the values quoted. The theoretical values employ only quantities directly calculable from the theory. That is, no parasitic remixing factor is used.

CONCLUSIONS

The results presented in Table III show markedly better agreement with theory than similar results from glass columns. Indeed, the $T_2/T_1 = 2$ data are in excellent quantitative agreement with the theory, without employing a parasitic remixing factor (see Fig. 3). It is felt therefore that no appreciable parasitics existed ni the column. Solutions of the theory which take into account the non-Maxwellian character of the gas as well as the temperature dependence of the thermal diffusion constant[7] may very well explain the discrepancies at higher temperatures. The temperature

dependence of the thermal diffusion constant can best be represented as a linear variation with $\ln T$. The temperature dependence alone cannot account for the whole of the discrepancy, since this will increase the theoretical values of $2A$, whereas some of the experimental deviations are in the other direction.

The improvement in performance with increasing number of spacers as noticed by Donaldson and Watson[5] was not observed (see Fig. 4). We feel that such improvement can occur when the construction is such that the spacers improve the geometry of the column. If the construction approaches the theoretical ideal, i.e., no irregularities in the wire-to-wall spacing, column absolutely straight, etc., spacers cannot improve the performance.

Finally, we believe that the Furry, Jones, and Onsager theory is adequate, but that appropriate solutions have not been effected for all cases.

[7] R. C. Srivastava, Proc. Phys. Soc. (London) A68, 294 (1955).

Color Centers in Alkali-Silicate Glasses Containing Alkaline Earth Ions

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Samples of alkali metal oxide-silica glasses with various kinds and amounts of alkaline earth oxide calcium oxide and silica were prepared, x-irradiated, and studied by spectrophotometry. Bleaching experiments with visible light were carried out. No effect of alkaline earth content upon the absorption spectra was detected.

Room temperature bleaching of a K_2O-SrO-SiO_2 glass with light of wavelength corresponding to the x-ray induced absorption band at 1.95 ev, decreased absorption generally but failed to create a new absorption band such as the Z_1 band found in KCl, containing $SrCl_2$, that has been irradiated and then bleached.

Comparisons are made with alkali-halide systems containing alkaline earth halides. It is suggested that there are inadequacies in the quasi-crystalline model of glass when applied to these glasses.

I. INTRODUCTION

IN an earlier report[1] on alkali silicate and borate glasses, the author presented evidence suggesting that the visible band found in x-irradiated samples is due to electrons trapped by oxygen vacancies adjacent to alkali ions and that the ultraviolet band is due to positive holes trapped by alkali ion vacancies which are adjacent to oxygen ions.

Warren and others[2] have demonstrated short-range order in glasses of simple composition and the author has used this to construct an analogy between the color centers of alkali-silica glasses and those in crystalline alkali halides. The attempt seems to be successful. The present work extends the study to alkali-silica glasses containing alkaline earth oxide.

X-ray studies[3] have indicated that the structure of Na_2O-CaO-SiO_2 glass is similar to that of Na_2O-SiO_2 glass with some of the sodium ions replaced by calcium ions.

In view of these facts, we have studied silica glasses containing alkaline earth oxide as well as alkali metal oxide to learn whether, in these glasses, the x-ray coloration can be compared with that in alkali halides containing alkaline earth halides and whether the comparison will support the "quasi-crystalline model" for glass.

Most commercial glasses are silicate and borosilicate glasses which contain alkali and alkaline earth ions. The method of preparation of the purest glass is the same as before.[4] The alkaline earth oxides we used were Merck guaranteed reagent grade carbonates. Every sample was annealed.

[1] R. Yokota, Phys. Rev. 95, 1145 (1954); 93, 896 (1954).

[2] B. E. Warren, J. Appl. Phys. 8, 645 (1937); Warren, Krutter, and Morningstar, J. Am. Ceram. Soc. 21, 259 (1938); I. Simon and H. O. McMahon, J. Chem. Phys. 21, 23 (1953); I. Simon and H. O. McMahon, J. Am. Ceram. Soc. 36, 160 (1953); R. Yokota, J. Phys. Soc. Japan 5, 295 (1950); 6, 489 (1951); M. L. Huggins, J. Phys. Chem. 58, 1141 (1954).

[3] J. Biscoe, J. Am. Ceram. Soc. 24, 262 (1941).

[4] R. Yokota, reference 2.

II. COLOR CENTERS IN ALKALI SILICATE GLASSES CONTAINING CALCIUM IONS

In all samples studied, we always observed three x-ray induced absorption bands similar to those found in the alkali silicate glasses. We denote these bands by A_1, A_2, and B, respectively, in order from long to short wavelengths.

The absorption resulting from x-irradiation (45-kv, 10 ma, tungsten target; samples 3 cm from the x-ray tube) of 15 hours at room temperature was measured by a Beckman DU spectrophotometer. The darkening reached almost complete saturation after 15 hours of x-irradiation.

The increase of absorption is given in Fig. 1 for the sodium silicate glasses containing calcium ions of molecular compositions represented by the formula $0.6Na_2O \cdot xCaO \cdot 2SiO_2$, where x is 0, 0.09, 0.18, and 0.27.

We can obtain an approximation to the complete absorption curve of the A_1 band by reflecting the curve of the lower energy side across the 1.99-ev line, although there is some arbitrariness in the choice of this wavelength. The figures show two facts: (A) The position of the peak and the half-width of the A_1 band are nearly the same. There is no evidence for a new band in the region of the A_1 band as a result of introducing calcium ions. Also, no new absorption band is apparent in the region of the A_2 or B band, although the intensity ratio of the A_1 to the A_2 band increases regularly with the calcium ion content. (B) The coloration of the glasses
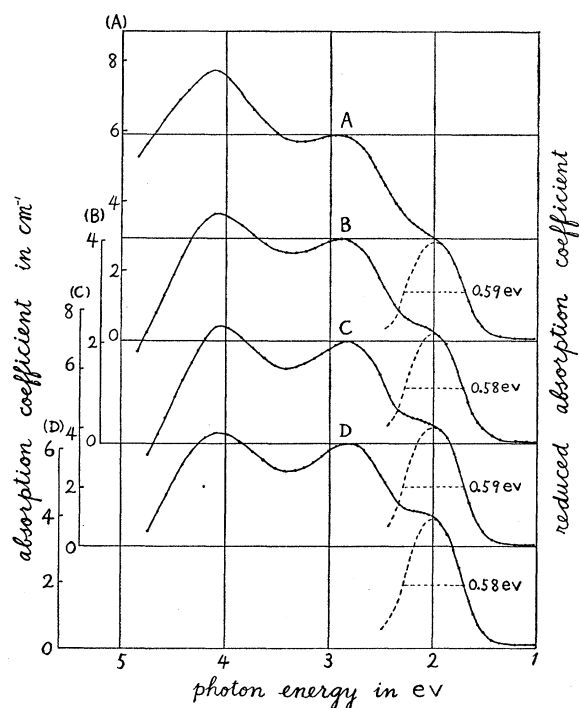

FIG. 2. Induced absorption bands in $0.6Li_2O \cdot xCaO \cdot 2SiO_2$ (Curves A and B) and $0.6Rb_2O \cdot xCaO \cdot 2SiO_2$ (Curves C and D) glasses. (A) and (C), $x=0$; (B) and (D), $x=0.18$.

containing calcium ions does not increase with the calcium ion content. This is markedly different from the case of the alkali halide crystals[5] in which, for example, the addition of $CaCl_2$ to NaCl enhances the extent of darkening at saturation over the entire region of observation at room temperature.

In the $0.6Na_2O \cdot 0.18CaO \cdot 2SiO_2$ glass, we measured at room temperature the absorption in the region of 1 to 5μ by the infrared monochrometer before and after x-irradiation at room temperature, but found no difference.

In the lithium, rubidium, and potassium silicate glasses containing calcium ions, the situation is the same as shown in Figs. 2 and 4. (The same procedure may be used for curves A and B in Fig. 2 since they apparently are similar to the other cases.)

We prepared samples of $0.8K_2O \cdot 0.2CaO \cdot 2SiO_2$ glass under oxydizing, nearly neutral, and reducing conditions using the methods described earlier.[1] The oxidized glass has the smallest A_1 band and the largest B band. In the reduced sample this ratio is reversed, and the neutral one has an intermediate ratio of sizes.

FIG. 1. Induced absorption bands in $0.6Na_2O \cdot xCaO \cdot 2SiO_2$ glasses. (A), $x=0$; (B), $x=0.09$; (C), $x=0.18$; (D), $x=0.27$
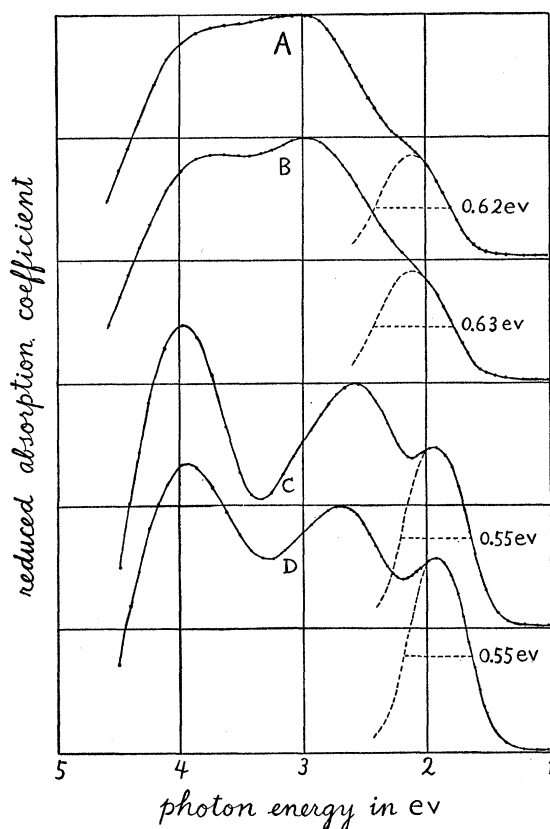
[5] H. W. Etzel, Phys. Rev. 87, 906 (1952).

III. ABSORPTION BANDS IN 2CaO·3SiO₂ GLASS

A calcium silicate glass of molecular composition $2CaO \cdot 3SiO_2$ was prepared by melting at 1650°C and then quenching and annealing. The x-ray-induced absorption bands are given in Fig. 3.

We observed a visible absorption band which extends from 1 to 2 ev, with a peak at 2.78 ev. This band is considered to be characteristic of the presence of calcium ion, and further, it is supposed to be due to electrons trapped by oxygen vacancies adjacent to calcium ions, because there is no x-ray induced visible absorption band in the SiO_2 glass prepared in the nearly neutral condition. We observed also an ultraviolet absorption band near 4.8 ev which does not exist in the silicate glass containing alkali ions.

IV. COLOR CENTERS IN POTASSIUM SILICATE GLASSES CONTAINING VARIOUS ALKALINE EARTH IONS

We prepared potassium silicate glasses containing various alkaline earth ions of molecular composition represented as $0.6K_2O \cdot 0.18RO \cdot 2SiO_2$, where R is Mg, Ca, Sr, or Ba. The increase of the induced absorption as a result of x-irradiation is measured at room temperature. Figure 4 shows that both the half-width and the position of the peak of the A_1 band are the same in each curve. This means that no new band overlaps the region of the A_1 band. Also no new band seems to appear in the region of the A_2 and B bands, although the intensity ratio of the A_1 to the A_2 band increases regularly in the order: Mg, Ca, Sr, and Ba.

V. ABSORPTION BANDS AT 90°K

The resolution of the absorption curve increases generally at low temperature.

The glass of molecular composition $0.6K_2O \cdot 0.18SrO \cdot 2SiO_2$ was darkened by x-irradiation at room temperature and the induced absorption bands were observed both at room temperature and liquid oxygen tempera-
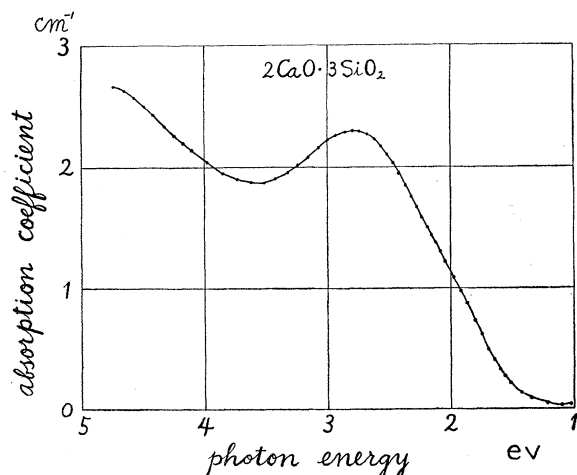
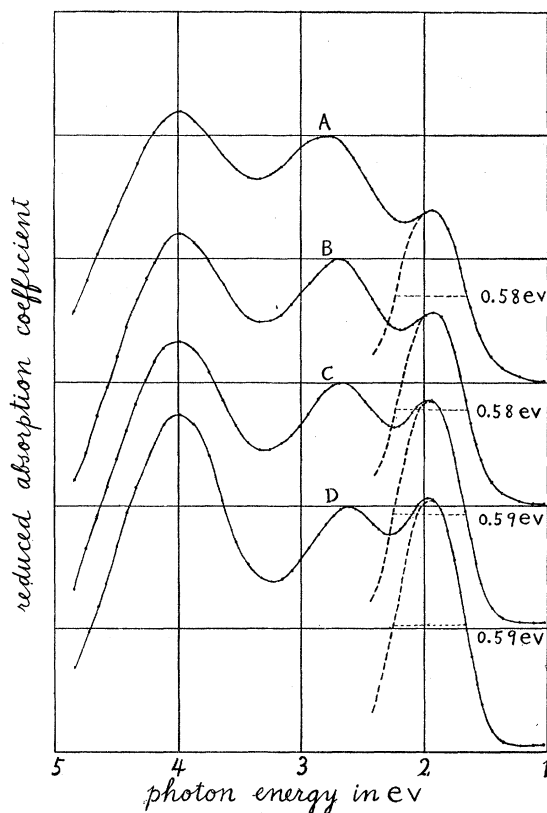Fig. 4. Induced absorption bands in $0.6K_2O \cdot 0.18RO \cdot 2SiO_2$ glasses. $(A), R = Mg; (B), R = Ca; (C), R = Sr; (D), R = Ba$.

ture with a cryostat similar to that of Casler, Prings-heim, and Yuster.[6] Curve A in Fig. 5 shows that no new band is resolved from the A_1, A_2, and B bands, although each band is sharper at 90°K.

In KCl containing $SrCl_2$ which has been darkened by x-irradiation at room temperature, the Z_1-band develops when the darkened crystal is irradiated in the F-band at room temperature.[7] Curve A in Fig. 5 shows the absorption spectra of the colored sample. This was subsequently bleached at room temperature with light of wavelength of the A_1 peak up to its saturation value. The absorption then was observed both at room temperature and at 90°K. As curve B in Fig. 5 shows, no new band is disclosed by this procedure.

VI. DISCUSSIONS AND CONCLUSIONS

We shall consider, as an example, the $0.6Na_2O \cdot xCaO \cdot 2SiO_2$ series where x is 0, 0.09, 0.18, and 0.27. Morey and Merwin[8] measured the density of Na_2O–CaO–SiO_2 glasses very accurately and comprehensively, giving the iso-density curves in triangular coordinates.

Fig. 3. Induced absorption bands in $2CaO \cdot 3SiO_2$ glass.

[6] Casler, Pringsheim, and Yuster, J. Chem. Phys. **18**, 887 (1950).
[7] Camagni, Chiarotti, Fumi, and Giulotto, Phil. Mag. **45**, 225 (1954).
[8] G. W. Morey and H. E. Merwin, J. Opt. Soc. Am. **22**, 623 (1932).

From these we can obtain the density of $0.6Na_2O \cdot xCaO \cdot 2SiO_2$ glass, by interpolation, to within ± 0.001 density units.

The largest ion present in glass is the oxygen ion. It is therefore interesting to consider the density data on a uniform basis of the glass volume containing one gram-atom of oxygen. Figure 6 indicates that the volume of $0.6Na_2O \cdot 2SiO_2$ glass contracts when CaO is introduced.

When $CaCl_2$ is added to KCl, the volume per gram-atom of chlorine increases, predominantly because of the fact that the Ca ion eliminates two K ions, substituting for one while the site of the other remains vacant.[9] Similar observations are made with NaCl containing $CaCl_2$. In view of this and the fact that the B band (attributed to positive holes trapped by Na ion vacancies) does not increase its intensity as shown in Fig. 1, it may be concluded that Na ion vacancies are not increased by the introduction of CaO.

This is in marked contrast to the alkali halide crystals. The reason may be as follows: The x-ray study[3] has indicated with some uncertainty that in $Na_2O-CaO-SiO_2$ glass each calcium must be surrounded by about 7 oxygens, if each sodium is assumed to be surrounded by 6 oxygens. The ionic radii of Na and Ca ions are nearly the same, the former being monovalent and the latter divalent. The network of glass has flexibility in the temperature range from the liquidus temperature to the glass transformation tem-
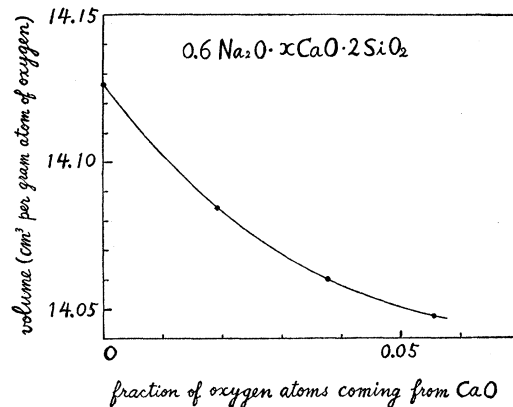

FIG. 6. Molar volumes in $0.6Na_2O \cdot xCaO \cdot 2SiO_2$ glasses.
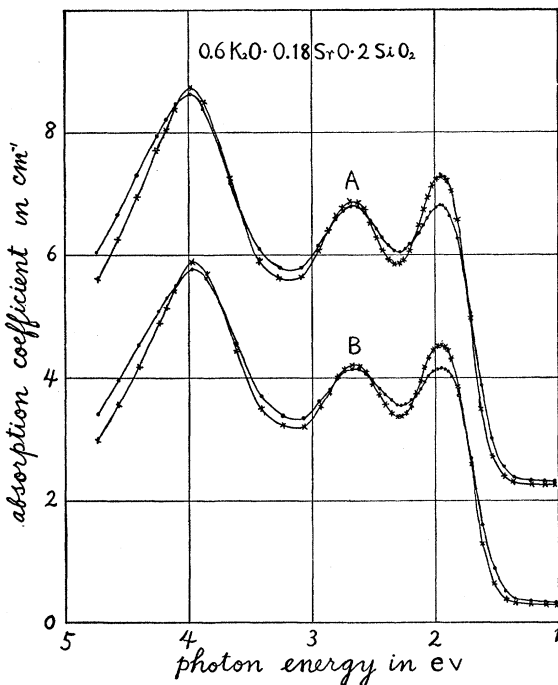
perature. While the glass cools through this temperature range, the Ca ion can coordinate more unsaturated single-bonded oxygens than the Na ion can, and so it preserves approximate electrical neutrality around itself without the generation of a Na ion vacancy. This state is frozen in at lower temperature. From this reasoning, a possible conclusion is that the Z_1 center, found in alkali-halide crystals containing alkali earth ions, cannot be formed in this glass and that the volume of $0.6Na_2O \cdot 2SiO_2$ glass contracts when CaO is introduced.

Oxygen may be coordinated in three ways: first, bonding two Si ions; second, bonding one Si and one Na ion; and third, bonding one Si and one Ca ion. We denote the first by $O_{(Si)}$, the second by $O_{(SiNa)}$, and the third by $O_{(SiCa)}$. There are three possible kinds of oxygen vacancies, namely $O_{(SiNa)}$, $O_{(SiCa)}$, and $O_{(Si)}$ vacancies. The first is most probable. The reason is as follows: (1) $O_{(Si)}$ is more tightly bound than $O_{(SiNa)}$ and $O_{(SiCa)}$, because the former bonds two Si and the latter bond only one Si. (2) $O_{(SiCa)}$ is more tightly bound than $O_{(SiNa)}$, because the ionic binding energy of Ca-O is roughly twice that of Na-O. This may be the reason why no absorption band attributed to electrons trapped by $O_{(SiCa)}$ vacancies are found.

There are three possible kinds of positive ion vacancies, that is, Na, Ca, and Si ion vacancies. By similar reasoning, Na ion vacancies are considered to be most probable. This may be the reason why no absorption band attributed to positive holes trapped by calcium ion vacancies are found.

Therefore, it is concluded that the absorption bands in alkali silicate glasses containing alkaline earth ions are the same as those in alkali-silicate glasses. Also, it is suggested that the "quasi-crystalline model" for glass is inadequate in the alkali-alkaline earth-silicate glasses, although there is definitely short-range order in these glasses.

The author wishes to express his gratitude to Mr. S. Nakajima for his assistance and to Mr. Y. Uemura for valuable discussions.

FIG. 5. Induced absorption bands in $0.6K_2O \cdot 0.18SrO \cdot 2SiO_2$ glass in which the circular dots and crosses represent data taken at room temperature and 90°K, respectively. Curve A is measured before bleaching and curve B after bleaching.

9 H. Pick and H. Weber, Z. Physik. 128, 409 (1950).