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Effects of High Pressure on the Thermoluminescence of γ-Irradiated α-Al_2O_3 Single Crystals*

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Thermoluminescent properties are reported here on γ-irradiated α-Al_2O_3 and ruby single crystals, before and after the specimens were subjected to hydrostatic pressures of 24 kbar for 255 min at 773°K and at 30 and 40 kbar for 30-min periods at room temperature. Glow-curve changes and peak resolutions occur for white sapphire in the temperature range of 340 to 623°K. The graphs show regularity with regard to glow-peak temperatures and their sensitivity to higher annealing temperatures after pressure. A single pressure-sensitive peak at ~503°K appears in ruby after applying pressure or after γ irradiation. Activation energies for several peaks as calculated from the results are also given.

INTRODUCTION

THERMOLUMINESCENCE of aluminum oxide and the effect of ionizing radiation on single crystals have been studied by several investigators.[1–5] The use of powder samples for luminescence studies might have complicated some results in that many peaks of unknown origin are observed during the warming cycle.[6] All past workers have restricted their glow experiments to effects of ionizing radiation. In the present work, glow curves (i.e., plots of light intensity versus temperature) were recorded for aged[7] single crystals of white sapphire and ruby. Glow curves are compared for specimens that were gamma irradiated (Co^{60}) approximately 2 years ago, then subjected to pressures of 24 kbar at 773°K for 255 min and at 30 and 40 kbar at room temperature for 30 min. The same specimens were then annealed for 4 h at 1073°K. Some of the specimens were then re-irradiated with Co^{60} γ rays and again subjected to pressures of 30 kbar.

Well-defined glow peaks were obtained in these experiments on a white sapphire specimen after it was subjected to high pressure. The peaks showed regularities in their resolution and grouping when they were compared to the complexity of glow curves which were obtained from γ-irradiated samples that were not subjected to pressures. Examinations similar to those made on white sapphire were carried out on ruby. A prominent glow peak appears as a result of γ irradiation *or* the application of pressure. It is of interest to find that, because of pressure effects, restriction must be placed on the type of materials used for geological "age dating" by thermoluminescence. The apparent cumulative radiation-damage effects must take into account possible errors which pressure factors would introduce.

Exciting light from a mercury source induced additional glow peaks not present in the unexcited (not γ irradiated and/or subjected to pressure) crystals. Upon light irradiation of γ-damaged and/or pressured specimens, glow peaks were induced in white sapphire at 355°K and appeared to be further resolved in ruby at 473 and 503°K.

EXPERIMENTAL

1. Samples

The samples used in this study were obtained from the Linde Company, Crystal Products Division about 2 years ago and were fabricated from alumina powder which showed the following spectroscopic analysis (Table I). The ruby material was fabricated from powder containing a Cr_2O_3 concentration of 0.75% but had an estimated 70% loss of dopant in the finished crystal.

The specimens used in this study were γ irradiated by a radiation source of approximately 4000 Ci of cobalt-60 in the form of five plates disposed about a cylindrical chamber.[7] The intensity of the gamma-ray field was

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* Studies have been made concerning the effects of high pressure on crystal-field strength by observing the spectrum in Al_2O_3, S. Minomura and H. G. Drickamer, J. Chem. Phys. **35**, 903 (1961); also in ruby, D. R. Stephens and H. G. Drickamer, *ibid.* **35**, 427 (1961).

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[1] O. Deutschbein, Ann. Physik **14**, 712 (1932), also G. F. J. Garlick and M. H. F. Wilkins, Proc. Roy. Soc. (London) **184**, 420 (1945), studied nonirradiated ruby and found light-induced luminescence, of a few milliseconds duration which was due to a forbidden transition in the Cr^{3+} impurity ion.

[2] Thermoluminescence of various crystal phases of polycrystalline aluminum oxide was studied in the 5 to 425°C region by J. K. Rieke and F. Daniels, J. Phys. Chem. **61**, 629 (1957).

[3] Saturation limits and annealing temperature of the γ-ray-induced coloration, defects and their effect on the optical properties of α Al_2O_3 were first reported by R. A. Hunt and R. H. Schuler, Phys. Rev. **89**, 664 (1953); and later by P. W. Levy and G. J. Dienes, "Report of the Conference of Defects in Crystalline Solids," H. G. Wells Physical Laboratory, University of Bristol, Physical Society, London, pp. 256–60, 1954 (unpublished); Phys. Rev. **94**, 1409 (1954).

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[5] W. D. Compton and G. W. Arnold, Discussions Faraday Soc. **31**, 130 (1961).

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TABLE I. Impurity content in alumina obtained by spectroscopic analysis, in %.

CaO	0.0030	Mn_2O_3	0.0001
Cr_2O_3	0.0008	NiO	0.0020
CuO	0.0003	SiO_2	0.0010
Ga_2O_3	0.0020	Na_2O	0.0010
Fe_2O_3	0.0025	Ag_2O	0.0001
PbO	0.0040	SnO_2	0.0002
MgO	0.0001		

determined as 1.4×10^5 rad/h by ceric sulfate dosimetry.[8] The white sapphire specimens were exposed for 1 h; the ruby had three successive 30-min exposures on the same day. Both the sapphire and ruby specimens remained in a clear-plastic box container during a period of 27 months.

After the first series of experiments were completed some of the samples were annealed at 800°C for 4 h and portions of each set were held as "background" controls. The remainder of the samples were exposed at room temperature for one hour to an 800-Ci source. The second set of experiments described below was conducted immediately after irradiation.

2. Pressure Apparatus

An unsupported tungsten-carbide piston $\frac{1}{2}$ in. in diameter was moved in a $\frac{1}{2}$ in. by 2 in. long supported tungsten-carbide pressure chamber. Talc was used as the pressure medium. Pressures up to 40 kbar were generated in the chamber and samples remained at this pressure for 30 min. A frictional correction for the single-stage piston was estimated from accurate results for a bismuth phase boundary previously determined as an absolute pressure indicator.[9] Essential features of the pressure chamber are given in Fig. 1. Details of this and similar apparatus have been published elsewhere.[10,11]

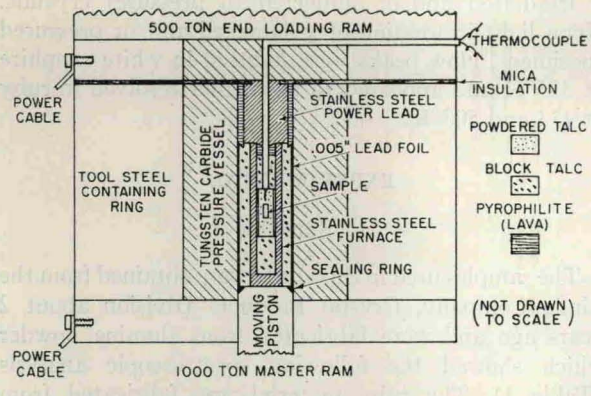

FIG. 1. Diagram of high-pressure cell and furnace assembly.

One run was made where white sapphire samples were subjected to a pressure of 24.0 kbar at a temperature of 500°C. The time of the run was 255 min and the samples were lowered to room temperature in approximately 3 sec by a rapid quench. The pressure was then gently released.

3. Thermoluminescence

The experiments were carried out in a lighted room.[12] The technique was essentially the same as was used previously[13,14] with one exception; the sample was in a black-box chamber only during the warming cycle. The heating rate was about 50° per min. Lower heating rates (lowest was 20° per min) produced no additional glow peaks and the resulting broadened peaks offered difficulty to establishing the temperatures for peak maximums. A compact source Mineralight Model V-41 Hg lamp, obtained from Ultra-Violet Products, Inc., San Gabriel, California, supplied the light for exciting the white sapphire and ruby crystals used in this study. Recorder tracings of glow curves obtained from several white sapphire and ruby specimens are reproduced in Figs. 2 through 6.

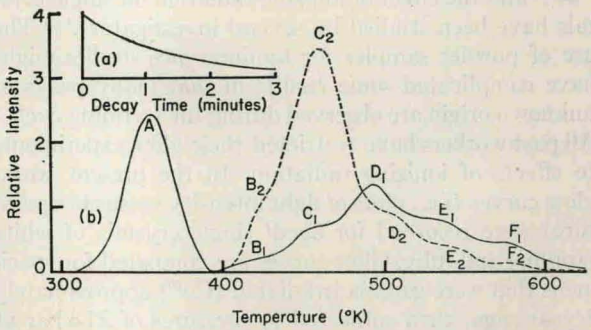

FIG. 2. Nonpressured sample: (a) Decay of light-induced luminescence, at 23°C, after 5-min exposure to mercury light, of an aged α-Al_2O_3 crystal having in its history a 1-h exposure to a Co^{60} source, over 2 years ago. (b) Glow curve (solid line) obtained from the sample used in (a), and glow curve (dash) obtained from an aged sample not exposed to uv light. (The heating rate was about 50°/min.)

RESULTS

1. White Sapphire

Nonpressured Sample

Curves for light-induced luminescence and the glow curves for an aged crystal are given in Fig. 2. The

[8] The term "aged" samples will mean that the specimens have in their history a one-hour exposure to a Co^{60} source. The intensity of the γ-ray field was determined as 1.4×10^5 rad/h by ceric sulfate dosimetry [J. Weiss, Nucleonics **10**, 28 (1952)]. The samples were investigated during a 3-week period, 27 months after the 1-h exposure.

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