inc., Rockford, IL; personal communication, 1994), phosphor-grade ZnS has been treated with H_2S .

Conclusions

The glow-in-the-dark materials used in the P-1000 pigments, as well, apparently, as many of the glow-in-the-dark toys, are made of zinc sulfide doped with copper (ZnS:Cu).

The emission of the ZnS semiconductor is not across the band gap, but involves interband traps associated with the Cu doping material. The phosphorescence decay of ZnS:Cu fits a second-order equation, consistent with recombination of relatively equal populations of holes and electrons ($n \sim p$).

The delocalized electrons in the conduction band must overcome a small but measurable activation energy of about 15 kJ/mol to fall back to the localized copper-site holes for the recombination that produces phosphorescence.

Acknowledgments

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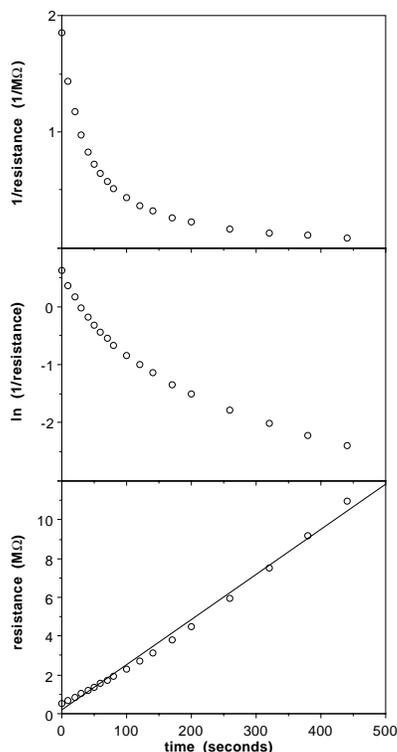


Figure 4. Top: Emission intensity (conductance or $1/\text{resistance}$) of a cadmium sulfide photocell measured with an ohmmeter for a Glow-Yo yo-yo after excitation with a 120-W flood lamp. Similar results were observed for all samples. Middle: Natural log of the emission intensity as a function of time. A linear plot is expected for first-order decay. Bottom: Inverse emission intensity as a function of time. A linear plot is expected for a second-order reaction. The slope of this line is the rate of the decay.

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10. The doping agent is identified as copper in the MSDS for Hanovia P-1000 pigment.

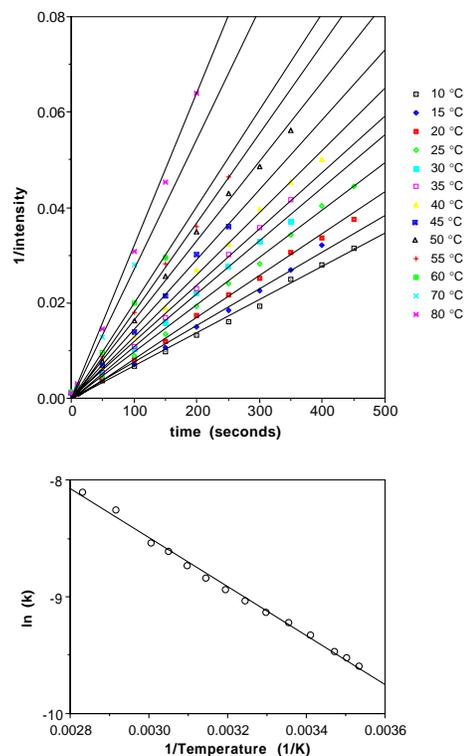


Figure 5. Top: Inverse emission intensity plotted every 50 s for Hanovia P-1000 pigment after excitation with a 120-W flood lamp and recorded with a spectrofluorophotometer. Data were taken for various temperatures between 10 and 80 °C. The slopes of the lines increase as the temperature increases, signifying a faster rate constant at higher temperature. Bottom: Natural log of the reaction rate constant plotted against inverse absolute temperature. The slope of this line is used to calculate the activation energy of the reaction according to the Arrhenius equation. For this set of data, the slope is $-E_a/R = -2100$ K, which corresponds to an activation energy of 17 kJ/mol.