

light-induced luminescence in a γ -irradiated sample at 23°C and not subjected to pressure, Fig. 2(a), is similar to that discussed in an earlier paper.¹³ Figure 2(b) shows (dashed curve) the effect remaining approximately 2 years after γ irradiation and the effect of mercury light (solid curve) on the emission of a similarly treated sample. The main peaks (B_1 , C_1 , D_1 , E_1 , and F_1 for the non-light-irradiated and A , B_2 , C_2 , D_2 , E_2 , and F_2 for the light-irradiated sample) were found to appear at 355, 419, 453, 500, 540, and at about 573°K, respectively.

Rieke and Daniels² have reported peaks similar to C_2 and D_2 for γ -irradiated α - Al_2O_3 powder. Absence in their results of the B_2 , E_2 , and F_2 peaks is perhaps due to instrumentation and/or sample structure characteristics.

The trap responsible for the C_2 peak in an aged sample is greatly influenced by uv light. An aged sample which was exposed for 5 min to uv light gave the luminescence

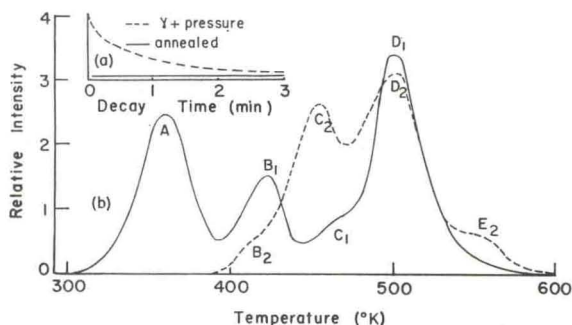


FIG. 3. Sample pressured to 40 kbar: (a) Mercury-light-induced luminescence (dash curve) of an aged α - Al_2O_3 crystal immediately after the crystal was subjected to 40 kbar of pressure (dashed curve) and after the crystal was subjected to 24 kbar and at 500°C (solid curve). (b) Glow curves obtained on aged α - Al_2O_3 samples immediately after 40 kbar pressure (dash) and after exposure first to mercury light after being pressured (solid).

decay curve of Fig. 2(a) and the thermoluminescence glow shown by the solid curve of Fig. 2(b). The trap responsible for the dominant C_2 peak in an aged sample, not exposed to uv energy, is greatly influenced by Hg light. The C_2 trap is ionized by the incident Hg radiation and the electron thus liberated is then captured by another luminescence center to form a new and dominant peak, A .

Pressured Sample

Representative luminescent decay and glow curves of aged crystals which were subjected to a pressure of 40 kbar for a period of 30 min are given in Fig. 3. The luminescence decay of a sample which was Hg irradiated after being pressured is given by the dashed curve in Fig. 3(a). It should be noted that in every case the decay was appreciably steeper for the first part of the curve for samples that were subjected to pressure when compared to curves for nonpressured samples, Fig. 2(a). A sample that was pressured to 24 kbar and heated to

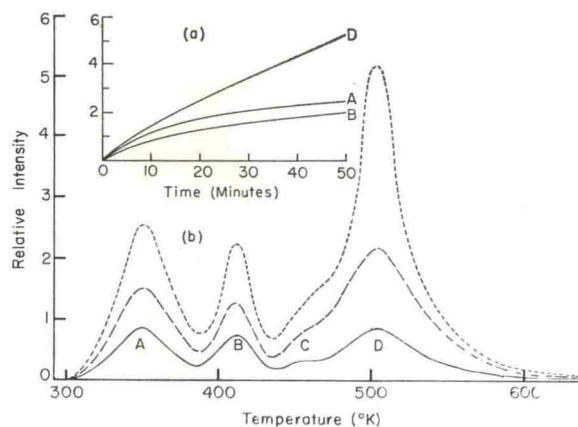


FIG. 4. (a) Dependence, in pressured samples, of intensities of the different glow peaks on time of exposure to mercury radiation. (b) Selective enhancement of glow peaks by radiation from a mercury light on an aged sample pressured to 40 kbar.

500°C while under pressure, for a period of 255 min, indicated an annealing out [solid line, Fig. 3(a)] of all luminescent centers.

The spectra for an aged sample which was annealed immediately after pressure shows main peaks B_2 , C_2 and D_2 comparable to those of Fig. 2(b). However, D is now the dominant peak and the resolved peaks E and F combined to form a peak E_2 at an intermediate temperature of about 560°K.

The exposure of a pressured specimen, before annealing, to Hg light [luminescence decay curve given in Fig. 3(a)] produced the solid-line glow curve of Fig. 3(b). Here again the trap effecting the C peak is destroyed and the A trap is enhanced. Complex changes at curves B , D , and E are noted.

Figure 4 shows the effect of additional irradiation with Hg light of a sample annealed after pressure was applied for 5 (solid), 15 (long dash), and 50 (short dash) min. Exposures were increased by 5-min time intervals, however only 3 curves are shown. Prolonged Hg irradiation of an aged and pressured crystal effected a faster rate of intensity increase in the D (500°K) trap such that the intensity increased by a factor of 10 or more. The intensity of glow peaks A and B have about the same rates of increase, Fig. 4(a). The intensities, Fig. 4(b), were reduced by a factor of 10 in order to keep peak heights on scale.

2. Ruby

As already reported in the literature,^{4,14} characteristic thermoluminescence in doped Al_2O_3 single crystals arises from transitions involving the impurities. Figure 5 shows glow peaks, for γ -damaged, pressured, and mercury-light irradiated ruby. The heating to 450°C of "as received" or virgin crystals not subjected to previous cycles of irradiation, pressure, heating, and cooling resulted in a glow curve which coincided with the black-body tracing of the heating element. Peak A at 473°K

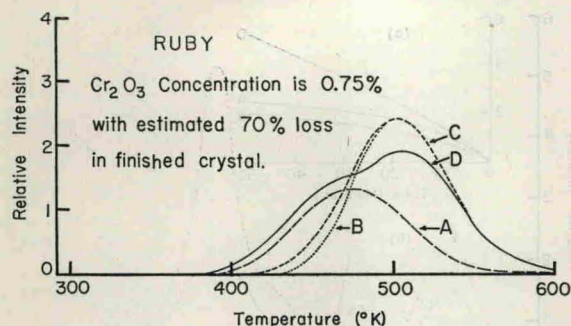


FIG. 5. Glow curves for as received and aged ruby: Sample was annealed after being γ damaged (long dash); as received sample pressured to 40 kbar (dot); sample γ damaged and pressured to 40 kbar (short dash); and sample γ damaged also pressured to 40 kbar and exposed for 5 min to radiation from a mercury-light source before annealing (solid curve).

is representative of glow peaks resulting from the annealing of aged (γ -irradiated two years ago) ruby specimens. Peak B, at 503°K, represents a typical glow curve obtained from virgin crystals which were pressured to 40 kbar. Glow peak C, at 503°K, represents annealing glow curves of aged ruby samples that were pressured to 40 kbar.

The compound peak D resulted from the annealing of an aged specimen which was pressured to 40 kbar and exposed to radiation from a mercury light source before the sample was heated. Slight variation in sample sizes made difficult any assignment of corresponding increases or decreases of intensity to the destruction of one type of luminescent center and favor by another in the process. It is intended to investigate, on identical samples, the distribution of luminescence intensities as a function of pressure, time under pressure, and time of exposure to uv light.

3. Kinetics of Thermoluminescence

The glow curves shown in Figs. 2 through 5 consist of a series of single or overlapping peaks, each of which corresponds to a particular type of electron trap. Each trap is emptied of its captured electrons as the rising temperature provides the necessary energy. The methods of calculating the number of electrons in the trap level and their activation energies require comment:

First Randall and Wilkins (Ref. 4, pp. 366–374) and later several other authors based their kinetic treatments on the assumption that the escape of the electron from a trap is the only event in a sequence of events leading to thermoluminescence which requires thermal activation. Elaborate analyses have been developed by Williams and Eyring,¹⁵ Hill and Schwed,¹⁶ Kikuchi¹⁷

¹⁵ F. E. Williams and H. Eyring, *J. Chem. Phys.* **15**, 289 (1947); also F. E. Williams, Ph.D. dissertation, Princeton University, 1946 (unpublished).

¹⁶ J. Hill and P. Schwed, *J. Chem. Phys.* **23**, 652 (1955).

¹⁷ T. Kikuchi, *J. Phys. Soc. Japan* **13**, 526 (1958).

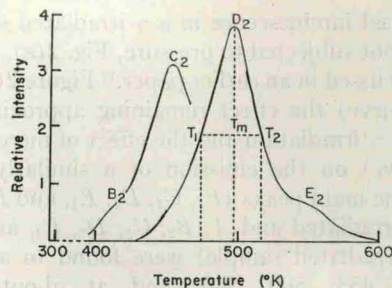


FIG. 6. Glow curves resolved by "saw-tooth" annealing of an aged sample which was pressured to 40 kbar.

and more recently by Medlin¹⁸ to account for the multiple peaks found in the glow curves. The simpler work of Hill and Schwed was extended by Bonfiglioli, Brovotto, and Cortese.¹⁹ They assumed that a transition of conduction-band electrons to a luminescence level n has a probability, p_n , which is temperature-independent. With increasing temperatures the trapped electrons are activated into the conduction band followed by their capture at various luminescence centers according to respective probabilities, p_n , which can differ by several orders of magnitude; the subscript n designates a particular center. A linear heating rate, R , results in light emission from a given luminescence level through second-order kinetics of the form

$$\frac{dN_n}{dt} = \frac{p_n N_n N_t}{R} e^{-E/kT}. \quad (1)$$

Here N_t is the number of electrons in the trap level, and N_n the number of luminescence centers.

Randall and Wilkins proposed that the energy of the trap level corresponding to an experimental peak is about $25 kT_m$, where k is the Boltzmann constant and T_m is the temperature of the peak maximum. A disadvantage is that this estimate is based on an assumed constant value for a frequency factor. Assuming the first-order reaction, Grossweiner²⁰ developed an estimate of trap depth which is

$$E = 1.51 k T_m T_1 / (T_m - T_1), \quad (2)$$

where k is the Boltzmann constant, T_m is the absolute temperature of the peak maximum, and T_1 is the temperature (on the low-temperature or leading edge of the glow curve) at which the intensity is one-half of the maximum value. This method also makes use of unaccountable¹⁵ assumptions concerning the frequency factor.

Hill and Schwed, and also Bonfiglioli used the slope in an Arrhenius plot (i.e., log intensity versus $1/T$) of the ascending portion of a peak to find activation energies, E . This method does not require an assumed fre-

¹⁸ W. L. Medlin, *Phys. Rev.* **122**, 837 (1961); **123**, 502 (1961).

¹⁹ G. Bonfiglioli, P. Brovotto, and C. Cortese, *Phys. Rev.* **114**, 951 (1959); **114**, 956 (1959).

²⁰ L. I. Grossweiner, *J. Appl. Phys.* **24**, 1306 (1953).