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Radiation-Induced Color Centers in Glasses

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The present state of studies on color centers in glasses has been reviewed. The current works on color centers are shown to be directed to classification of the color centers (trapped hole or trapped electron ?), use of color center phenomena as a tool for elucidating the glass structure and investigation of inorganic radicals in glass as a solution medium. Investigation of high pressure effect on color centers, conducted in our laboratory, is presented as an example of their applications to the problem of glass structure.

I. INTRODUCTION

Since the color centers in glasses were first investigated systematically by Yokota[1] more than fifteen years ago, an enormous number of works have been published on this subject.[2] A wide range of glass compositions including major and minor constituents has been covered. Novel methods such as electron spin resonance technique have been employed. Dielectric measurements, luminescence phenomena and infrared spectra have also been applied, besides uv and visible spectroscopy. Indicator atoms of Ce, Eu *etc.* have been conveniently utilized for elucidating classification of the centers. Kinetic studies on their formation have been made. All these studies contributed to the better understanding of nature (type and structure) of color centers and, in some cases, threw some doubt upon their type proposed at the initial stage of the color center study.

In this paper the present knowledge on their nature is reviewed first. Although their nature has not been clarified thoroughly, there have been a number of works aimed at elucidating glass structure on the basis of color center phenomena and studying inorganic radicals in glass as a solution medium. Finally the effect of high pressure on color centers in glasses studied in our laboratory is reported as an application of their study for the problem of glass structure.

The subjects in this paper have been limited to the color centers or defects produced by electromagnetic radiations : γ-rays, x-rays and uv radiation. A comprehensive review has been published by Lell, Kreidl and Hensler in 1966,[2] which should be consulted by the reader interested in this matter, and so, the studies published later than 1966 have been stressed when possible.

II. GENERATION OF COLOR CENTERS IN GLASSES

When exposed to high energy radiations such as γ- and x-rays, oxide glasses take a variety of colors depending upon their composition. Generally, the radia-

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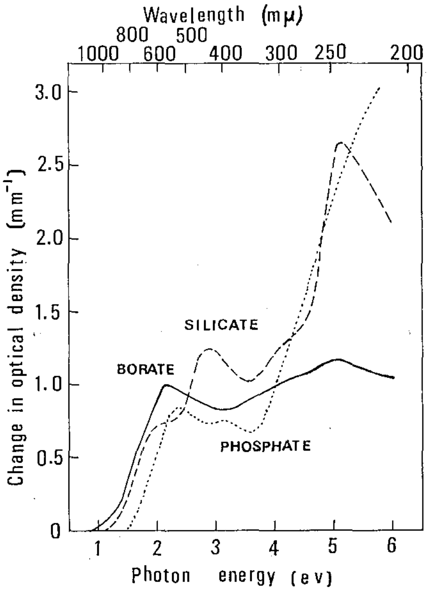


Fig. 1. Radiation-induced absorption in a silicate glass ($2\,SiO_2 \cdot 0.35\,Na_2O \cdot 0.3\,CaO$), a borate glass ($B_2O_3 \cdot 0.35\,Na_2O \cdot 0.3\,CaO$) and a phosphate glass ($P_2O_5 \cdot 0.35\,Na_2O \cdot 0.3\,CaO$) (Bishay and Ferguson[3]).

tion colors are brown, purple and red, respectively, for silicate, borate and phosphate glasses. Absorption curves[3] of irradiated glasses are shown in Fig. 1.

These radiation-induced colors in glasses were attributed[1] to the formation of "color centers" similar to those found in irradiated or additively colored alkali halide crystals.[4] That is, trapped electrons and holes associated with ion vacancies were made responsible for the colors. The presence of trapped electrons or holes in irradiated glass was confirmed[5] by ESR technique. The existence of ion vacancies in glasses might have been suspected, because glass was believed to have a random and originally defective structure in contrast to crystal consisting of regular arrays of atoms or ions. If we pay attention to the presence of short range order of atomic arrangement in glasses, however, it would be natural to assume that various defects, *e. g.*, ion vacancy or interstitial ion, are found also in glasses. Then, the occurrence of color centers in glass similar in nature to those in alkali halide crystals can be understood. Kats and Stevels[6] classified the possible defects in glasses.

III. NATURE AND STRUCTURE OF COLOR CENTERS

1. Assignment of optical absorption bands

One of the most important and fundamental subjects in the study of color centers in glasses is to assign the observed optical absorption bands to trapped electrons or holes. There is no unambiguous way for the assignment, and the two contradictory views have been presented.

Radiation-induced absorption spectra[6] of alkali silicate glasses containing 30

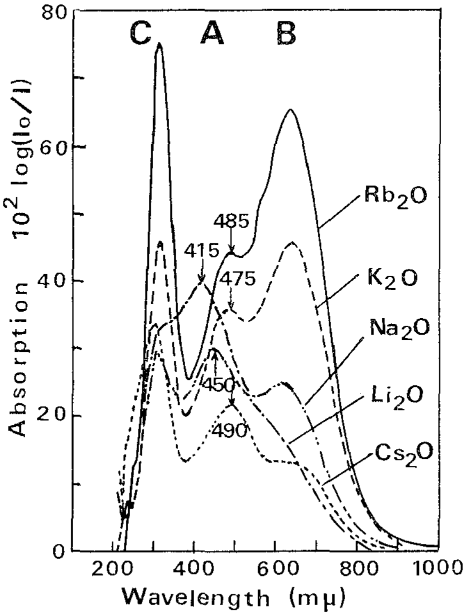


Fig. 2. Radiation-induced absorption of alkali silicate glass with 30 mole % of different types of alkali (Kats and Stevels[6]). Exposure to 10^6 r x-rays.

mole % alkali are shown in Fig. 2. The figure shows the color center bands stable at room temperature. Three series of absorption bands are distinguished; two of them are in the visible region, the wavelength range of the bands being 415-490 mμ (A) and 620-630 mμ (B), respectively, and the other is at 310 mμ (C) in uv region. The above designations A, B and C are employed for convenience throughout this paper to indicate the center responsible for the absorption band as well as the band itself.

Much effort has been made to assign each series of bands to a particular type (trapped electron or hole?) of color center. Briefly, the methods of assignment are mainly based on:

1. Comparison of the behavior of a band in glasses with the bands in alkali halide crystals.
2. Use of competition of trapping sites and multivalent ions for electrons or holes.

Yokota attributed the visible bands A and B to trapped electron at oxygen vacancy neighboring alkali ion and the uv band C to trapped hole at alkali ion vacancy neighboring oxygen ion on the basis of the following observations:[1]

a. The visible bands A and B shift to shorter wavelengths in the order of decreasing ionic radius of the alkali ion in glass (K→Na→Li) as is the case with F center in alkali halide crystal. In alkali halides the F center band, attributed to an electron trapped at a halogen ion vacancy and surrounded by alkali ions, shifts to shorter wavelengths with decreasing radius of the alkali ion (K→Na→Li).[7]

b. The oxidized glass seems to exhibit the smallest A and B bands and the largest C band, and the situation is the reverse for the reduced glass. The oxidizing condition may decrease the number of oxygen vacancy (electron-trapping site) and the reducing condition may increase it.

c. The intensity and position of the two visible bands (A and B) change regularly with the Na_2O content, but those of the C band hardly change. In other words, the former are associated with alkali ion (an electron trapped in oxygen vacancy has an alkali ion or ions nearby) and the latter has no relation with alkali ion (a hole trapped in alkali ion vacancy has no surrounding alkali ions).

Yokota's assignment was supported by Kats and Stevels.[6]

Later, however, Stround[8] proposed the different assignment. He made a detailed examination of the behavior of cerium ions on x-irradiation with the glass SiO_2 75 %, Na_2O 25 % (wt.). The assumption was made that a Ce^{3+} ion, lower valence state of cerium, traps a hole produced by irradiation before it is captured by intrinsic hole trap. As shown in Fig. 3,[8] the radiation-induced absorption at 450 mμ (A band) and 620 mμ (B band) decreased with increasing Ce^{3+} concentration. For Ce^{3+} concentration sufficiently large, the Ce^{3+} ions captured essentially all the holes. The above results led to the assignment of the visible bands at 450 mμ (A) and 620 mμ (B) to trapped hole centers. These two bands are not caused by trapped electrons, since neither is formed by photo-ionization of Ce^{3+} ions with ultraviolet light (production of free electrons) although the traps causing these two bands are present during uv irradiation.[9]

Similar discussion on the nature of the color centers was made by Mackey, Smith and Nahum[10] using the sodium disilicate glasses containing Eu^{3+} ions. By

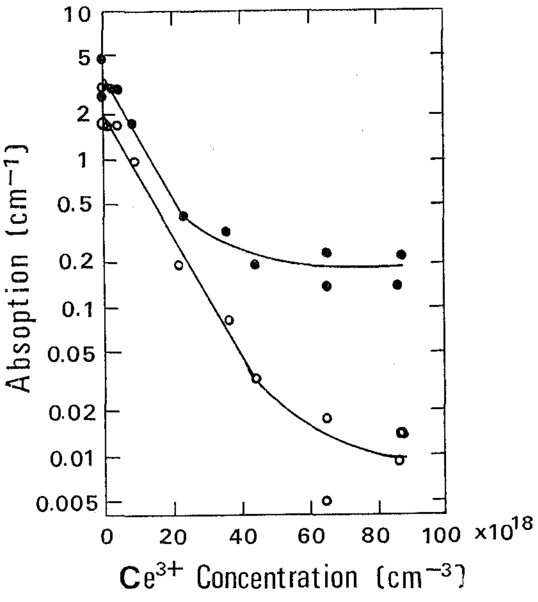


Fig. 3. Change of radiation-induced absorption as a function of Ce^{3+} concentration (Stroud[8]).

● Change at 450 mμ in glasses with negligible Ce^{4+}.

○ Change at 620 mμ in glasses with negligible Ce^{4+}.

melting glass in oxidizing condition, europium was incorporated entirely as Eu^{+3}, higher valence state of europium ions. The added Eu^{3+} ions were assumed to have an electron trapping cross section proportional to its concentration and to compete with intrinsic defects (traps) for electrons generated by the x-rays. Kinetic equations for trapping and recombination of electrons and holes were related to optical observations on glasses. It was shown first that the inverse of the initial growth rate of trapped electron band should have a linear dependence on Eu^{3+} concentration. This was tested and confirmed to hold for the 305 mμ band (C band), as shown in Fig. 4.[10] Second, the kinetic analysis showed that the initial growth rate of absorption bands of trapped holes should be unaffected by addition of Eu^{3+}. Actually, the 460 mμ (A) and 620 mμ (B) bands were independent of Eu^{3+} concentrations for small x-ray doses, as shown in Fig. 5.[10] Thus, the band peaked at 305 mμ (C band) was attributed to trapped electron and the other two bands at 460 mμ (A band) and 620 mμ (B band) to trapped

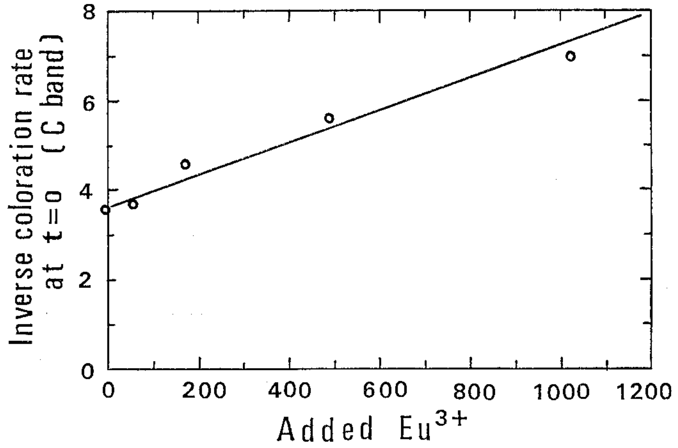


Fig. 4. Relation between the inverse of the initial rate of growth of the 305 mμ (C) band and the added Eu^{3+} concentration (Mackey, Smith, Nahum[10]).

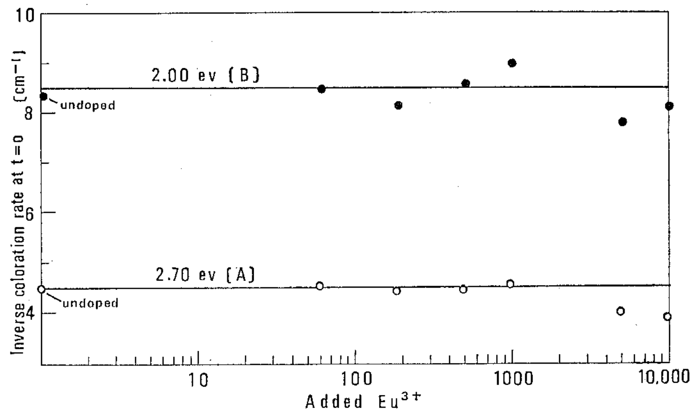


Fig. 5. Independence of the Eu^{3+} concentration for initial rate of coloration in the 460 mμ (A) and 620 mμ (B) bands (Mackey, Smith and Nahum[10]). X-irradiation at 350°K.

hole. It was claimed that the behavior of the absorption bands upon thermal bleaching, change of glass composition and luminescence supported this classification.

It should be noted that the following three assumptions were made[9] implicitly in the analysis. First, the addition of a low concentration of polyvalent ions, generally less than 10^{20} ions/cm^3, to glass does not alter the glass structure radically. Second, melting of glass under controlled condition (reducing or oxidizing) has no effect other than affecting the valence state of polyvalent ions. Third, the primary effect of ionizing radiation is the supplying already existing charge traps with electrons or holes.

It is also important to note that these assignments were independent of the sign of the *g*-shift obtained by ESR measurements.[9]

The assignment of the absorption bands in borate[9,11] and phosphate glasses[9,12,13] were also conducted and the visible bands (see Fig. 1) were attributed to holes trapped at non-bridging oxygens. It is interesting to note that the similarity in absorption is striking[2,3] for all the three glasses (silicate, borate and phosphate), as seen in Fig. 1, and that the visible bands are all attributed to trapped hole centers.

2. Electron spin resonance measurement

The *g*-shift (the difference between the *g*-value of the free electron, 2.0023, and the measured *g*-value) determined by ESR technique is said to give the sign of a trapped charge; a positive *g*-shift indicates a trapped hole and a negative

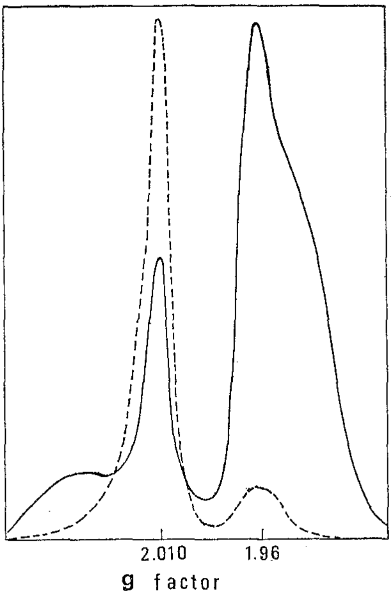


Fig. 6. ESR spectrum of $Na_2O \cdot 3SiO_2$ glass exposed to 10^5 r x-rays (Stroud, Schreurs and Tucker[9]).
--- No cerium added,
—— 35×10^{18} Ce^{3+}/cm^3, 0.3×10^{18} Ce^{4+}/cm^3.
Divide the solid curve ordinates by 12.5.

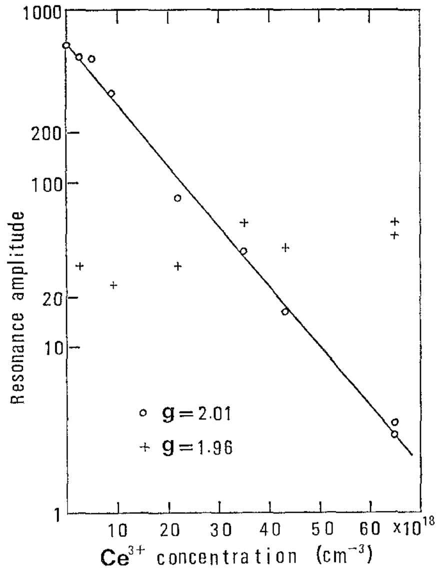
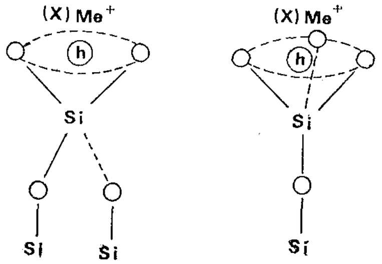


Fig. 7. Effect of Ce^{3+} concentration on the ESR spectra caused by x-ray irradiation of soda-silica glass (Stroud, Schreurs and Tucker[9]).

g-shift a trapped electron.2) This is not always a reliable method of classification of a trapped charge, however.12) Actually, the assignment of the ESR spectra as well as optical bands (A, B and C) was made independently of the sign of the g-shifts.9,12)

It was confirmed that the ESR spectrum of irradiated soda-silica glass consists of two strong resonances centered at $g=2.01$ and $g=1.96$, respectively, as shown in Fig. 6.9,12) As the solid curve in the figure shows, addition of Ce^{3+} ions to the glass reduces the $g=2.01$ line drastically, while no effect is observed on the $g=1.96$ line. Figure 7 shows the dependence of the size of the resonance lines on Ce^{3+} concentration.9,14) The size of the $g=2.01$ line depends exponentially on Ce^{3+} concentration and, accordingly, it is assigned to trapped holes. The $g=1.96$ line is assigned to trapped electrons because its size is independent of the Ce^{3+} concentration. Further experiments on the thermal bleaching, variation with glass composition and dependence on the radiation dose indicated that the $g=2.01$ ESR line changes with the optical absorption in the visible (A and B bands) and the $g=1.96$ line is not related to these optical bands. Therefore, it was assumed that the holes which give rise to one or both the visible absorption bands (A and B bands) also cause the ESR line at $g=2.01$.

Schreurs15) made a detailed study of the multiplicity of the $g=2.01$ hole band and confirmed that there are two overlapping hole spectra in the $g=2.01$ region. The dependence of the two hole ESR spectra on such variables as the type of alkali ion (Li through Cs), the alkali-to-silica ratio, the microwave power, and the bleaching temperature was investigated and the models for the two centers were proposed, as shown in Fig. 8.



(a) (b)

Fig. 8. Models for HC$_1$ (A center) and HC$_2$ (B center) (Schreurs15)). The number of Me$^+$ ions (alkali ions) in the neighborhood of the trapped holes is not specified.

The center more dominant in the low-alkali silicate glasses, called HC$_1$ (Hole center 1), was considered responsible for the 475 mμ optical band (A band). The model for this center (Fig. 8 a) is a hole trapped on a Si-O network tetrahedron with some alkali ions nearby, which has two nonbridging and two bridging oxygens. The hole belongs to the two nonbridging oxygens equally.

The center more dominant in the high-alkali silicate glasses, called HC$_2$, might probably be responsible for the 650 mμ band (B band). The proposed model is a hole trapped on a Si-O network tetrahedron, which has one bridging oxygen and three nonbridging oxygens. The hole belongs to the three nonbridging oxygens equally.

IV. STUDIES ON GLASS STRUCTURE AND INORGANIC RADICALS

The current problems on the color centers in glasses are classified into the following three categories:

1. Detailed examination of the structure of color centers in simple glasses.
2. Utilization of the color center as a tool for studying glass structure.
3. Studies of formation and behavior of inorganic radicals (transition ions, noble metals, halogens and others) in glass regarded as solution medium.

In the first category Bray and his co-workers made ESR measurements on irradiated alkali borate glasses[16] and reached the conclusion that the ESR centers can be attributed to holes trapped in the π orbitals of oxygens which are shared between one 3-coordinated boron and one 4-coordinated boron in the glass network. ESR measurements of the glasses with various compositions are being made.[2,17]

Bishay and co-workers conducted the works belonging to the second category extensively. ESR as well as optical spectra were examined on simple glasses whose compositions were systematically varied. Change in glass structure was observed at compositions containing about 25, 33 and 45 mole % PbO in PbO-B_2O_3 glasses,[18] at about 2-5 mole % and 10-16 mole % TiO_2 in TiO_2-containing barium silicate glasses[19] and at compositions containing about 22.5 and 27.5 mole % BaO in barium silicate glasses.[20]

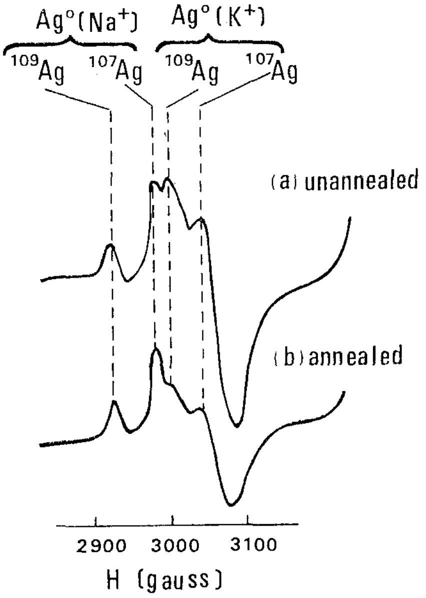


Fig. 9. Low-field parts of ESR spectra by $A_g{}^0$ in 6.7 Na_2O·13.3 K_2O·80 SiO_2 glass (Imagawa[21]).

Imagawa[21)] studied the ESR spectra of neutral silver atom Ag° produced in Ag^+-containing alkali silicate glasses by γ-irradiation. In $20(Na_2O+K_2O)\cdot 80\ SiO_2$ glasses, Ag° neighbored by K^+, $Ag^\circ(K^+)$, and Ag° neighbored by Na^+, $Ag^\circ(Na^+)$, were distinguished from each other as shown in Fig. 9. The relative peak height of $Ag^\circ(K^+)$ against $Ag^\circ(Na^+)$ decreased when the glass was annealed, indicating that in thermodynamic equilibrium the amount of $Ag^+(K^+)$ decreases with decreasing temperature near the glass-transition range. From the observation that Ag° (accordingly, Ag^+) is neighbored by only one kind of alkali ion in mixed alkali glass, it was deduced that monovalent cations exist in pairs in silicate glass.

The work of the third category can be said to have started with the study of solarization,[22)] color change of glass by exposure to sunlight. In the glass containing two kinds of polyvalent ions A^{+n} and B^{+m}, exposure to sunlight results in the formation of, for example, $A^{+(n+1)}$ and $B^{+(m-1)}$ as a result of electron transfer from A^{+n} to B^{+m}. Accordingly, the color due to A^{+n} or B^{+m} disappears and a new color due to $A^{+(n+1)}$ or $B^{+(m-1)}$ appears. A number of combinations of polyvalent ions have been known. Another class of radicals are formed in photosensitive glasses[23)] containing noble metal ions such as Ag^+, Au^+ and Cu^+, which change to Ag°, Au° and Cu° (superfix 0 means neutral atom), respectively, on exposure to uv ray.

The use of γ- and x-rays for irradiation gave a great number of radicals. The most studied among all may be cerium which proved to prevent the irradiation coloration of glasses effectively. It was already stated that cerium exists as Ce^{3+} or Ce^{4+} ions in glasses and that on irradiation a Ce^{3+} ion traps a hole, changing to Ce^{4+}, and Ce^{4+} ion traps an electron, changing to Ce^{3+}. Some other reactions leading to radical formation are as follows:

$Eu^{3+}+e \longrightarrow Eu^{2+}$ Mackey and Nahum[25)]
$Fe^{2+}+h \longrightarrow Fe^{3+}$ Tucker[14)]
$Pb^{2+}+e \longrightarrow Pb^+, Pb^\circ$ Ghosh[26)]
$\left.\begin{array}{l} Ag^{+}+h \longrightarrow Ag^{2+} \\ Ag^{+}+e \longrightarrow Ag^\circ \end{array}\right\}$ Tucker;[14)] Yokota and Imagawa;[27)] Feldmann and Treinin[28)]
$Au^{+}+e \longrightarrow Au^\circ$ Imagawa[29)]
$\left.\begin{array}{l} Tl^{+}+e \longrightarrow Tl^\circ \\ Tl^{+}+h \longrightarrow Tl^{2+} \end{array}\right\}$ Gosh;[30)] Bishay and Maklad[31)]
$Nb^{5+}+e \longrightarrow Nb^{4+}$ Kim, Reardon and Bray[32)]
$Cd^{2+}+e \longrightarrow Cd^{+}$ Imagawa[33)]

In these examples the radicals were expressed as ions for simplicity. It should be born in mind, however, that the radicals produced by irradiation are not exactly the same[34~36)] in optical absorption as the ionic species of the identical valence normally present in glass before irradiation. In rigid network of glass, Ce^{4+}, as an example, produced by irradiation would retain the environment of Ce^{3+} from which it was formed.

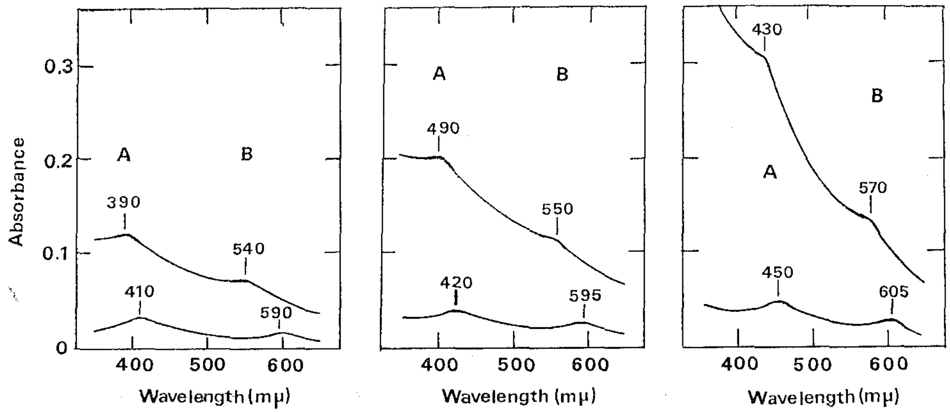
Also halogen radicals have been studied. Halogen ions in glasses are paid attention to, particularly, regarding the photochromic glasses[37)] which are made by precipitating silver (or thallium[23)]) halide crystals in glasses. Treinin and his co-workers followed the photochemistry of halogen radicals in low-melting $B_2O_3 \cdot 2H_2O$ glass and metaphosphate glasses[38] irradiated with x-rays and uv light and identified dihalide molecule ions of various types by their optical and ESR spectra. Griscom, Taylor and Bray[39] examined the ESR spectra of glasses prepared from mixtures of alkali halides and boron oxide and subjected to γ-rays. Certain new resonances were found and attributed to V-type centers (for example, Cl_2^- molecule ions) formed from halogen ions (Cl^-) as a result of trapping a hole. Inclusion of small amounts of KCl or LiCl in borate glasses resulted in nearly total suppression of the usual boron-oxygen-center (trapped hole center present in borate glass without halogen) resonance, indicating that the dissolved Cl^- ions are efficient hole traps. Photochemical reactions of halogen ions dissolved in silicate glasses were investigated by Matsuda and his co-workers.[40]

V. HIGH PRESSURE EFFECT ON COLOR CENTERS IN GLASS

As an example of application of color center spectra for obtaining information on glass structure, the work on high pressure effect on them, conducted in the author's laboratory, will be described.[41]

The high pressure effect[42] characteristic of glass as distinct from crystals is the persistence of the densification (permanent increase in density) after removal of high pressure. Increase in density or refractive index of glass, however, exhibits only the average value of densification of the whole glass network. One of the methods employed for examining the change of the local structure of glass or the local shrinkage at a particular site is to measure the optical absorption representing the local structure. This type of study has been applied to the color center sites (defect sites).

Silicate glasses of the compositions SiO_2 70 %, BaO 10 %, R_2O 20 % in mole, where R=Li, Na and K, were exposed to Co-60 γ-rays of 1×10^7 r and subjected



(a) (b) (c)

Fig. 10. Effect of high pressure on the spectra of γ-irradiated glasses. (a), (b) and (c) correspond to lithium, sodium and potassium glasses, respectively. The bottom curves are those before application of pressure and the top curves are those after application of pressure.

to a high pressure of 50 kilobars. Absorption spectra of the γ-irradiated glasses before and after the application of the pressure, measured with a microspectrophotometer, are shown in Fig. 10. It is seen for all the three glasses that the two visible bands on each absorption curve shift to shorter wavelengths when the glasses are densified. As designated before, the bands peaking at about 400 mμ are due to A center and those peaking at about 600 mμ are due to B center.

We tried to determine the local shrinkage at the sites of the color centers from the value of shift of the absorption peaks. To achieve this the behavior of the color centers in alkali halide crystals was referred to. Ivey[7)] proposed a general relation between the peak wavelength λ and ionic distance (lattice constant) r that holds for various types of trapped electron centers in alkali halides having cubic crystal structure:

$$\lambda = C\, r^n. \tag{1}$$

Here C and n are functions of the type of the color center only and not dependent on the kind of crystal. The range of the n value is, approximately, from 1 to 2, depending upon the type of the trapped electron center. For trapped hole centers in alkali halide crystals no such relation has been proposed. A few experimental data from the literature[4)] indicate, however, that the peak wavelength increases with increasing lattice constant as is the case with trapped electron centers. Assuming that eq. (1) holds for this case,

$$n = 0.6 - 1.1 \tag{2}$$

was obtained. For both trapped electron and trapped hole centers, therefore,

$$n = 0.6 - 2.0. \tag{3}$$

The formulae (1) and (3) were derived for color centers in alkali halide crystals. The color centers in glasses, however, have possibly the similar structure; they are associated with cation or anion vacancies or like. It might be said that the oxide glasses have divalent oxygen ions as anion instead of monovalent halogen ions in alkali halides. It is suggested[43)] that the relation (1) seems to hold for alkaline earth oxides which have oxygens as anion. Further, it should be noted that various types of color centers were included when formulae (1) and (3) were obtained; F, M, R and U centers and V_1, V_2, V_3, V_4 and V_k centers. Considering these, application of these formulae may be justified.

When the peak wavelength of the color center (A or B center) in the glass before and after application of pressure are denoted by λ_o and λ_p, respectively,

$$\lambda_o = k\, r_o^n, \qquad \lambda_p = k\, r_p^n, \tag{4}$$

where r_o and r_p are "lattice constants" of the glass. Suffix o and p refer to the value before and after application of pressure, respectively. When the local shrinkage s_l is defined as the degree of decrease in the local volume,

$$s_l = \frac{v_o - v_p}{v_o} = \frac{r_o^3 - r_p^3}{r_o^3} = 1 - \left(\frac{r_p}{r_o}\right)^3. \tag{5}$$

Here v_o and v_p are local volumes. From eqs. (4) and (5)

$$s_l = 1 - (\lambda_p/\lambda_o)^{3/n}. \tag{6}$$

Table 1. Bulk and Local Shrinkages Due to Application of Pressure at 50 Kbars.

	Bulk shrinkage	Local shrinkage	
		at A center	at B center
Lithium glass	0.040	0.073-0.221	0.125-0.359
Sodium glass	0.025	0.072-0.219	0.112-0.326
Potassium glass	0.018	0.070-0.210	0.087-0.259

Introduction of the observed values of λ_o and λ_p into eq. (6) gave the local shrinkages at the color center sites shown in Table 1. Since the value n can not be specified, only the range is shown, the lower limit of the value of shrinkage corresponding to $n=2$ and the higher limit to $n=0.6$. The bulk shrinkages were obtained from the density measurements.

It is seen from the table that the local shrinkage is much larger than the bulk shrinkage for both A and B centers and for all the glasses examined. It can be said that the part of structure where there is some kind of defect is densified very much. The defect may be an alkali ion vacancy or a site where an alkali ion displaces from the normal position.[15] Previously, we obtained the local shrinkage at the Co^{2+} ion in glass[44] by measuring the shift of the crystal field absorption band due to application of pressure and found that for silicate glass the local shrinkage at the Co^{2+} site is much smaller than the bulk shrinkage. This result is interpreted to show that a Co^{2+} ion suppresses more or less the occurrence of entanglement (cause for densification[45]) of the local network by filling the void. On the contrary, the result on the color centers mentioned above demonstrates that the vacancy sites allow the entanglement to occur easily, by increasing the space of the void.

VI. CONCLUDING REMARKS

Present state of our knowledge on the color centers in glasses has been reviewed. Much is left to be done for obtaining clearcut models of the color centers in glasses, while the work directed to the use of color center phenomena for obtaining informations on glass structure are conducted. If applied properly, the study on the color centers will be useful for the elucidation of short range order of glass structure, particularly at the defect sites.

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