

## Thermoluminescence in Sodium Silicate by uv Excitation

S. A. A. Winer and R. Chen

Citation: *The Journal of Chemical Physics* **51**, 4530 (1969); doi: 10.1063/1.1671823

View online: <http://dx.doi.org/10.1063/1.1671823>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/51/10?ver=pdfcov>

Published by the **AIP Publishing**

---

### Articles you may be interested in

[The structure of sodium silicate glass](#)

*J. Chem. Phys.* **93**, 8180 (1990); 10.1063/1.459296

[A molecular dynamic calculation of the structure of sodium silicate glasses](#)

*J. Chem. Phys.* **71**, 4570 (1979); 10.1063/1.438210

[Thermoluminescence in Vitreous Sodium Silicate](#)

*J. Chem. Phys.* **44**, 2262 (1966); 10.1063/1.1727032

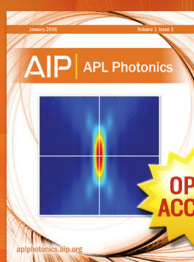
[Experimental Study of the Mechanism of Thermoluminescence in Irradiated Sodium Chloride](#)

*J. Chem. Phys.* **23**, 652 (1955); 10.1063/1.1742071

[The Scattering of Light by Sodium Silicate Solutions](#)

*J. Chem. Phys.* **17**, 664 (1949); 10.1063/1.1747356

---



Launching in 2016!

The future of applied photonics research is here

OPEN  
ACCESS

**AIP** | APL  
Photonics

has a half-width roughly that of the energy separation of the individual crystal bands. This is seen with special clarity in the results of laser Raman studies<sup>50</sup> on these glasses and crystals shown in Fig. 7. In Fig. 7 the crystalline material is the compound  $\text{TlNO}_3 \cdot \text{Cd}(\text{NO}_3)_2$ , the presence of two separate  $A_1'$  bands, at 1032 and 1057  $\text{cm}^{-1}$ , showing that the crystal contains two distinct nitrate ion environments. The spectra of two different vitreous mixtures, of compositions 1:1  $\text{NaNO}_3\text{-Cd}(\text{NO}_3)_2$  and 1:1  $\text{AgNO}_3\text{-Cd}(\text{NO}_3)_2$ , are compared with this crystal spectrum in the two parts of Fig. 7. (The spectra in each part were obtained with different instruments—see Fig. 7 caption.) Although the glass and crystal samples differ in their monovalent cations, the effect of disordering the particles is essentially the same—the two sharp peaks are replaced by a broad band having a half-width roughly that of the crystal spectrum.

The observation implies that in the amorphous phase there is a *distribution* of environments for the nitrate ions spanning the range provided by the component crystals, and an equivalent range of perturbations of the “free ion” frequencies by the “crystal” field. The 3- $\text{cm}^{-1}$  splitting of this band just resolved in the vitreous  $\text{NaNO}_3\text{-Cd}(\text{NO}_3)_2$  sample is probably significant, and indeed the preparation of glasses in

<sup>50</sup> Performed by one of us (J.W.) in the course of study at the Laser Raman Institute held at the University of Maryland (1968).

which exist two distinguishable nitrate environments has recently been reported by Hester and Krishnan.<sup>51</sup>

### CONCLUDING REMARKS

It should be clear from the preceding discussion that the collective aspects of vibrational spectra in ionic liquids deserve more attention than has been accorded them in the past. Of importance would appear to be studies in which greater variations in cation masses than achieved in this study are introduced, and in which the spectral consequences of lowering sample temperatures to liquid-nitrogen temperatures, are determined. The results of such work, and also the effect of pressure to  $\sim 30$  kbar on lattice band and nitrate ion frequencies will be presented in a subsequent publication.

### ACKNOWLEDGMENTS

We thank John Lyford IV for helpful discussion of, and assistance with, the ir experimental aspect of this work, and Professor W. B. White for some helpful comments on the manuscript. We are indebted to Dr. A. J. Eastaerl for the samples of  $\text{ZnCl}_2$ , pyridinium chloride,  $(\text{PyH})_2\text{ZnCl}_4$ , and the glass-forming  $\text{ZnCl}_2$ -pyridinium chloride solutions. This work was supported by a grant from the Purdue University I.D.L. program.

<sup>51</sup> R. E. Hester and K. Krishnan, *J. Chem. Soc.* **1968**, 1955.

## Thermoluminescence in Sodium Silicate by uv Excitation\*

S. A. A. WINER AND R. CHEN†

*Department of Physics, Polytechnic Institute of Brooklyn, Brooklyn, New York 11201*

(Received 5 June 1969)

Thermoluminescence (TL) in sodium silicate, known to be excitable by x rays and gamma irradiation, was found to be excited by uv light. Only the glow peak appearing below room temperature (RT) is excitable whereas additional peaks that had been found above RT after  $\gamma$  irradiation do not appear. This fact indicates that  $\gamma$  rays may create new defects while uv light can only excite existing imperfections. The observed peak at about 130°K is found to consist of many overlapping components corresponding to a continuum of activation energies between 0.16 and 0.38 eV. The emission, which was found to be in the visible, peaked at  $\sim 500$  m $\mu$ . The dependence of TL intensity on the uv excitation dose and the decay of phosphorescence were also studied.

### INTRODUCTION

Thermoluminescence (TL) in various glasses excited by exposure to  $\alpha$  particles from an Ra source was reported by Nyswander and Lind<sup>1</sup> as early as 1926. Nyswander and Cohn<sup>2</sup> found a few years later uv-

excited TL in glasses consisting of 45.5% zinc oxide and 54.5% boric acid. Various glasses were found to produce TL after being excited, usually by gamma rays or x rays. A review article by Ridone<sup>3</sup> on luminescence in the glassy state discusses the results in detail. Kikuchi<sup>4</sup> studied the TL of sodium silicate ( $0.6\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ ) excited by x rays and found a very broad peak at about 140°K. This peak consisted of many overlapping peaks corresponding to many traps in the

\* Research Supported by National Science Foundation Grant SDP-GU-1557.

† Present address: Department of Physics and Astronomy, Tel-Aviv University, Ramat-Aviv, Tel-Aviv, Israel.

<sup>1</sup> R. E. Nyswander and S. C. Lind, *J. Opt. Soc. Am.* **13**, 651 (1926).

<sup>2</sup> R. E. Nyswander and B. E. Cohn, *J. Opt. Soc. Am.* **20**, 131 (1930).

<sup>3</sup> G. E. Ridone, “Luminescence in the Glassy State,” in *Luminescence of Inorganic Solids*, P. Goldberg, Ed. (Academic Press Inc., New York, 1966), Chap. 8, pp. 419-464.

<sup>4</sup> T. Kikuchi, *J. Phys. Soc. Japan* **13**, 526 (1958).

range 0.22–0.40 eV. Kikuchi suggested the possibility that the trapping levels were distributed continuously and uniformly. He attributed these continuous trapping levels to the randomness of the O–Si–O bond angle. The phosphorescence decay curves recorded by Kikuchi did not follow the simple monomolecular or bimolecular laws, showing again that probably many trapping levels were involved.

Bettinali and Ferraresso<sup>5</sup> used a sodium silicate sample containing higher proportions of Na<sub>2</sub>O, 28.5% Na<sub>2</sub>O to 71.5% SiO<sub>2</sub> as compared to 23% Na<sub>2</sub>O and 77% SiO<sub>2</sub> used by Kikuchi. They excited the sodium silicate samples by gamma irradiation and found a broad peak at ~133°K consisting, as before, of many components. Apart from this peak, they found two single peaks, at 350 and 400°K, both corresponding to a trapping level at 0.8 eV but having slightly different emission spectra. The low-temperature peak saturated at relatively low doses, the high-temperature ones did not saturate even at very high doses of the gamma irradiation.

In the present work, sodium silicate of the same composition as Kikuchi's samples was excited by uv light and yielded the broad low-temperature peak. The continuous nature of the activation energies was revealed by thermally bleaching portions of the peak and measuring the activation energies by the initial rise method.<sup>6,7</sup>

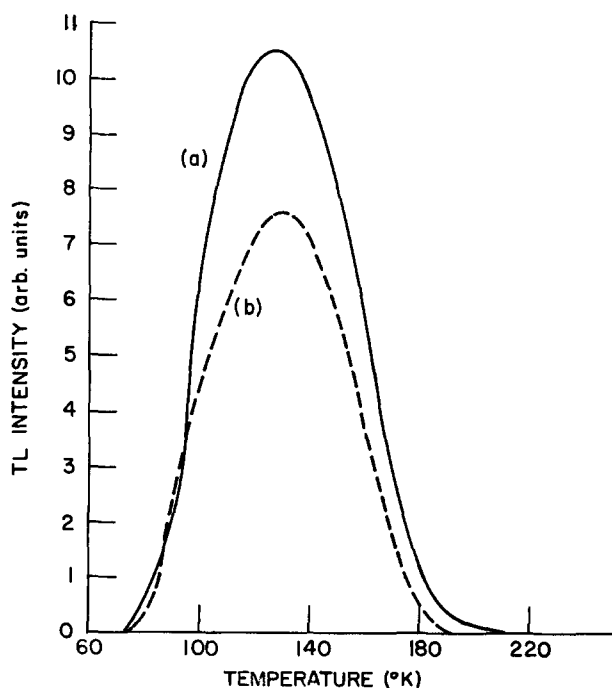


FIG. 1. Representative uv excited glow curves in sodium silicate, Samples 1 [Curve (a)] and 2 [Curve (b)].

<sup>5</sup> C. Bettinali and G. Ferraresso, *J. Chem. Phys.* **44**, 2262 (1966).

<sup>6</sup> G. F. J. Garlick and A. F. Gibson, *Proc. Phys. Soc. (London)* **60**, 574 (1948).

<sup>7</sup> R. Chen and G. A. Haber, *Chem. Phys. Letters* **2**, 483 (1968).

The dependence of the maximum intensity on the dose of uv excitation light was also studied. The results are similar to those previously reported<sup>5</sup> for the low-temperature peak using gamma irradiation. A possible reason for the appearance of the high-temperature peaks only after gamma irradiation is discussed.

The decay of phosphorescence after uv excitation at liquid-nitrogen temperature (LNT) was also investigated. The results were plotted, as a function of time, both on semilog and log–log papers. Assuming the involvement of only one trapping level in a process, one expects a straight line on the semilog paper if the process is of first-order kinetics.<sup>8</sup> When the kinetics is of second order,<sup>6</sup> one expects a straight line having a slope of 2. For other cases Adirowitch<sup>9,10</sup> proved that a straight line will result using log–log paper except for a short initial period of time. The possible slopes in this general case vary between 0.5 and 3.0.

## EXPERIMENTAL

The sodium silicate solutions came from two sources, Allied Chemical (Samples 1) and Fisher Scientific Company (Samples 2). The ratio between Na<sub>2</sub>O and SiO<sub>2</sub> was 23.5:76.5 in both cases. The samples were prepared by spreading sodium silicate solution on aluminum platelets (7×9 mm) and allowing them to dry for at least 24 h. The samples were then inserted into the sample holder of a vacuum cryostat, and could be cooled down by liquid nitrogen or heated by a suitable heater. The samples were excited at LNT by a 150-W Engelhard–Hanovia high-pressure xenon arc lamp whose emission has substantial components in the uv region between 200 and 400 mμ. The light emitted from the sample during the heating process was measured by a thermocooled photomultiplier (E.M.I. 9558Q). A rough analysis of the emission spectrum was done by introducing Kodak Wratten Filters between the sample and the monochromator. The output of the photomultiplier was measured by a Keithley 610A electrometer and recorded by one of the pens of a Leeds and Northrup type “G” double-pen chart recorder. The other pen was used for the simultaneous recording of the output of an Omega Chromel–Alumel thermocouple, thus providing the temperature measurement. The heating rate used was about 15°K/min.

## RESULTS

No TL emission was found after extensive excitation through a Kodak Wratten Filter No. W2A which absorbs the uv below 400 mμ and transmits practically all the visible. Thus we know that the excitation is due to

<sup>8</sup> J. T. Randall and M. H. F. Wilkins, *Proc. Roy. Soc. (London)* **A184**, 347 (1945).

<sup>9</sup> D. Curie, *Luminescence in Crystals* (Methuen and Co., Ltd., (London) 1963).

<sup>10</sup> E. I. Adirowitch, *J. Phys. Radium* **17**, 705 (1956).

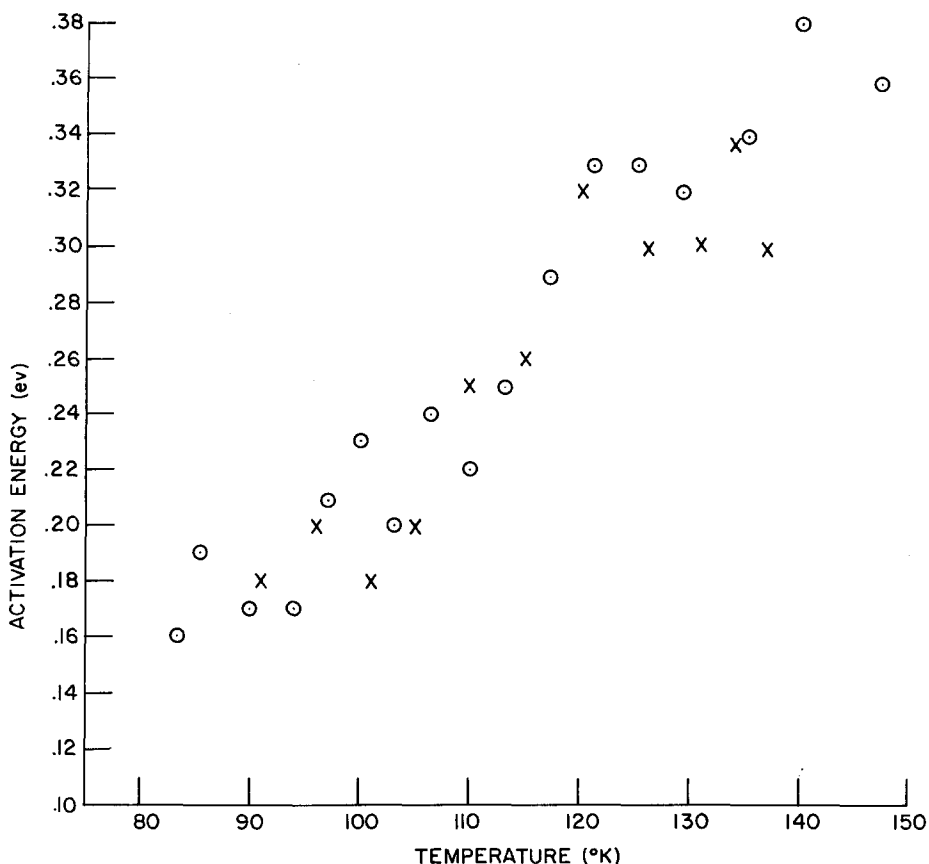


FIG. 2. Activation energies of sodium silicate found by the initial rise method vs temperature.  $\circ$ , Sample 1;  $\times$ , Sample 2.

the uv light. Figure 1 shows the glow curves found in sodium silicate after the uv excitation. Curve (a) gives the glow of Sample 1 (Allied Chemical) having a peak at  $\sim 127^\circ\text{K}$ . Curve (b) shows the glow of Sample 2 (Fisher Scientific) having a peak at  $\sim 130^\circ\text{K}$ . Both curves were recorded after uv excitation for 30 min. Under certain excitation conditions, a comparatively weak peak appeared in Sample 2 at  $\sim 250^\circ\text{K}$ . No glow was found above RT even after very extensive excitation. Kodak Wratten Filters Nos. W4, W16, and W98 were used for an approximate spectral analysis of the main peak. Filter No. W16, transmitting only above  $520\text{ m}\mu$ , absorbed practically all the glow emission and so did No. W98 which transmits around  $450\text{ m}\mu$ . Using filter No. W4 (high transmission above  $450\text{ m}\mu$ ) the measured light intensity was reduced by  $\sim 50\%$ . This together with the results with the W16 and W98 filters shows that the main emission is in the vicinity of  $500\text{ m}\mu$ . This result seems to be similar to the emission spectrum given by Bettinali and Ferraresso<sup>5</sup> for the peaks appearing above RT (after  $\gamma$ -ray excitation) and for the fluorescence. Better analysis of the emission spectrum by a monochromator was not possible because of the relatively low intensity of the emission.

The activation energies of the various components of the main peak were found by the initial rise method.<sup>6,7</sup>

Straight lines were found for  $\ln I$  vs  $T^{-1}$ , the slopes of which are  $-E_i/k$ . In this way the activation energies  $E_i$  were calculated. Figure 2 gives the results for the activation energies as a function of temperature. The values of activation energy seem to increase with temperature from 0.16 to 0.38 eV.

Some measurements of the decay of phosphorescence at liquid-nitrogen temperature were also made. Representative results are given in Fig. 3. The phosphorescence intensity as a function of time is given for Sample 1 [curve (a)] and for Sample 2 [curve (b)] on a log-log scale. The plotted curve is not a straight line. A plot of the same results on a semilog scale resulted in a curve which also is not a straight line.

Some measurements were made of the dependence of the emission intensity on the dose of uv excitation. The dose was varied by using different excitation times. The emission intensity was found to be approximately linear with the exciting dose at low doses and tended to saturation at higher ones. This resembles the results of Bettinali and Ferraresso<sup>5</sup> for gamma-ray excitation for the peak occurring below RT. Note that no trace of the peaks reported to appear above RT after gamma-ray excitation was found even when the excitation dose was an order of magnitude higher than the saturation dose of the low-temperature peak.

## DISCUSSION

Thermoluminescence below RT in sodium silicate samples, known to be excitable by gamma rays and x rays, was shown here to be excited by uv light. Some of our results using uv excitation resemble the results found after x- and  $\gamma$ -ray excitations. Thus, the main peak at  $\sim 130^\circ\text{K}$  is seen to consist of many overlapping components with a continuum of values for the activation energies. The shift in the temperature of the peak—about  $130^\circ\text{K}$  here instead of  $\sim 133^\circ\text{K}$  with gamma excitation and  $\sim 140^\circ\text{K}$  after x irradiation—is not necessarily a result of the different excitation. It may result, for example, from the use of different heating rates or from the slight difference of the ratio of the amounts of  $\text{Na}_2\text{O}$  and  $\text{SiO}_2$  between our samples and those of Bettinali and Ferraresso. Since we have a broad peak consisting of many components, the difference between the various cases may be considered quantitative rather than qualitative. Only the relative intensities of the various components might have changed slightly.

The range of activation energies was found by us to be 0.16 to 0.38 eV whereas Kikuchi<sup>4</sup> reported values of 0.22 to 0.40 eV. Apart from possible differences due to the different excitation, it seems that our results are somewhat more reliable, since Kikuchi used an approximate formula for calculating  $E_i$ . He also assumed that the frequency factor is the same for all trapping levels and that it has the value of  $10^{10} \text{ sec}^{-1}$ . This is not necessarily justified.

The fact that the phosphorescence decay curves obey neither the exponential decay law nor Adirowitch's formula<sup>9,10</sup> indicates that even at a constant low temperature, more than one trap is involved in the process.

The fact that only the peak at  $\sim 130^\circ\text{K}$  appears after the low energy excitation (uv and x rays) while the distinct high-temperature peaks (having appeared after  $\gamma$  excitation) are not excitable by these low energies reveals an important possibility. It seems that the low-temperature glow results from trapping of electrons in existing traps by uv, x rays, or  $\gamma$  irradiation. The higher than RT peaks seem to correspond to traps associated with defects which are created by the  $\gamma$  irradiation. This agrees very well with another result given by Bettinali and Ferraresso,<sup>5</sup> namely, that the  $133^\circ\text{K}$  peak could be saturated by  $8 \times 10^4 \text{ R}$ . This dose is sufficient to fill practically all the existing traps, whereas the high-temperature peaks are not saturated even by  $3 \times 10^7 \text{ R}$ . It has been found that the emission spectrum in our case resembles the spectral contents of the peaks above RT reported by Bettinali and Ferraresso. This indicates that, although different traps are responsible for the TL below and above RT, both glows may be attributed to the same center or group of centers.

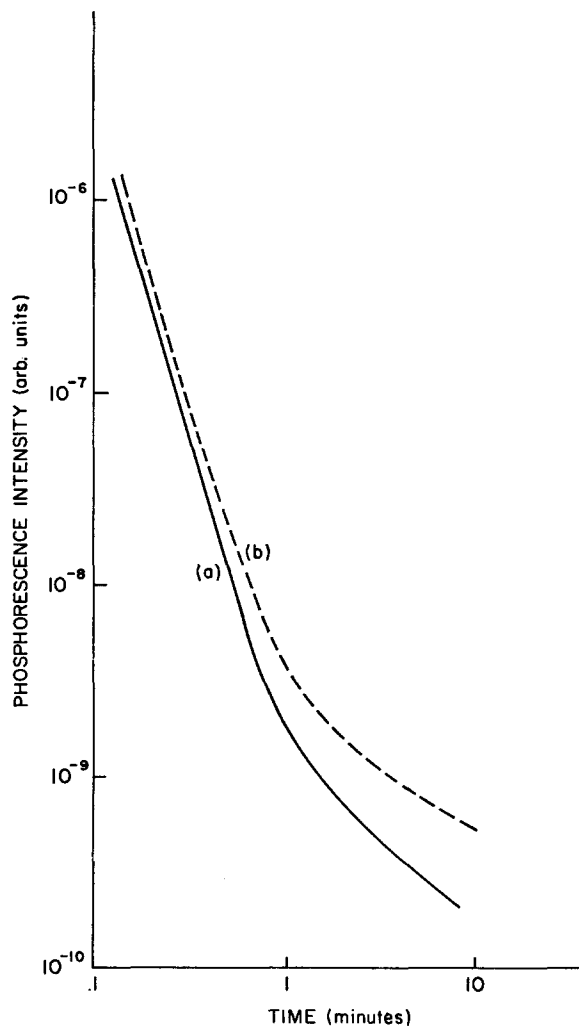


FIG. 3. Phosphorescence decay curves at LNT, for Sample 1 [Curve (a)] and Sample 2 [Curve (b)].

Sodium silicate (water glass) has been used<sup>11</sup> as glue for preparation of  $\text{ZnS:Er}^{3+}$  powder samples. One has to make sure in such a case that TL peaks of sodium silicate would not be interpreted as resulting from the examined powder. We checked this point for the samples used by Halperin *et al.* and found that the  $\text{ZnS:Er}^{3+}$  emission was at least two orders of magnitude higher than that of the sodium silicate. This shows that in this specific case, the reported results correspond solely to the ZnS powders.

## ACKNOWLEDGMENT

We would like to express our thanks to G. A. Haber for reading the manuscript and for making some useful comments.

<sup>11</sup> A. Halperin, W. Y. Chu, G. A. Haber, and J. J. Dropkin, *International Conference on II-IV Semiconducting Compounds* (W. A. Benjamin Inc., New York, 1967), p. 68.