Color Centers in Alkali Silicate and Borate Glasses

RYOSUKE YOKOTA

Matsuda Research Laboratory, Tokyo-Shibaura Electric Company, Kawasaki-shi, Japan

The color centers induced by x-ray irradiation in the alkali silicate and borate glasses and the mixed alkali glasses are studied. By preparing samples of various compositions in the reducing and in the oxidizing condition, and by optical and thermal bleaching, it is concluded that the visible band is due to electrons trapped by oxygen vacancies neighboring alkali ions and that the ultraviolet band is due to positive holes trapped by alkali ion vacancies neighboring oxygen ions.

I. INTRODUCTION

THE study of color centers in quartz and fused quartz was reported by the author.[1] It was established that in fused quartz, prepared in the reducing condition, there is an oxygen vacancy which can trap one or two electrons.

Most commercial glasses are silicate and borosilicate glasses which contain alkali and alkali-earth ions.

Prizbram[2] reported very briefly the position of the peak of the visible part of the induced absorption bands in alkali borate glasses by the β and γ irradiation of radium.

II. PREPARATION OF SAMPLES AND EXPERIMENTAL METHODS

We prepared the samples by melting the raw materials in a platinum crucible in air with an electric furnace whose heater was a platinum ribbon.

As raw materials, we used lithium, sodium, potassium, and rubidium[3] carbonates, and boric acid, all of which were Merck guaranteed reagent grade. The quartz powder was made from pure quartz which had no absorption up to 210 mμ. We used also the purest SiO_2 made from distilled pure tetraethylsilicate; however, the results obtained were the same as those derived using pure quartz powder.

In this method of preparation, the samples are made in nearly neutral condition, that is, in neither an oxidizing nor a reducing condition. The glass specimens were annealed and polished.

We measured the absorption with a Beckman DU spectrophotometer at room temperature.

Some of the samples were hygroscopic. Therefore every sample was inserted into a moisture-tightened vessel containing silica gels during the x-irradiation and absorption measurements.

III. COLOR CENTERS IN ALKALI DISILICATE AND DIBORATE GLASSES

We have studied the alkali disilicate and diborate glasses, because crystals of the same composition are known to exist and the glass is considered[4] to have a local order of arrangement similar to that of the crystal of the same composition. A comparative study of crystal and glass may be possible in future.

The increase of absorption resulting from x-irradiation (45-kv, 10-ma tungsten target) for two hours at room temperature is given in Fig. 1 for silicate glasses and in Fig. 2 for borate glasses. The ordinates of these curves are the reduced absorption coefficient, i.e., the ratio of the absorption coefficient to the value at maximum.

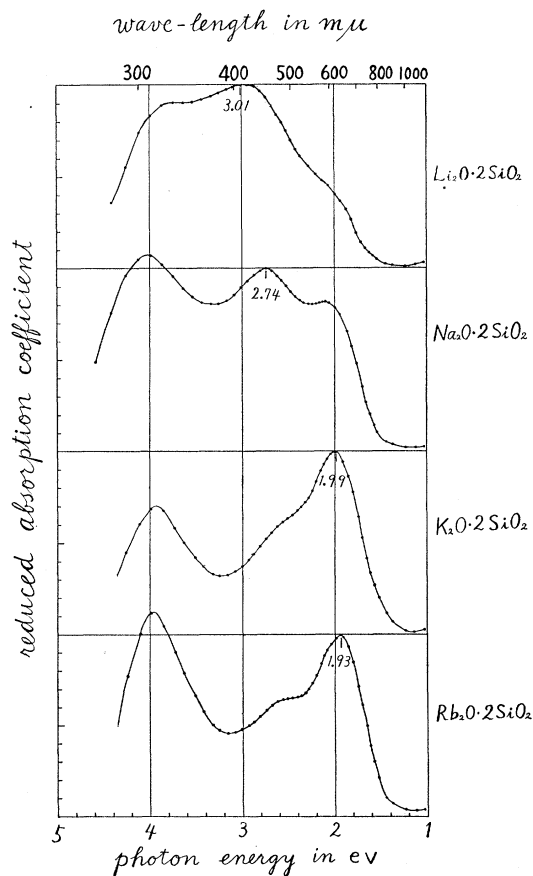Figure 3 gives the induced absorption bands of alkali

FIG. 1. Induced absorption bands of alkali disilicate glasses.

---

[1] R. Yokota, J. Phys. Soc. Japan 7, 222, 316 (1952); Phys. Rev. 91, 1013 (1953).
[2] K. Prizbram, Z. Physik 130, 269 (1951).
[3] The rubidium carbonate is cp grade made in the Fisher Scientific Company (U. S. A.).
[4] R. Yokota, J. Phys. Soc. Japan 5, 295 (1950); 6, 489 (1951).

diborate glasses which are colored under different conditions of x-irradiation (100-kv, 3-ma tungsten target, at 45°C). The peak of the ultraviolet band is clearly observed.

We denote each band in the silicate glasses, measured from the long wavelength side, by A_1, A_2, and B. The corresponding bands in borate glasses are designated A and B, respectively.

The comparison of the peaks in Figs. 1 and 2 with the well-known F bands in the crystals of LiCl, NaCl, KCl, and RbCl obtained by Pohl[5] shows that the relation between the position of peak and the half-width in
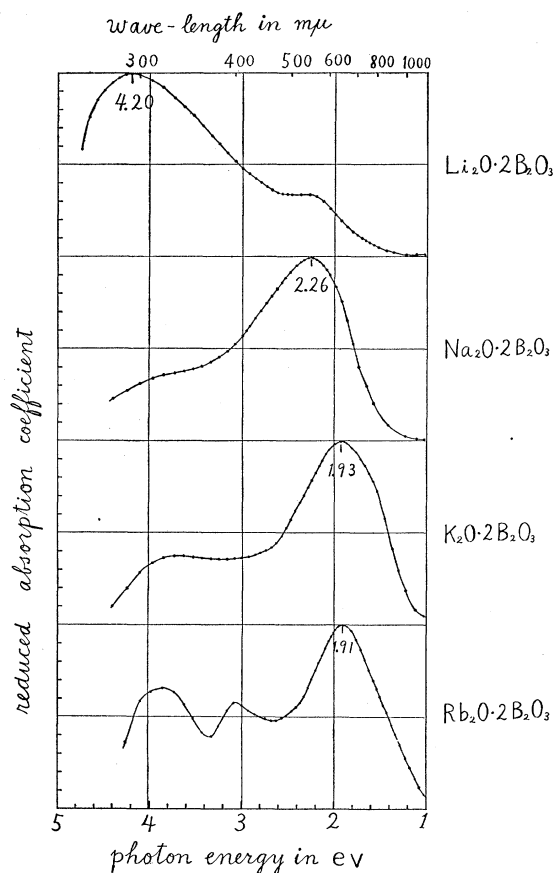

FIG. 2. Induced absorption bands of alkali diborate glasses.

the visible bands in glasses resembles that found for the F bands in alkali halide crystals.

In the discolored $Na_2O \cdot 2SiO_2$ glass, each band is bleached, along with other bands, by the irradiation with light lying in that band. All bands are bleached simultaneously by heating.

We prepared $K_2O \cdot 2SiO_2$ glass by melting potassium carbonate, quartz powder, and a very small amount of silicon powder whose purity is 99.98 percent. This glass is entirely transparent in both the visible and ultra-

[5] R. W. Pohl, Proc. Phys. Soc. (London) **49** (extra part), 3 (1937); Physik. Z. **39**, 36 (1938).
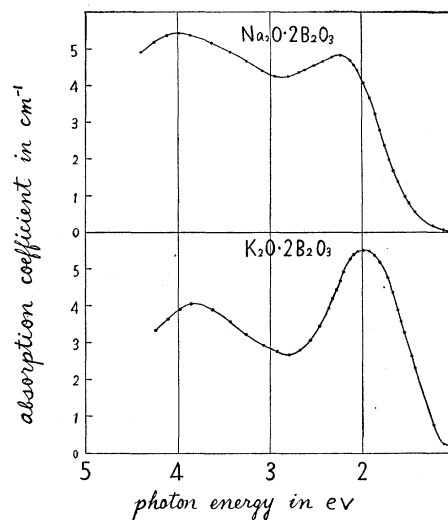

FIG. 3. Induced absorption bands of $Na_2O \cdot 2B_2O_3$ and $K_2O \cdot 2B_2O_3$ glasses (100-kv, 3-ma tungsten target, at 45°C).

violet regions; that is, the silicon does not act as a decolorizer, but acts as a reducing agent.

Furthermore, we prepared $K_2O \cdot 2SiO_2$ glass by melting potassium nitrate (Merck guaranteed reagent grade) and quartz powder in a sintered pure alumina crucible. It is well known that nitrate is more oxidizing than carbonate when the raw materials react at high temperature.

The induced absorption bands in these glasses, under the same condition of x-irradiation, are given in Fig. 4 together with those of the glass prepared in the nearly neutral condition.
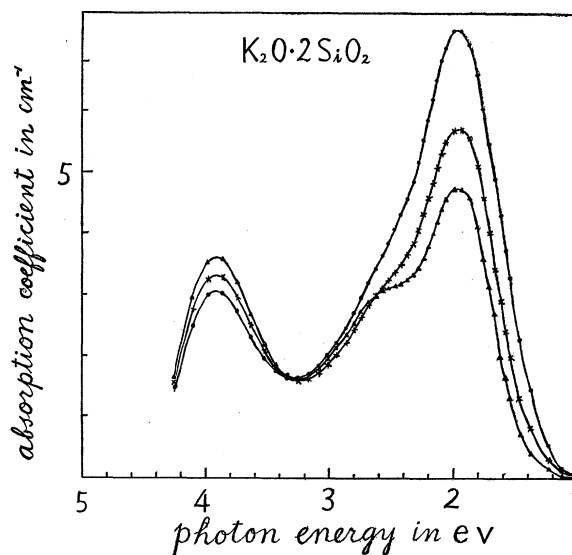

FIG. 4. Induced absorption bands of $K_2O \cdot 2SiO_2$ glass prepared in different conditions. The circular dots represent the glass prepared in reducing condition; the crosses represent the glass prepared in nearly neutral condition; and the triangles represent the glass prepared in oxidizing condition.

The oxidized glass has the smallest A_1 and A_2 bands and the largest B band. The reduced one has the reverse, and the neutral one has intermediate ratio of sizes.

IV. COLOR CENTERS IN Na₂O—SiO₂ GLASSES AND MIXED ALKALI GLASSES

We prepared $Na_2O - SiO_2$ glasses by melting sodium carbonate and quartz powder. The increase of the induced absorption as a result of x-irradiation is given in Fig. 5. For reference, in some cases the ordinates are given by the measured absorption coefficient. Figure 5 shows that the intensity and position of the
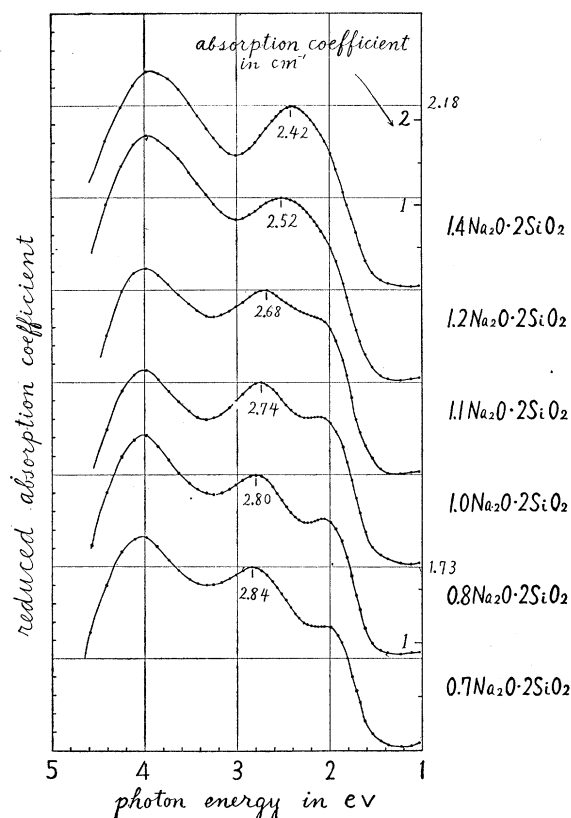

FIG. 5. Induced absorption bands in Na₂O—SiO₂ glasses.

peaks of the A_1 and A_2 bands change regularly with the Na₂O content, but those of the B band hardly change.

The situation is the same in $K_2O - SiO_2$ glasses.

We prepared the mixed alkali glasses of the molecular compositions represented as $xNa_2O \cdot (1-x)K_2O \cdot 2SiO_2$ and $xNa_2O \cdot (1-x)K_2O \cdot 2B_2O_3$, where x is 0, 0.25, 0.5, 0.75, and 1. The induced absorption bands in these glasses are given in Figs. 6 and 7. The figures show two facts: (A) the relative intensity and the peaks of the two visible bands in silicate glasses and the peak of the A band in borate glasses change approximately with the molecular fraction of Na₂O in K₂O. (B) The peak
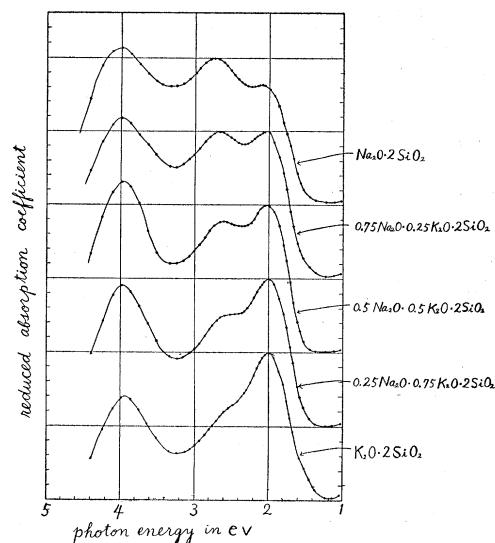

FIG. 6. Induced absorption bands in xNa₂O · (1−x)K₂O · 2SiO₂ glasses.

of the B band is nearly indifferent to the molecular composition, although some differences exist in potassium and sodium glasses.

These facts give additional evidence that the visible bands are due to electrons trapped by oxygen vacancies neighboring alkali ions, whereas the B band is due to positive holes trapped by alkali ion vacancies neighboring oxygen ions.

V. DISCUSSION AND CONCLUSIONS

We represent the molecular compositions of the alkali silicate glasses as $(M_2O)_x(SiO_2)_{1-x}$, where x is the molecular fraction of M₂O. There are two kinds of oxygens, one bonding two Si ions and the second bonding one Si and one alkali ion. We denote the former
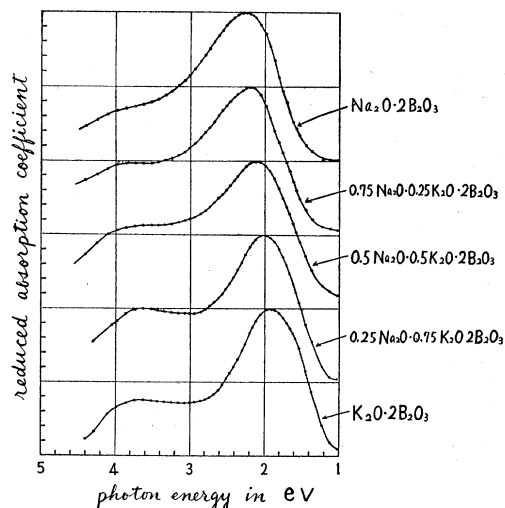

FIG. 7. Induced absorption bands in xNa₂O · (1−x)K₂O · 2B₂O₃ glasses.

by O^{Si}, and the latter by O^{SiM}. The molecular fractions of O^{Si} and O^{SiM} are equal to $2-3x$ and $2x$, respectively, as the following simple reasoning shows.[6]

There are two possible kinds of oxygen vacancies, namely, O^{SiM} vacancies and O^{Si} vacancies. The former are more probable than the latter. The reason is as follows: (1) O^{Si} is more tightly bound than O^{SiM}, because O^{Si} bonds two Si and O^{SiM} bonds only one Si. As the preparing temperature of the glass is about 1300°C and the melting point of SiO_2 crystal is 1713 ±10°C, the number of O^{Si} vacancies is considered to be very much smaller than the number of O^{SiM} vacancies. (2) In $Na_2O - SiO_2$ glasses, the number of O^{Si} decreases as Na_2O increases whereas the number of O^{SiNa} increases. Figure 5 shows that the A_1 and A_2 bands increase as Na_2O increases.

[6] B. E. Warren and A. D. Loring, J. Am. Ceram. Soc. 18, 269 (1935).

There are two possible kinds of positive ion vacancies, namely, the alkali ion vacancies and Si ion vacancies. The former are more probable than the latter. The reasoning is as follows: (1) The Si ions are very tightly bound by four oxygens arranged at the corners of a tetrahedron. Since the preparing temperature of the glass is about 1300°C, the number of Si ion vacancies is considered to be very much smaller than that of the alkali ion vacancies. (2) In $Na_2O - SiO_2$ glasses, the number of Si ions decreases as Na_2O increases whereas that of Na ions increases. Figure 5 shows that the relative intensity of the B band and the A_1 and A_2 bands is nearly independent of the Na_2O content.

In the alkali borate glasses the situation is nearly the same.

In conclusion the author wishes to express his gratitude to Professor A. von Hippel for his aid in reading the manuscript, to Mr. S. Nakajima for his assistance, and to Mr. Y. Uemura for his helpful discussions.

Anisotropy of Fluorescence of Some Organic Crystals

S. C. Ganguly and N. K. Chaudhury
Research Laboratory, Bangabasi College, Calcutta, India
(Received April 22, 1954)

A mathematical relationship between the intensities of polarized fluorescence in different perpendicular directions and the molecular orientations with respect to the crystal axes has been established, and particular reference is made to the plane aromatic molecules. It is emphasized that the knowledge of intensities of polarized fluorescence in different directions of a crystal may, in favorable cases, give direct information regarding the orientation of the molecule and the nature of oscillators responsible for giving fluorescent light.

1. INTRODUCTION

IN some recent communications[1] we have emphasized the fact that the oscillators responsible for the emission of fluorescent light of the crystal of anthracene, chrysene, phenanthrene, pyrene, and similar other crystals with planar molecules have definite directions —independent of the incident electric vector—making definite angles with the b axis in the (001) plane, and the light emitted by the molecules is completely polarized.[2] In each of these cases this angle happened to agree well with that made by the plane of the constituent molecule of the crystal lattice with the (001) plane. Following Perrin[3] and Krishnan,[4] we assumed in these papers that a radiating molecule is equivalent to a single linear electric oscillator. This picture of a

radiating molecule may be regarded as extremely one-sided, because it neglects the spatial character of radiative transition in a molecule. Such a picture is quite understandable in dye molecules where a molecule possesses a strong electric moment in a particular direction but it fails to present a commendable view in molecules lacking that. We can illustrate the difference between the two cases with the help of an azo-benzene molecule and a benzene molecule. A molecule of azo-benzene possesses a strong electric moment along the bond length in the molecule and absorption of light is the greatest when the incident light is polarized in the direction of the bond.[5] A molecule of benzene is planar and, because the π electrons are constrained to move in the plane of the molecule,[6] the virtual oscillators

[1] S. C. Ganguly and N. K. Chaudhury, J. Chem. Phys. 19, 617 (1951); 21, 554 (1953).
[2] S. C. Ganguly and N. K. Chaudhury, Z. Physik 135, 255 (1953).
[3] F. Perrin, Compt. rend. 180, 581 (1925).
[4] K. S. Krishnan and P. K. Seshan, Indian Acad. Science 8A, 487 (1934); Current Sci. (India) 3, 26 (1934); Z. Crystallogr. A89, 538 (1934).

[5] E. J. Bowen, *Chemical Aspects of Light* (Clarendon Press, Oxford, 1942), p. 11.
[6] C. V. Raman and K. S. Krishnan, Compt. rend. 184, 449 (1927); Proc. Roy. Soc. (London) A113, 511 (1927); K. S. Krishnan et al., Proc. Roy. Soc. (London) A113, 511 (1927); Trans. Roy. Soc. (London) A231, 235 (1933). K. S. Krishnan, Presidential Address, Section of Physics, Proceedings of the 27th Indian Science Congress, Part II (1940).