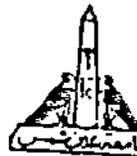


-30- CORRELATION OF THE VISIBLE INDUCED CENTERS IN SODA-SILICA
GLASS AND SMOKY QUARTZ.

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Abstract

A similarity in position's, shape's and width's at half-maxima of the visible induced bands in oxidized soda-silica glass and smoky quartz has supported the view that the bands at about 1.9 eV and 2.58 eV in smoky quartz are not related to substitutional aluminium in the quartz structure as it was reported earlier. This has been further substantiated by the development of a band at about 3.0 eV in smoky quartz whose intensity correlates with the visually observed smoky color. It is believed that the two bands H_3^+ and H_2^+ in irradiated soda-silica glass as well as the two bands A_1 and A_2 in smoky quartz have the same origin related to paramagnetic oxygens in the silica structure.

Introduction

Several investigators have studied the optical absorption caused by x-irradiation in a large number of simple soda-silica glasses. Smith and Cohen (1964) studied the coloration produced by x-irradiation in highly pure oxidized soda-silica glasses. Gaussian resolution of the induced absorption spectra showed three absorption maxima at about 1.96 eV (632nm), 2.7 eV (460nm) and 4.1 eV (302nm). The bands were attributed to sites introduced to the glass network where electrons or holes could be trapped.

By studying the effects of Ce^{3+} and Ce^{4+} in the oxidized soda-silica glasses, Stroud et. al. (1966) were able to show that the visible bands were due to trapped holes, while the other bands in the near ultra-violet (at about 4.0 and 5.27 eV) were assigned to trapped electrons. The same conclusions were reached by Mackey et. al. (1966, 1970), who assigned the two centers at 1.99 eV and 2.7 eV to two distinct trapped holes H_3^+ and H_2^+ which proved to have a common structural precursor.

Color centers were also observed and reported in natural smoky quartz and irradiated colorless quartz by many investigators. Two optical absorption bands, designated A_1 and A_2 about 2.0 eV (620nm) and 2.7 eV (460 nm) respectively, were usually assigned to the smoky color produced by x-irradiation of naturally colorless quartz. The A_1 and A_2 bands were attributed to an aluminium atom replacing a silicon atom in the quartz structure with an alkali or hydrogen in a nearby interstitial location providing charge balance (Griffiths et.al, 1955; Mackey (1963).

Nassau and Persoett (1975, 1977) performed a series of irradiation and heat treatment experiments on a large number of natural and synthetic quartz. In some of the studied samples, the A_1 and A_2 optical absorption bands

were present without any smoky color. The smoky color, however developed upon further irradiation and was accompanied by a new absorption band A_3 at about 2.9 eV (427nm) whose intensity correlated with the substitutional aluminium content, and an ESR signal due to substitutional aluminium. Accordingly, the authors suggested that the smoky color in quartz due to substitutional aluminium was associated with A_3 optical band at 2.9 eV rather than the A_1 and A_2 bands proposed earlier.

The purpose of the present study is to investigate the correlation if any, between the two induced hole centers H_2^+ and H_3^+ in irradiated soda-silica glass and the visible induced centers in crystalline silica, and to assign models for the various present bands.

Experimental

Soda-silica glasses were prepared using ultra-pure sodium carbonate (Alpha grade) for Na_2O and corning purified fused silica for SiO_2 .

Batches were prepared to yield glasses of the composition $Na_2O \cdot 3.0 SiO_2$.

The batch constituents were then thoroughly mixed and melted in a Pt-Rh crucible in a high temperature pot furnace with Kanthal elements. To reduce the

volatilization losses, the furnace temperature was slowly raised and then maintained at 1200°C for the hour, after which the melt was allowed to cool gradually to the room temperature. The glass samples were then ground and carefully polished, cerium oxide being used to obtain the final highly polished surfaces for optical measurements.

The natural smoky quartz sample was a Brazilian crystal.

Optical spectra were taken at room temperature by means of a recording spectrophotometer in the range 1 to 6.0 eV.

The specific absorbance in cm^{-1} , $\alpha = \left(\frac{1}{t}\right) \log_{10} (I_0/I)$, where t is the sample thickness in cm., was calculated without reflectance correction. X-irradiation experiments were carried out at room temperature at tube settings of 45 KV and 35 mA.

A curve resolver, a modified analog computer, was used to resolve the bands. Band parameters, viz., width at half maximum with absorption maximum (α_m) and energy at maximum absorption band positions were obtained from the resolved absorption curves.

Results and Discussion

Figure (1) shows the optical absorption spectra of Na_2O , 3.0SiO_2 glass melted under oxidizing conditions prior to and after 30 mins, of x-ray irradiation. The unirradiated glass was colorless and showed no absorption bands in the visible region of the spectrum. The effect of x-irradiation on the absorption spectrum is best illustrated by a difference spectrum. This spectrum is obtained by subtracting the spectrum taken before irradiation from the one measured after irradiation and is referred to as the induced spectrum.

Figure (2) shows the induced spectrum of the oxidized soda-silica glass together with Gaussian resolution for the absorption bands. The absorption is resolved into three bands at about 1.98, 2.68 and 4.0 eV (widths at half-maxima are 0.5, 1.08 and 1.16 eV respectively) being characteristic of oxidized soda-silica glasses. The absorption band positions are in proper agreement with those reported by Mackey et.al. (1966, 1970). As was mentioned earlier, the bands H_3^+ and H_2^+ (1.98 and 2.68 eV) were assigned to two distinct hole centers, while the band E_3^- (4.0eV) was assigned to a trapped electron.

Figure (3) illustrates an approximate gaussian resolution for an irradiated natural Brazilian smoky

quartz. A striking similarity in band positions and shapes was observed between the A_1 and A_2 bands at 1.9 and 2.58 induced in irradiated natural smoky quartz and the bands at about 1.98 and 2.68 eV induced in irradiated sodium silicate glass. The slight differences in positions and widths at half-maximum between the two spectra as presented in Table (1) were not entirely unexpected. These differences can be interpreted in view of the regular arrangement of the SiO_4 tetrahedron in the case of quartz compared to the random network on glass.

Table 1
Comparison of Band Parameters in Smoky Quartz
to those in Soda-Silica Glass

Absorption Band	Smoky Quartz		Na ₂ O. 30SiO ₂ Glass	
	Peak position eV	Width at half-max. eV	Peak position eV	Width at half-max. eV
A_1 or H_3^+	1.9	0.7	1.98	0.5
A_2 or H_2^+	2.58	0.8	2.68	1.08

The band at about 3.0 eV in smoky quartz resembles the A_3 band observed by Nassau and Prescott (1978) with peak position varying between 2.58 and 3.1 eV, and width at half-maximum varying between 1.3 and 1.7 eV. They

attributed the half-maximum varying between 1.3 and 1.7 eV. They attributed the changes in the band position and width to non-equivalent of silicon sites by aluminium. The positions and widths at half-maxima of the gaussian resolved bands that provided satisfactory fit in smoky quartz together with those given by Nassau and Prescott are given in table 2.

Table (2)
Positions and width at Half-maxima ($\frac{W}{2}$) of Approximate Gaussian Resolved Bands in Smoky Quartz as Compared to those given by Nassau and Prescott (1975, 1977 and 1978).

Absorption band	The study		Nassau and Prescott	
	band Position	$W_{1/2}$	band Position	$W_{1/2}$
A ₁	1.9	0.7	1.8	0.7
A ₂	2.58	0.8	2.5	0.8
A ₃	3.05	1.1	2.85-3.1	1.3-1.7
B	3.98	1.28	3.9	1.2
C	5.0	--	.0	--

The observed similarity of the A₁ and A₂ bands in smoky quartz and the H₃⁺ and H₂⁺ bands in soda-silica glass strongly supports Nassau's and Prescott's conclusion

regarding the A_1 and A_2 bands and their non-correlation to the substitutional aluminium hole centers in the quartz structure. This is further substantiated by the development of the band at 3.05 eV in the absorption spectra of smoky quartz. The intensity of this band increased in accordance with the intensity of the smoky color.

Conclusion

The H_3 and H_2 absorption bands in x-irradiated soda-silica glasses and the A_1 and A_2 bands in smoky quartz may be associated with a defect in the silica structure which persists even when the long range order is destroyed on transition from the crystalline lattice to the more random vitreous state. It is well known that the introduction of an alkali into the silica network breaks up the siliconoxygen bond forming one non-bridging oxygen for each alkali ion. During irradiation this defect losses an electron and results in a trapped hole center, with the hole restricted to the non-bridging oxygen. The released electron can be trapped in a nearby precursor defect which comprises an electron trap, or the Na^+ ion can trap the released electron and become a neutral atom. Since the sodium atom is sufficiently small, it is free to migrate through the network to an electron-trapped defect. This defect may accept the charge and the sodium atom becomes an ion again. However, that the two centers

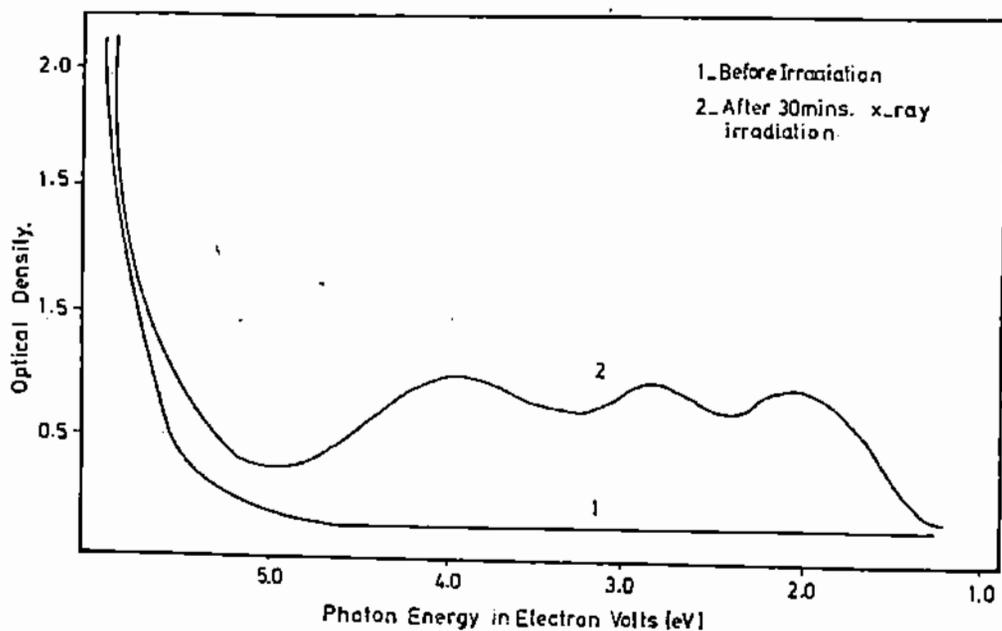


Fig.(1):The optical absorption spectra of sodium silicate glass melted under oxidizing conditions before and after 30 mintes x_ray irradiation.(sample thickness 0.09 cm).

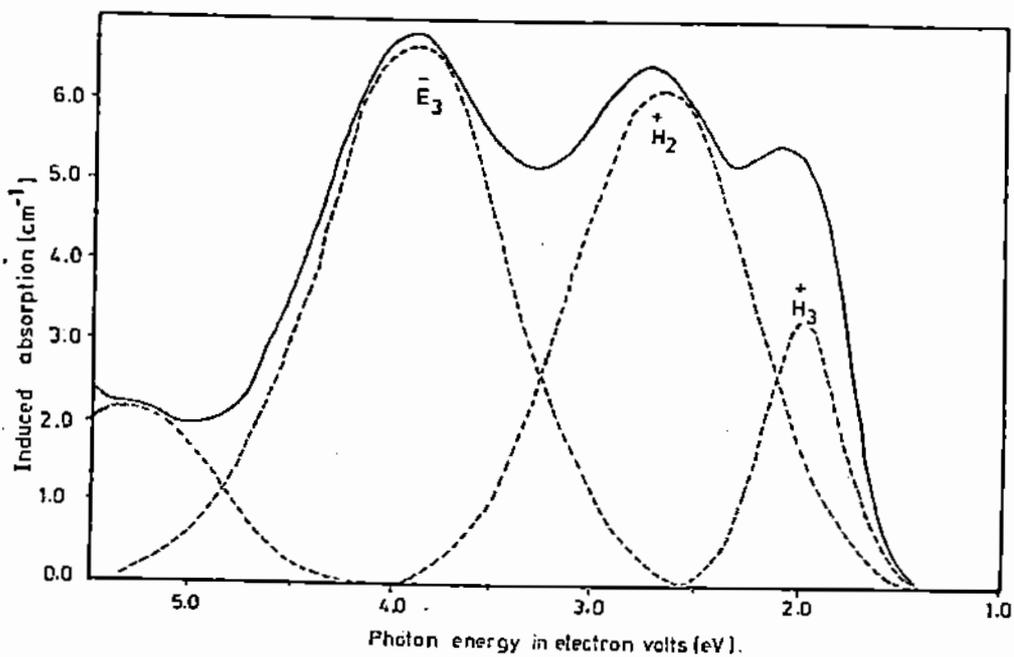


Fig. (2) : Approximate gaussian resolution of the induced absorption spectrum of sodium silicate glass.

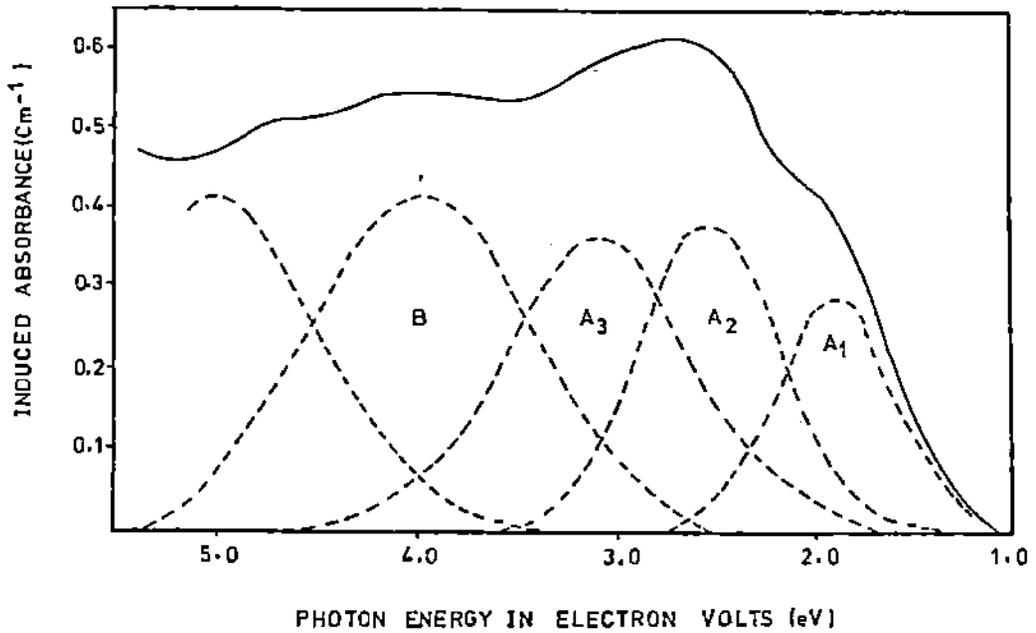


Fig.(3). Approximate gaussian resolution of the induced absorption spectrum of natural smoky quartz.

H_3^+ and H_2^+ are transitions of the same center is unlikely in the light of earlier observation by Mackey et. al. (1970) to the effect that their intensity ratio varies strongly during the coloring and bleaching processes, and that their rate of annihilation varies with increasing the titanium concentration in the glass.

We can, therefore, consider the idea that the two centers differ in the number of non-bridging oxygens as suggested by Schreurs (1967). We may also suspect that the origin of the two bands in smoky quartz is related to paramagnetic oxygens similar to their origin in glass. It is obvious, however, that further studies must be carried out to clarify this problem. It would be helpful in investigating the nature of these bands in quartz, to illuminate the samples at low temperature with light that falls mainly in the 1.98 eV region, and study the variations in the intensity ratio of the two bands with further x-irradiation and/or bleaching.

References

1. Griffiths, J.H.E.; Owen, J. and Ward, I.M., Defects in Crystalline Solids, Rep. Bristol Conf., Physical Soc., London (1955) 81.
2. Mackey, J.H., J. Chem. Phys., 39 (1963) 74.
3. Mackey, J.H.; Boss, J.W. and Kopp, M. Phys. Chem. Glasses, 11 (1970) 205.
4. Mackey, J.H.; Smith, H.L. and Halperin, A., J. Phys. Chem. Solids, 27 (1966) 1759.
5. Nassau, K. and Prescott, B.E., Phys. Status Solidi, A29 (1975) 659.
6. Nassau, K. and Prescott, B.E., Mineral. Mag., 41 (1977) 301.
7. Nassau, K. and Prescott, B.E., Am Mineral., 63 (1978) 230.
8. Schreurs, J.W.H., J. Chem. Phys., 47 (1967) 818.
9. Smith, H.L. and Cohen, A.J., J. AM. Ceram. Soc., 47, (1964) 564.
10. Stroud, J.S., Schreurs, J.W.H. and Tucker, R.F., Proc. of the 7th Inter. Con. on Glass, Brussels, 1966.