RELATIONSHIP BETWEEN E.S.R. SPECTRA AND DOSE IN ELECTRON-IRRADIATED BOROSILICATE GLASSES.*

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RESUMEN

Se han llevado a cabo estudios de la resonancia del espín electrónico (R.E.E.) en vidrios de borosilicato activados con cobalto e irradiados con electrones de 1 MeV. Los vidrios expuestos a dosis entre 10^3 rad exhiben un espectro de R.E.E., tal que la intensidad de la única línea es función creciente de la dosis recibida y tendiente a la saturación. A partir de las gráficas obtenidas se discute el decaimiento de los centros paramagnéticos en el tiempo. Se discute además, la posibilidad de usar la relación encontrada para utilizar los vidrios como dosímetros. Se comparan los resultados con el método común de transmitancia óptica.

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ABSTRACT

Electron spin resonance (E.S.R.) spectra have been observed for electron-irradiated cobalt-activated borosilicate glasses. The glasses were exposed to doses between 10^3 and 10^6 rad and display an E.S.R. spectrum such that the intensity of the only line is an increasing function of the doses having a tendency to saturation. Graphs were obtained which show the decay of the paramagnetic centers. The relationship between intensity and dose opens the possibility of using these glasses as dosimeters. The results have been compared with the usual method of optical density.

INTRODUCTION

Large-scale use of gamma-ray or electron-beam doses in different products made it necessary to develop a more convenient dosimeter than the usual ones based on some chemical techniques. Radiation-induced changes in absorption, luminescence and other properties of solids have been used to measure low doses of ionizing radiation by Friedman and Glover[1] and Schulman et al.[2] For high doses, radiation-induced absorption changes in glass are large enough to measure doses directly, as Schulman, Klick and Rabin[4] have pointed out. In particular a cobalt-activated borosilicate glass has been extensively used[5], with a linear response up to 10^6 rad, where saturation effects begin to appear. The dose received by the irradiated cobalt-glass plate is determined by comparing the transmissivity of air with that of the glass at 500$m\mu$ in the Bausch and Lomb Spectronic 20 Colorimeter Spectrophotometer.

Electron irradiation not only causes glass coloration but also paramagnetic centers. Coloration has been studied by Kreidl and Hensler[6] and E.S.R. studies of glasses containing boron were first reported by Yasaitis and Smaller[7] and recently by Lee and Bray[8] and Karapetyan and Yudin[9].

In the present work curves were obtained showing the creation of paramagnetic centers as a function of dose and their de-excitation in time. It is proposed,

by comparison with the colorimetric methods, to use these curves for high-dose measurements and the utilization of the de-excitation curves is discussed.

EXPERIMENTAL PROCEDURE

The apparatus used to obtain the E.S.R. spectra was a Varian V-4502-15 spectrometer operating at a microwave frequency in the X-band near 9.4 GHz with 100 kHz field modulation. The spectrometer provides a recorder tracing of the first derivative of the resonance absorption curve. E.S.R. data were obtained at room temperature.

The glasses used were of the type F-0621 provided by Bausch and Lomb Co., with a nominal molar-volume composition of: SiO_2 62%, B_2O_3 21%, Na_2O 11%, Al_2O_3 6%, Co_3O_4 0.1% and the appropiate dimensions (15 x 6 x 1.5 mm) to allow readings to be taken in the Spectronic 20 colorimeter with the adaptor. The glass plates exhibit the characteristic blue color of cobalt in a non-saturated solution.

The glass samples were irradiated at room temperature with an electron beam of 1 MeV and 10 μA, (the output of the Van de Graaff accelerator at the Institute of Physics of the University of Mexico) during time intervals varying from 0 to 300, corresponding to doses as high as 160 Krep. The E.S.R. spectra were determined within the first hour after irratiation.

The samples for the E.S.R. spectrometer were prepared from the commercial plates by cutting them with a mechanical saw to final dimensions of 6 x 2.5 x 1.5 mm. No great difference was detected sawing the samples after or before irradiation.

Because different samples were irradiated for different time intervals, all the results were normalized by referring them to a standard sample.

Line width and g factor were measured with the help of a nuclear magnetic resonance indicator, Magnion Model G-502, using as standard the D.P.P.H. ($g = 2.0036$) reported by Holden et al.[10]. A Varian 0.1% pitch in KCl was used as intensity standard.

EXPERIMENTAL RESULTS

Before irradiation no paramagnetic resonance was observed in the samples. After irradiation, the glasses showed a resonance peak and were colored to different tones of green and brown.

The g value of the resonance is 2.0144, measured at the point where the derivative curve crosses the horizontal base line, and the line width, i.e., the separation between the positive and negative maxima points in the derivative curve, is $\Delta H = 49.4 \pm 0.3$ gauss where the error quoted corresponds to one standard deviation.

Figure 1 shows the peak-to-peak height against irradiation time and dose. Using an equation similar to the one proposed by Roch[11],

$$h = h_s (1 - e^{-\alpha t})$$

where h is the peak-to-peak height taken from the derivative curve, h_s is the same height at saturation, α is the slope at the origin and t the irradiation time, we fitted the curve to the experimental points with $h_s = 7.0$ and $\alpha = 0.024 \pm 0.003$.

Since the causes of errors are multiple, (amplifier and detector stability, klystron-power variations, variation in the Q-cavity when the sample is changed, etc.) we estimate an over-all error of 3% in the measurements.

Figure 2 shows the decrease in time of the number of paramagnetic centers measured by means of the variation in the peak-to-peak height after irradiation. The samples were kept at room temperature in closed jars. Studies of the temperature-dependence of the de-excitation in time of the paramagnetic centers are being carried out.

DISCUSSION

It is evident from the figures that the measurements of dose as a function of the height has the same characteristics as measurements made by the colori-

metric method[12] but with the advantage that the determinations can be made more accurately. It is evident that this situation is seriously dependent upon the quality of the glass (homogeneity and lack of mechanical stresses).

Fading of coloration of irradiated crystals and glasses in storage is a well-known phenomenon. Since de-excitation of the paramagnetic centers is appreciable in our case, means are required to prevent its interference with the usefulness of the glass as a dosimeter. First one should standradize so that all peak-to-peak height measurements are made at a given time after the irradiation as we did. Second, decay curves can be done and a reduction factor can be obtained to be applied to glass plates read days or weeks after exposure.

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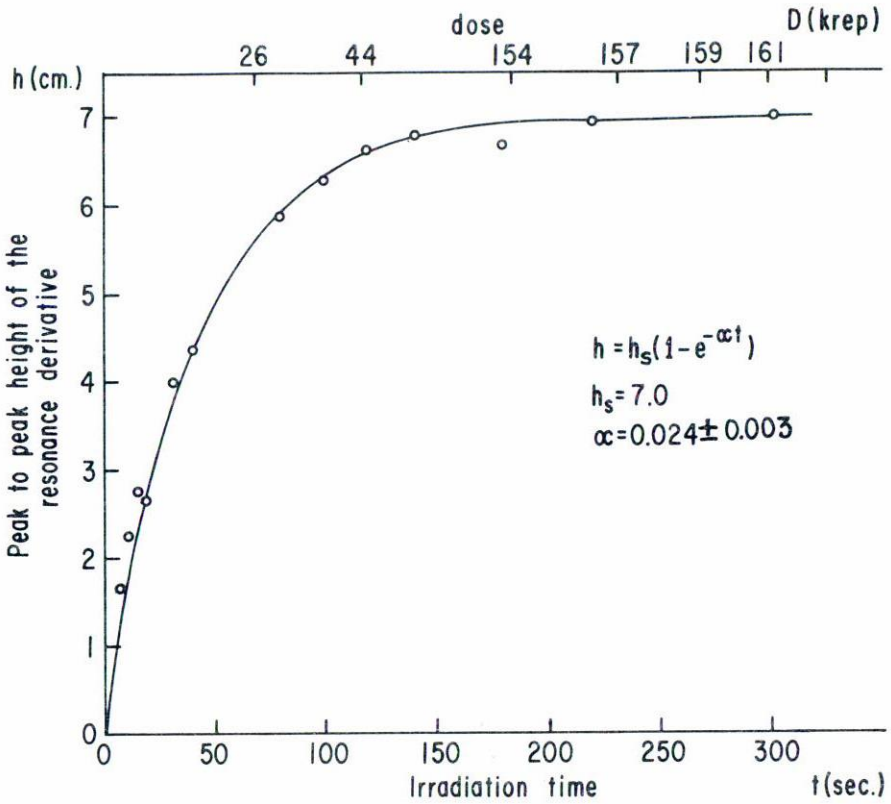
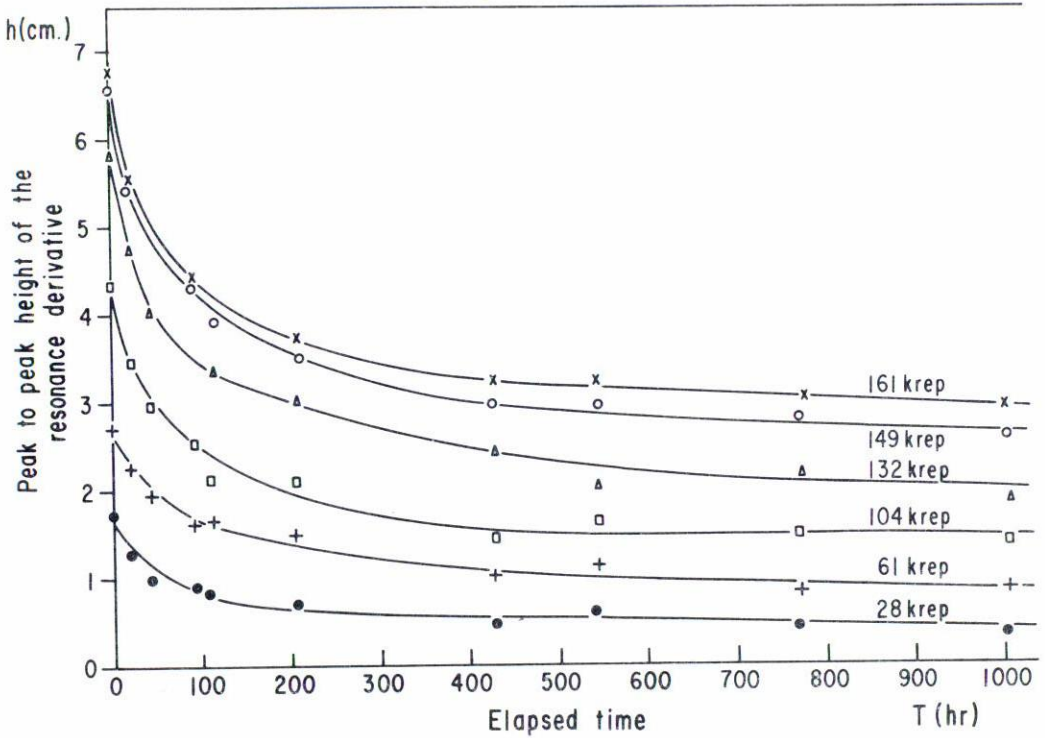


Height of the Resonance Derivative as a Function of Dose in Cobalt-Activacted Borosilicate Glasses

Fig. 1



Decay Curves for Electron-Irradiated Cobalt-Activated Borosilicate Glasses

Fig. 2