MASTER

SCR-79

Sandia Corporation

REPRINT

**RADIATION-INDUCED COLORATION
IN GLASS**

by

W H Cropper

August 1959

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Preprinted for: AMERICAN CERAMIC SOCIETY, GLASS DIVISION
Symposium on Radiation Effects
Wernersville, Pennsylvania. October 1959.

SCR-79

SANDIA CORPORATION REPRINT

RADIATION-INDUCED COLORATION IN GLASS

by

W. H. Cropper

August 1959

✱✱

ABSTRACT

General aspects of radiation-induced coloration in glass are discussed. It is considered that the most significant initial effect of the radiation is to produce free electrons and positive holes in a track. The decay of the track from the initial condition is described in some detail, assuming (a) that the rate of diffusion of electrons from the track is small compared to the rates of other processes, and (b) that "primary" processes which form color centers can be considered independent of "secondary" processes which cause destruction of color centers. A method of calculation is described which gives the concentration of color centers formed at various doses. With plausible assumptions for the parameters, agreement with the data of Schulman⁴ on a silver phosphate glass is obtained. The treatment of glasses less simple than the silver phosphate case is also discussed. *auth*

TABLE OF CONTENTS

	Page
Introduction	5
The Model	5
Description of the Track Processes	6
Description of the Processes Causing Color-Center Destruction	12
Applications to Special Cases	15
List of References	18

LIST OF ILLUSTRATIONS

Figure	Page
1 - Calculation of the concentration of color centers, M_O' for values of the dose, x ; M_O' has units cm^{-3} and x is in roentgens	13
2 - Calculation of color-center formation at various doses in a silver phosphate glass	17

RADIATION-INDUCED COLORATION IN GLASS

Introduction

Ionizing radiation induces color-center formation in most types of glass. The radiation causes production of free electrons, and these are either returned to the ions from which they came (positive holes), or they are captured elsewhere at one of the numerous and varied trapping centers present in the glass. The latter process usually leads to color-center formation, since most glasses contain at least one type of trap which is a color-center precursor. The traps may be natural to the base glass, being located at defects such as negative ion vacancies, or they may be associated with certain added positive ions.

The present paper gives an approach to the elementary processes which lead to color-center formation. It is considered that the energy of the primary and secondary particles of the radiation is dissipated in a track, and that the free electrons and positive holes are initially produced there. The decay of the track from this initial condition may then involve the following:

- (a) Recombination of positive holes and electrons;
- (b) Interaction between trapping centers and electrons to form color centers;
- (c) Diffusion of electrons away from the track;
- (d) Diffusion of positive holes away from the track;
- (e) Interaction between positive holes and color centers;
- (f) Spontaneous decay of color centers;
- (g) Destruction of color centers in regions of localized high temperatures and electronic excitation.

The Model

Under certain conditions all of the above processes may be important, and a theoretical calculation of the color-center yield becomes very complicated. In the present treatment a useful simplification is introduced by separating the processes which may be of importance in the track (processes (a), (b), and (c)) from

those which are slower (processes (d), (e), and (f)) and occur after the track has mostly decayed. It will be shown below that process (g) does not significantly affect color-center production at the concentrations usually encountered. Thus the problem can be considered in two stages: (1) the initial production of electrons in the track and their subsequent competitive capture by positive holes and trapping centers, and (2) the effects of slower processes, all of which contribute to the destruction of color centers. These two stages will be considered to be independent of each other, and will be discussed separately.

Description of the Track Processes

We now turn to a brief description of a track and the differential equations which describe its decay. As an example the track of an average Compton recoil electron from a 1-mev gamma photon will be described.

We first calculate m_0 and n_0 , the initial number of positive holes and electrons present in the track:

$$m_0 = m_1 + M' \quad (1)$$

$$n_0 = m_1 \quad (2)$$

where m_1 is the primary yield of free electrons or positive holes, and M' is the number of color centers contained in the track. For the present case m_1 may be calculated as follows:

$$m_1 = \frac{4.5 \times 10^5}{30} = 1.5 \times 10^4,$$

since the electron has 450 kev energy, and it is assumed that approximately 30 ev are required to produce one electron.

The effective volume of the track may be estimated:

$$v = \frac{4\pi}{3} (10^{-6})^3 (5 \times 10^3) = \sim 10^{-14} \text{ cm}^3,$$

it being assumed that the track ($\sim 6 \times 10^6 \text{ \AA}$ in length) is composed of 5×10^3 "spurs," each with an initial radius of $\sim 100 \text{ \AA}$, and in which ~ 3 free electrons

are produced. We will also require the rate of production of tracks. Designating this rate by $A \text{ cm}^{-3} \text{ sec}^{-1}$, where I is the dose rate in r sec^{-1} , we have:

$$A = (86)(2.7)/(1.6 \times 10^{-12})(4.5 \times 10^5) = 3.2 \times 10^8 \text{ r}^{-1} \text{ cm}^{-3}.$$

It is assumed that a dose of 1 r deposits 86 ergs/gm, and that the density of the glass is 2.7 gm cm^{-3} . Thus the number of free electrons produced per unit volume per unit dose is given by,

$$Am_1 = 4.8 \times 10^{12} \text{ r}^{-1} \text{ cm}^{-3}.$$

To obtain the color-center yield, we will multiply this number by α , the fraction of the electrons which are captured by the color-center-producing traps.

It can now be established that process (g) does not usually give significant destruction of color centers. It would be expected that a mechanism for radiation-induced destruction of color centers would involve localized high temperature, or electronic excitation in regions where ($\sim 30 \text{ ev}$) free electrons are stopped. Seitz and Kochler⁵ discuss this mechanism in connection with production of displacement damage; they conclude that the probability for a process with activation energy ϵ , induced by deposition of energy E in a spherical region of radius r' is very small outside a radius r given by

$$r = \frac{4}{(324 \pi)^{1/6}} \left(\frac{E}{\epsilon} \right)^{1/3} r',$$

with $E = 30 \text{ ev}$, $\epsilon = 1 \text{ ev}$, $r' = 2A$,

$$r < 10 \text{ \AA}.$$

Thus, since the color-center concentration is usually less than $5 \times 10^{18} \text{ cm}^{-3}$, it follows that less than 0.02 color centers are destroyed by this mechanism per electron produced. Then, unless α has a value appreciably less than 0.1, process (g) can be neglected.

The decay of a track according to processes (a), (b), and (c) is described by the following differential equations:

$$\partial n / \partial t = D \nabla^2 n - k_2 M n - k_3 m n \quad (3)$$

$$dm / dt = -k_3 m n \quad (4)$$

in which

- m = Number of positive holes in the track;
- n = Number of free electrons in the track;
- M = Number of trapping centers in the track;
- D = Diffusion coefficient for free electrons;
- k_2 = Rate constant for electron-trapping-center interactions;
- k_3 = Rate constant for electron-positive-hole interactions.

An exact simultaneous solution of Equations (3) and (4) is quite difficult. An approximate solution can usually be obtained by neglecting the diffusion term of Equation (3). A comparison of the magnitude of the $D \nabla^2 n$ -term and the $k_2 M n$ -term justifies this procedure:

$$k_2 M n / D \nabla^2 n > \left[k_2 M n \right]_0 / \left[D \nabla^2 n \right]_0 = \sim k_2 M b^2 / D,$$

where b is the initial radius of the spur. It is commonly assumed that for electrons in a solid phase $D < 10^{-2} \text{ cm}^2 \text{ sec}^{-1}$. Fowler⁶ finds that in polyethylene the specific rate of electron-trapping-center interactions in units of $\text{cm}^3 \text{ sec}^{-1}$ (i.e., $k_2 v$) is $\sim 7 \times 10^{-10}$; for the corresponding rate constant in the track, $k_2 = \sim 7 \times 10^4 \text{ sec}^{-1}$. For the case of glass, we assume $k_2 > 10^4 \text{ sec}^{-1}$. The number of trapping centers in the track is assumed to be that of the case described in the section, Applications to Special Cases, $M = 5 \times 10^6$. Frequently assumed values for b lie in a rather wide range. Samuel and Magee¹ assume $b < 20 \text{ \AA}$; Lea² takes $b = 150 \text{ \AA}$; in the present case we assume $b < 100 \text{ \AA}$. With these limits on the parameters, we have

$$k_2 M n / D \nabla^2 n > 10.$$

The relative value of the $k_3 mn$ -term may also be estimated:

$$k_2 Mn / k_3 mn > [k_2 Mn]_0 / [k_3 mn]_0 = k_2 M / k_3 m_0 = \sim 500 (k_2 / k_3),$$

with $M = 5 \times 10^6$, and $m_0 = 10^4$. Since k_2 and k_3 may conceivably differ by as much as two orders of magnitude, we cannot conclude that the $k_3 mn$ -term in Equation (3) is negligible in comparison with the $k_2 Mn$ -term.

It may be concluded then that as a first approximation Equations (3) and (4) may be written

$$-dn/dt = k_2 Mn + k_3 mn \quad (5)$$

$$-dm/dt = k_3 mn, \quad (6)$$

and n may be obtained in terms of m as follows:

$$n = m - M' + (k_2 M / k_3) \ln (m / m_0).$$

Therefore

$$-dm/dt = k_3 m \left[m - M' + (k_2 M / k_3) \ln (m / m_0) \right]. \quad (7)$$

It is of interest to obtain the number of positive holes remaining after all of the free electrons have gone to positive holes or trapping centers. This will be the steady-state concentration of m , for which $dm/dt = 0$, and is evidently given by solutions of the equation

$$m_f + (k_2 M / k_3) \ln (m_f / m_0) = M', \quad (8)$$

where m_f is the steady-state number of positive holes in the track. The number of electrons which have gone to positive holes in the track will be $m_0 - m_f$, and if α is the fraction of the initial m_1 electrons which have gone to traps

$$m_0 - m_f + \alpha m_1 = m_1$$

and

$$\alpha = [y m_1 - (1 - y) M'] / m_1 \quad (9)$$

where $y = m_f / m_0$.

An expression can now be written for the rate of formation of color centers:

$$\frac{dM'_0}{dt} = A m_1 \alpha = A I [y m_1 - (1 - y) M'] ,$$

where M'_0 is the bulk concentration (cm^{-3}) of color centers. In terms of the dose, $x = It$:

$$\frac{dM'_0}{dx} = A [y m_1 - (1 - y) M'] . \quad (10)$$

Equation (10) can be integrated for various values of M' and y . Values of y are obtained from

$$y(1 + z) + r \log y = z , \quad (11)$$

where

$$r = 2.303 k_2 M / k_3 m_1$$

$$z = M' / m_1 .$$

Table I contains results of calculations of α , y , and x for various values of the variable z and the parameter r .

At low doses ($< \sim 10^5 r$) Equation (10) is approximately

$$\frac{dM'_0}{dx} = A m_1 \alpha_0 ,$$

where α_0 is a constant given by

$$\alpha_0 + r \log \alpha_0 = 0 .$$

TABLE I

Calculation of the Dose for Various
Values of the Parameter r and the Variable z

z^*	$r = 0.5$			$r = 5$			$r = 50$		
	y	α	$x(10^{-5})^{**}$	y	α	$x(10^{-5})^{**}$	y	α	$x(10^{-5})^{**}$
0	0.278	0.278	0	0.718	0.718	0	0.957	0.957	0
0.01	0.282	0.275	0.112	0.719	0.716	0.0437	0.957	0.957	0.0328
0.1	0.317	0.249	1.18	0.725	0.698	0.449	0.958	0.956	0.328
1	0.562	0.125	18.4	0.776	0.551	5.55	0.959	0.917	3.34
2	0.693	0.080	51.1	0.815	0.445	11.2	0.960	0.881	9.36
4	0.809	0.046	159.4	0.864	0.318	28.0	0.963	0.816	14.2
6	0.862	0.032	325	0.892	0.246	50.4	0.966	0.786	22.1
8	0.892	0.025	548	0.911	0.202	78.5	0.968	0.759	30.6
10	0.911	0.020	830	0.925	0.171	112	0.970	0.667	39.6
20	0.953	0.0105	3090	0.957	0.0955	365	0.977	0.513	94.8
40	0.976	0.0053	12000	0.977	0.0508	1660	0.984	0.348	258
60	0.984	0.0036	26400	0.984	0.0350	2780	0.988	0.268	481
80	0.988	0.0026	46800	0.988	0.0256	4870	0.990	0.206	752
100	0.990	0.0022	72700	0.990	0.0203	7550	0.992	0.172	1080

*The bulk concentration of color centers, M'_O , is related to z by $M'_O = zm_1/v$, where v is the volume of the track.

**Dose is calculated in roentgens and is given by

$$x = (1/Av) \int_0^z (dz/\alpha).$$

In the above the approximate value $v = \sim 10^{-14} \text{ cm}^3$ is used, so that

$$x = (3.12 \times 10^5) \int_0^z (dz/\alpha).$$

Thus in this dose range M'_O varies linearly with dose, according to

$$M'_O = A m_1 \alpha_O x \quad (12)$$

$$= (4.8 \times 10^{12}) \alpha_O x \text{ cm}^{-3}.$$

At higher doses all of the terms of Equation (10) are necessary, and M'_O becomes a function of x raised to a power less than unity. This is shown in Figure 1 where the results of Table I have been plotted in terms of $\log M'_O$ versus $\log x$.

It has been assumed in the above that all of the electron traps are color-center-producing. In many cases more than one kind of color-center-forming traps will be present, and the fraction of the total absorbed energy, α_i , which is distributed to the color center of interest is given by

$$\alpha_i = k_i M_i \alpha / k_2 M,$$

where k_i is the specific rate for the interaction between electrons and the i^{th} trapping center, and M_i is the number of electron traps of the i^{th} type in the track. The rate of formation of the i^{th} color center is then given by

$$\frac{dM'_i}{dx} = A m_1 \alpha_i, \quad (13)$$

where M'_i is the concentration of the i^{th} color centers. In general the behavior of the ratio M_i/M is difficult to predict. Therefore, general calculations from Equation (13) are not easily made. In the following section the simplest case is treated, that in which all trapping centers produce color centers.

Description of the Processes Causing Color Center Destruction

As mentioned before, the basic assumption of this treatment is that processes (d), (e), and (f) do not proceed significantly until processes (a), (b), and (c) are nearly complete. Equation (10) developed in the last section has provided a description of the latter processes; we now include processes (d), (e), and (f) and attempt to write an equation for the over-all effect.

Figure 1. Calculation of the concentration of color centers, M'_O for various values of the dose, x ; M'_O has units cm^{-3} and x is in roentgens.

In general

$$\frac{dM'_0}{dx} = Am_1 \alpha - R,$$

where R expresses all of the slow color-center-destroying processes, and α is given by Equations (9) and (11). Probably R can be separated into first- and second-order processes, so that

$$\frac{dM'_0}{dx} = Am_1 \alpha - (k_4/I)M'_0 - (k_5/I)(M'_0)^2 \quad (14)$$

can be written. First-order destruction of color centers probably results from escape of electrons from rather shallow traps; second-order processes may be the result of annihilation interactions between color centers and positive holes.

Therefore it would be expected that k_4 of Equation (14) should be given by

$$k_4 = Ae^{-E/kT} \quad (15)$$

where E is the activation energy for the escape of the electron from its trap, and A is a "frequency coefficient." If A is of the order of magnitude 10^{13} sec^{-1} , and $I = \sim 10^2 \text{ r sec}^{-1}$, the term involving k_4 in Equation (14) may be important at room temperatures in comparison to the first term for $M'_0 > 10^{18} \text{ cm}^{-3}$ and $E < \sim 1 \text{ ev}$.

The specific rate of the interaction between color centers and positive holes is determined by the rate of diffusion of the two species, so that

$$\begin{aligned} k_5 &= B \sigma D \\ &= B \sigma D_0 e^{-E'/kT} \end{aligned} \quad (16)$$

where B is a coefficient with a value ~ 10 , σ is a "reaction diameter" ($\approx \sim 1\text{\AA}$), D_0 is the diffusion coefficient of the species at high temperatures, and E' is the activation energy for a single jump in the diffusion process. D_0 depends rather strongly on the size of the species involved and the structure of the lattice; data taken on the diffusion of positive ions in various crystals indicate that D_0 should have values in the range $10 - 10^{-4} \text{ cm}^2 \text{ sec}^{-1}$. Thus k_5 might lie in the range

$$k_5 = (10^{-6} - 10^{-11}) e^{-E'/kT} \quad (17)$$

and this term may be expected to be significant at room temperature if $E' < 0.75 - 1.0$ ev and $M'_O > 10^{18}$ cm⁻³.

The color-center concentrations and activation energies mentioned are not unlikely. Therefore, it is to be expected that rather extensive fading will take place at high concentrations of color centers after the irradiation and during the irradiation, if the dose rate is low. In the following section the extent of this effect in actual cases is discussed.

Applications to Special Cases

In order to apply Equation (10) to experimental results, it is necessary to relate the calculated quantity M'_O , the bulk concentrations of color centers, to the measured quantity, μ , the absorption coefficient. The necessary relationship is provided by the Smakula relation³:

$$M'_O = \frac{18mc}{\pi e^2 h} \frac{n'}{(n' + 2)^2} \left(\frac{\mu_m W}{f} \right) \text{ cm}^{-3}, \quad (18)$$

where μ_m is the absorption coefficient (cm⁻¹) at the wavelength of the maximum of the absorption peak, W is the half-maximum width (in ev) of the band, f is the oscillator strength of the absorbing center, n' is the index of refraction of the medium, and the constants m , c , e , and h have their usual significance. Substituting values for the general constants and using $n' = 1.5$, Equation (18) becomes

$$M'_O = \sim 2 \times 10^{18} \left(\frac{\mu_m W}{f} \right) \text{ cm}^{-3}. \quad (19)$$

This may be combined with Equation (12) to give

$$\mu_m = \frac{2.4 \times 10^{-4} f \alpha_O}{W} x \quad (20)$$

for the linear portion of $\mu_m - x$ plot. Using the latter, values for $f \alpha_O$ can be obtained. Table II gives two results obtained in this manner.

TABLE II

Type of glass	W(ev)	$f\alpha_0$	Reference
Silver phosphate	1.5	0.8	3
Cobalt silicate	1.9	0.4	4

If f can be considered to be about unity, the resultant values of α_0 are indicated to be the range 0.4 - 0.8, and one may conclude that values of r are in the range 1 - 50. Thus we arrive at

$$k_3/k_2 = 20 - 1000$$

for $M = 5 \times 10^6$. This result seems reasonable, since the color-center-producing traps should usually be shallower than the positive holes.

The calculation described under Description of the Track Processes has been carried out for the case of the silver phosphate glass used by Schulman⁴ in which the concentration of silver ions was $\sim 5 \times 10^{20} \text{ cm}^{-3}$, and $M = 5 \times 10^6$. The parameter r was assigned the value $r = 5$. It was also assumed that all of the traps form color centers; this assumption seems justified with the very high concentration of Ag^+ ions present. The result of this calculation, neglecting all decay processes, is shown in Figure 2, Curve A.

It is likely that Ag-color center in a phosphate glass are quite stable and do not undergo appreciable thermal decomposition. Thus we apply Equation (14) to this case neglecting the second term on the right. Curve C was obtained assuming

$$k_5/I = 1.8 \times 10^{-28} \text{ cm}^3 \text{ r}^{-1},$$

and

$$k_5 = 5.4 \times 10^{-26} \text{ cm}^3 \text{ sec}^{-1},$$

and that one month's time elapses after the irradiation (the situation in Schulman's experiments⁴). It is thus implied from Equation (16) that the activation energy for one diffusion jump is 0.8 - 1.1 ev. Lacking definite information on the mechanisms

Figure 2. Calculation of color-center formation at various doses in a silver phosphate glass. Curve A takes into account only the processes of the track; Curve C includes a second-order decay process and assumes that one month's time elapses after irradiation; Curve B assumes the second-order decay process and gives the color-center concentration immediately after the irradiation; circles represent the data of Schulman⁴; ordinate: log of color-center concentration in cm^{-3} ; abscissa: log of dose in roentgens.

of the decay processes, we cannot establish that Curve C is an accurate indication of the color-center concentration at various doses. However, since the assumptions and the agreement with Schulman's data are reasonable, we conclude that second-order decay processes are possible. Curve B was obtained assuming second-order decay processes and that the measurement was made immediately after the irradiation (dose rate: 300 r sec^{-1}).

REFERENCES

1. A. H. Samuel and J. L. Magee, "Theory of Radiation Chemistry. II. Track Effects in Radiolysis of Water," J. Chem. Phys. 21, 1080 (1953).
2. D. E. Lea, Actions of Radiations on Living Cells, Cambridge Press, Second Edition, (1956).
3. A. Smakula, Zeits. f. Physik 59, 603 (1930).
4. J. H. Schulman, C. C. Klick, and H. Rabin, "Measuring High Doses by Absorption Changes in Glass," Nucleonics 13 (2), 30 (1955).
5. F. Seitz and J. S. Koehler, "Displacement of Atoms During Irradiation," Solid State Physics 2, 305 (1956).
6. J. F. Fowler, "X-Ray Induced Conductivity in Insulating Materials," Proc. Roy. Soc. (London) 236A, 464 (1956).