

## Letters to the Editor

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### Luminescence of Beryllium Oxide\*

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**I**N the course of a survey of the luminescence of metallic oxides, some interesting properties of beryllium oxide have been noted. When irradiated by alpha particles, an intense ultraviolet fluorescence was observed. From the spectral sensitivity of the detector, it was estimated that a considerable emission occurs at wavelengths of 2500Å or less.

Although earlier investigators have reported a visible blue luminescence from BeO under action of a vacuum discharge, apparently no mention has been made of the fact that the spectrum extends far into the ultraviolet. Under alpha irradiation, white powdered BeO yielded an emission band extending from above 4000Å into the ultraviolet to ~2000Å. The spectrogram was obtained in a small Hilger quartz spectrograph. Bombardment of a combustion tube of sintered BeO gave the same result. BeO has been reacted with other materials, such as SiO<sub>2</sub>, to produce numerous phosphors but does not itself appear to have been studied in detail. A comparison of the intensity of the ultraviolet fluorescence of powdered BeO and of NaCl-Ag under alpha-particle excitation is shown in Table I.

Nine different samples of BeO were obtained from eight different suppliers, and all exhibited a detectable long-period phosphorescence as well as energy storage at room temperature (20°C) when excited by cathode rays, x-rays, or ultraviolet light. Irradiation by alpha particles resulted principally in fluorescence. One sample of BeO, excited by cathode rays, decayed over a period of 400 minutes on a  $\log I - \log t$  plot with a slope of -0.83. The decay of both visible and ultraviolet portions of the spectrum followed the same law. Spectrographic analyses showed that B, Mg, Al, Si, and Fe could be present as impurities. The afterglow which immediately followed excitation could be considerably enhanced in the case of the less pure samples by ignition at 1400°C. Under cathode-ray excitation, this afterglow equaled in intensity that of the best samples of NaCl-Ag. The purest material was obtained from Johnson, Matthey, and Company, Ltd., and although it had good fluorescent response for alpha and beta particles, phosphoresced only faintly under irradiation by excitants of all types. Ignition of this particular material had

TABLE I. Ultraviolet fluorescence.

Phosphor <sup>a</sup>	Yield
NaCl + 0.0008 percent AgCl	31
NaCl + 0.004 percent AgCl	71
NaCl + 0.02 percent AgCl	370
NaCl + 0.10 percent AgCl	1160
NaCl + 0.22 percent AgCl	3150
NaCl + 0.50 percent AgCl	4630
NaCl + 1.00 percent AgCl	3730
BeO	1060
BeO (ignited)	990

<sup>a</sup> AgCl concentrations in weight percent.

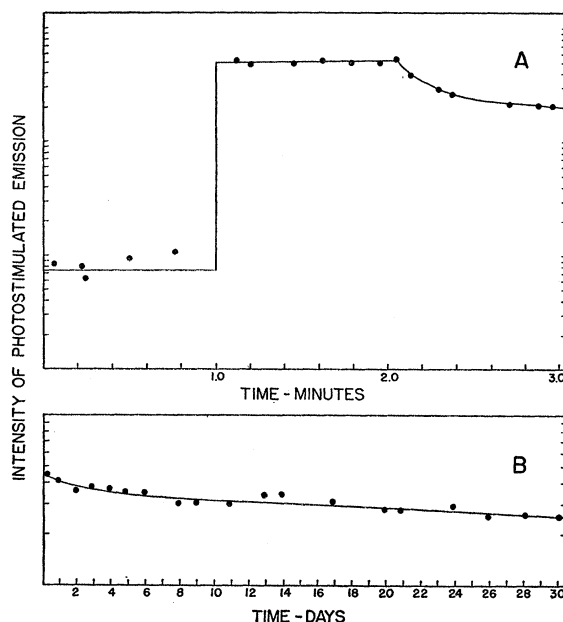


FIG. 1. Photostimulated emission of x-rayed beryllium oxide. In Fig. 1(A), photostimulated emission occurs during one minute of stimulation and is followed by a post-stimulation afterglow. Figure 1(B) is a plot of the decay of the energy stored in x-rayed BeO. Excitation and all measurements carried out at room temperature (20°C).

small effect upon the phosphorescence and energy storage. The alpha-particle-excited fluorescence of all samples seemed to remain unchanged by ignition.

A sample of BeO obtained from Fisher Scientific Company, Inc., was ignited at 1400°C and irradiated by 20-kev x-rays and stored in darkness. After twenty-two hours, the excited phosphor was photostimulated by light from a tungsten lamp for one minute. The emission during stimulation and the post-stimulation afterglow are shown in Fig. 1(A). A similar specimen was x-rayed, and bursts of ultraviolet of duration six seconds were drawn from it by photostimulation at intervals of 24 to 48 hours over a period of thirty days. This photostimulated emission is approximately proportional to the amount of energy remaining stored in the beryllium oxide. These data are plotted in Fig. 1(B), where it is clear that a large fraction of the stored energy remained after thirty days—more than in any other phosphor studied in this laboratory. Under identical conditions of photostimulation, the emission from BeO was less than one percent of that from transparent samples of NaCl-Ag of the same area. However, the transmission of the powdered BeO is low, and only light released near the surface could be measured.

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### Restoration of $F$ and $V_1$ Centers Following Low-Temperature Bleaching

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**T**HE following observations were made in the course of experiments with single crystals of KCl colored at 113°K by 180-kv x-rays.

The freshly colored crystals contain a large fraction (up to 50 percent) of unstable  $F$  centers which require a thermal activation of only 0.02 eV in order to decay, presumably by tunneling of electrons to neighboring positive hole centers. This is revealed by

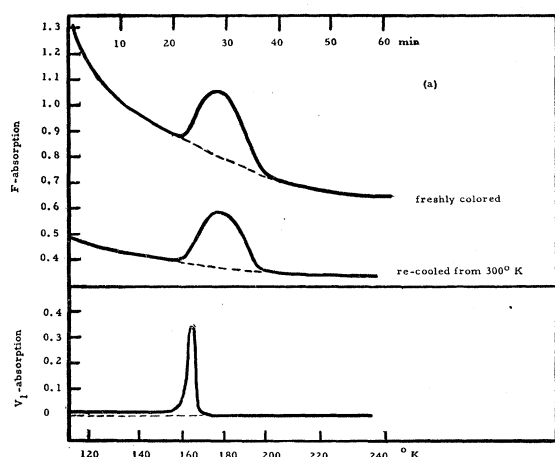


FIG. 1.  $F$  and  $V_1$  absorption during warming after optical bleaching at  $113^\circ\text{K}$ .

a steep drop in the " $F$ -absorption glow curve," i.e., the curve giving the absorption in the maximum of the  $F$  band as a function of time or temperature during gradual warming of the crystals. The unstable centers are removed by raising the crystal to room temperature so that the absorption glow curve obtained after re-cooling to  $113^\circ\text{K}$  shows only a slight fall entirely explained by the broadening and shift of the maximum of the  $F$  band with rising temperature.

Optical bleaching by  $F$  irradiation occurs at  $113^\circ\text{K}$  with a saturation value of 30 percent of the  $F$  centers bleached, and is followed by a partial recovery in the dark in which up to  $\frac{1}{3}$  of the bleached  $F$  centers reappear within about 10 minutes. The effects are similar to those reported by Markham, Platt, and Mador<sup>1</sup> on x-rayed KBr at  $78^\circ\text{K}$ . But their explanation of the recovery in terms of a dissociation of  $F'$  centers cannot apply in our case where  $F$  irradiation has been found to reduce and not to enhance the  $F'$  band. Instead, we believe that the recovery is connected with a narrow (0.17 eV) absorption band at  $8750\text{\AA}$  which we have found to appear during optical  $F$  bleaching.

The result of main interest concerns a large-scale restoration phenomenon which occurs if the crystals are first bleached at  $113^\circ\text{K}$  by  $F$  irradiation and then slowly warmed in the dark ( $2.3^\circ\text{K}$  per min). The  $F$ -absorption glow curves observed under these conditions for a virgin crystal and a crystal recooled from room temperature (Fig. 1(a)) show a large peak around  $175^\circ\text{K}$  superimposed on the normal absorption glow curves discussed above. This means that  $F$  centers are temporarily recreated and subsequently bleached thermally. The thermal bleaching can be

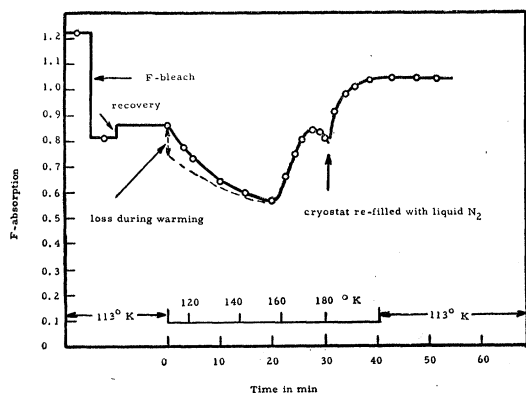


FIG. 2. Restoration of optically bleached  $F$  centers by warming and recooling.

prevented and the restored absorption be arrested by rapid re-cooling from a temperature near the restoration peak (Fig. 2). It is seen that nearly all the optically bleached  $F$  centers can be regained by this procedure.

Even more remarkable is the fact that simultaneously with the  $F$  centers,  $V_1$  centers are recreated as revealed by a sharp peak in the absorption glow curve obtained by observing the absorption in the maximum of the  $V_1$  band during warming. The curve shown in Fig. 1(b) refers to a crystal recooled from room temperature so that at the beginning of the experiment it did not contain any  $V_1$  centers but only more stable higher  $V$  centers. The fact that the peak occurs slightly below that for the  $F$  centers and is very much sharper implies a very short lifetime of the restored  $V_1$  centers in accordance with their low dissociation temperature of  $128^\circ\text{K}$  as observed by Dutton and Maurer.<sup>2</sup> It appears very significant that the height of the  $V_1$  restoration peak, representing only a fraction of the total number of transient  $V_1$  centers involved, is about twice as large as the height of the original  $V_1$  band present in the crystals immediately after x-raying.

In explanation of the effects described we offer the following tentative suggestions: Crystals x-rayed at low temperature contain a large number of positive holes in so far optically unidentified  $V_x$  centers. Electrons released by  $F$  irradiation are trapped at these centers to form complex metastable centers (possibly associated with the peak at  $8750\text{\AA}$ ) which on breakup by thermal activation yield unstable  $F$  centers and  $V_1$  centers in close proximity to each other.

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<sup>1</sup> Markham, Platt, and Mador, Phys. Rev. **92**, 597 (1953).  
<sup>2</sup> D. Dutton and R. Maurer, Phys. Rev. **90**, 126 (1953).

## Effect of Hydrostatic Pressure on the Superconducting Transition of Tin and Thallium

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THE dependence on pressure of the magnetic threshold field of superconductivity has been measured for tin and for thallium for pressures transmittable by liquid helium. The experimental technique consisted of measuring the difference of the threshold fields of two similar ellipsoidal single crystals at the same temperature. The pressure on one ellipsoid was held fixed while the pressure on the other was varied by means of tank helium gas. The transition was followed by means of 60-cycle ac susceptibility measurements.

The summary of results to date on tin and thallium is given in Table I, which contains a review of previous determinations of the pressure coefficients. The values for tin marked by asterisks are deduced from data on wires in tension, in which the hydrostatic stress is one-third the tensile stress for isotropic materials. The rather good agreement among the tin data between the pressure coefficients directly measured in hydrostatic experiments and those deduced from wire straining suggests that in the latter the shear components have a small or negligible effect on the superconducting transition in tin. This speculation is now being checked with a thin-walled tin cylinder stressed in pure shear.

No ready explanation is at hand for reconciling the results of the present work on thallium and those of Kan, Lazarev, and Sudovstov<sup>1</sup> with those recently reported by Chester and Jones,<sup>2</sup> differing as they do in both magnitude and sign. The technique employed by Chester and Jones results in massive plastic deformation at room temperature while that used by Kan *et al.* may produce some plastic deformation near the ice point. To examine the effects of mild plastic deformation, an ellipsoid was machined from a single crystal twisted  $180^\circ$  over the 1.2-cm length of the ellipsoid. The threshold curve and pressure coefficient for this sample were the same as for the undeformed crystal.