Memoirs of the Faculty of Engineering, Nagoya University
Vol. 28, No. 2. (1976)

ON THE OPTICAL PROPERTIES OF IRRADIATED COBALT GLASS AND OTHER GLASSES

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(received October 22, 1976)

Abstract

The optical properties of cobalt glass and other glasses, when they are irradiated by γ-ray, electron beam and neutron flux, are investigated. The change of their transmissivity is studied over 320~1000mμ wave length range. Fading phenomena, time variation and temperature dependence are studied. The time dependence of the fading is expressed by the formula which is proportional to $t^{-\lambda}$ approximately (λ is constant). From the excitation curve, four or more centers can be assigned. Refering to the ESR-measurements and other works, the structure of these centers are determined and the production mechanism is discussed. These interpretation can explaine the experimental results well.

CONTENTS

1. Introduction

It has long been known that the window glass can become colored on a prolonged exposure to very strong sunlight. The improvement and development of radiation source or techniques made to be clear that the irradiation or γ-ray, electron beam and neutron flux produced more strong coloration. And this coloration becomes to be used for radiation dosimetry (especially for high dose radiation, $10^5 \sim 10^7 r$). For this purpose, the window glass is not appropriate, because it has a large coloration but a large fading. To avoid this difficulty, many attempts using various glass with some impurity have been done[1]. On this line, our study have started. At first, we attempt to examine the possibility of cobalt glass as radiation dosimeter. In the course it has been found that the cobalt glass has small fading. During few hours after exposure, it showed unstable behaviour. However, after this period its fading behaviour is approximated by the formula which is proportional to $t^{-\lambda}$, where λ is constant and t is elapsed time after exposure. This property is almost similar for the irradiation of γ-ray, electron and neutron. This is established by the measurement using light at three wave length 350, 400, and 450mμ.

To know about the reason of this coloration, we attempt to measure the trasmissibity over wave length range 350$\sim$1000mμ. The transmissibity curve shows some numbers of the excitation band. This excitation is caused by the irradiation. Of course, original glass has the variation of transmissivity, but obviously this excitation is caused by the irradiation. It has been known today that the various properties of glass are based on the local property of glass. The structure of glass were investigated by many authors[1]. From their works, it is known that the glass has original network, e. g. Si-O network for silicate glass. The contamination of impurities and the defect of original net-work (e. g. nonbridging oxygen) induced the free electron traps or positive vacancies, so various kinds of centers are produced. The irradiation set many electrons to be free and produce many defects. This process will be the origin of these excitation bands. Thus absorption bands are ascribed to each centers formed by irradiation. This phenomena are similar as alkali-halide-case, so the analysis of these centers are investigated on the basis of alkali-halide-like model. The structure of these centers are recognized, and the model of these centers can interprete the properties of the irradiated cobalt glass. Thus this consideration can extend to other glasses. In latter case, the data is deficient and the quality is limited, so we can not induce the definite answers. However, we can obtain some results from the analogy of cobalt glass' results and other works'.

We started this work hoping to use glass-dosimeter efficiently, but in this course we understand to have to know the structure of glass. The knowledge of the structure of centers formed in glass is necessary for the effecient use of glass dosimeter. In 2. we describe our expenimental details and obtained results. Mainly we do experimets on cobalt glass, but add the results of other glasses (phosphate glass, etc.). These results obtained are analyzed in 3. In this section we propose the possible structure and the production mechanism of these centers. In 4, the property of glass as dosimeter is discussed. Some comments on the procedure of the usage are given. Finally we summarize the experimental and thoretical results in 5.

2. Experiments and Results

2. 1. Experiment

The cobalt glasses were made by Ohara Optical Glass Mfg. Co.. The size of each pieces of glass is 4.5×13.5×1.5 mm, and sometimes thickness 2 mm is used too. The composition is shown in Table I. This size is determined by considering its homogeneity, distortion which may occur in cutting and spot area of the spectrophotometer.

Table I
The composition of cobalt glass

SiO_2	69%
Na_2O	18%
CaO	10%
MgO	1.0%
B_2O_3	1.0%
CoO	1.0%

When they are irradiated with γ-ray, they, are covered with the same kind of glass at the both sides in order to get the equilibrium for secondary electrons. On the side part, this effect is included too, since the spot area is narrow by 5 mm. The decrease of radiation dose by this covering is about 1.5% of total.

A Beckmann-type spectrophotometer is used for the measurement of transmissivity of glass. The used range in wave length is from 320 mμ to 1000 mμ.

Let us take the intensity of light transmitted glass before and after irradiation I and I′ respectively, so the transmissivity is I/I_0 and I'/I_0 where

$$I=I_0e^{-\mu d}$$

and

$$I'=I_0e^{-\mu' d}$$

d is the thickness of glass, μ and μ' are the absorption coefficient before and after irradiation, and I_0 is incident intensity. The increase of the absorption coefficient $\Delta\mu$ can be represented as follows,

$$\Delta\mu=\frac{1}{d}\left[ln\frac{I'}{I_0}-ln\frac{I}{I_0}\right]=\frac{1}{d}[lnI'-lnI]$$

In many cases the measurement of tranmissivity are done at few hundreds hours after exposure. The number of times of measurements is nearly ten for each materials. Between the successive measurements, materials are kept at a constant temperature.

As sources of radiation, Co-60 source at Nagoya University and Nagoya Agency of Industrial Science and Technology, Ministry of International Trade and Industry, linear accelerator at the same Agency, nuclear reactor JRR-1, JRR-3 and IRR-4 at Tokai Research Establishment, J. A. E. R. I. and Cs-137 source at National Institute of Genetics are used.

2. 2. Transmissivity

The variation of transmissivity is shown in Fig. 1. In this figure, the transmissivity before and after irradiation is shown too. In Fig. 2, the increase of the absorption coefficient is shown. On that case, glasses were irradiated by Co-60 γ-ray. The radiation dose is from 10^4r to 10^6r, mainly 10^5r.

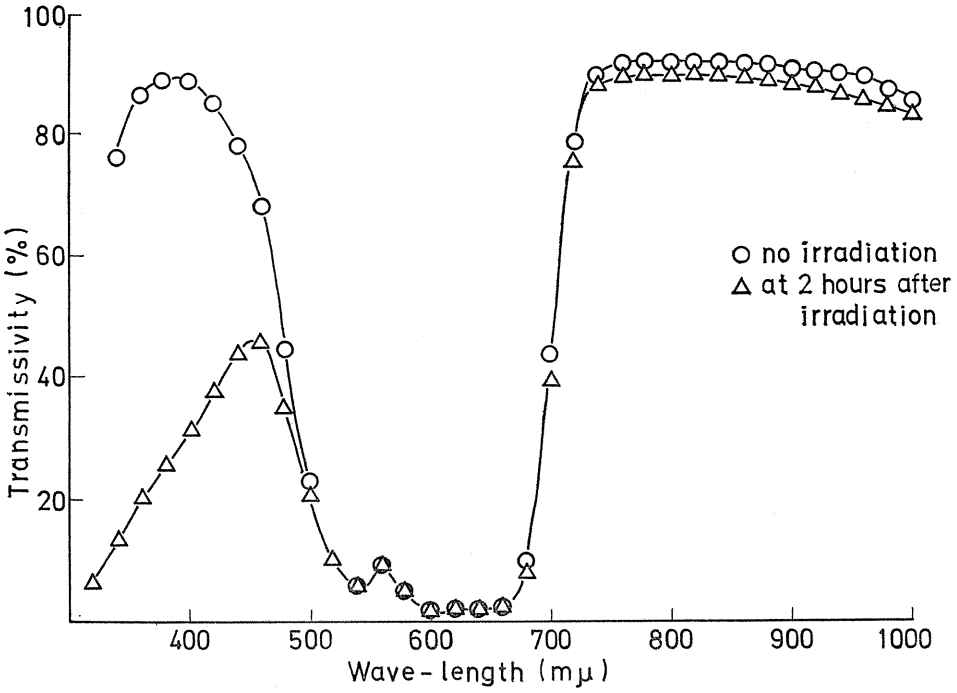

Fig. 1. The change of transmissivity of cobalt glass (γ-ray).

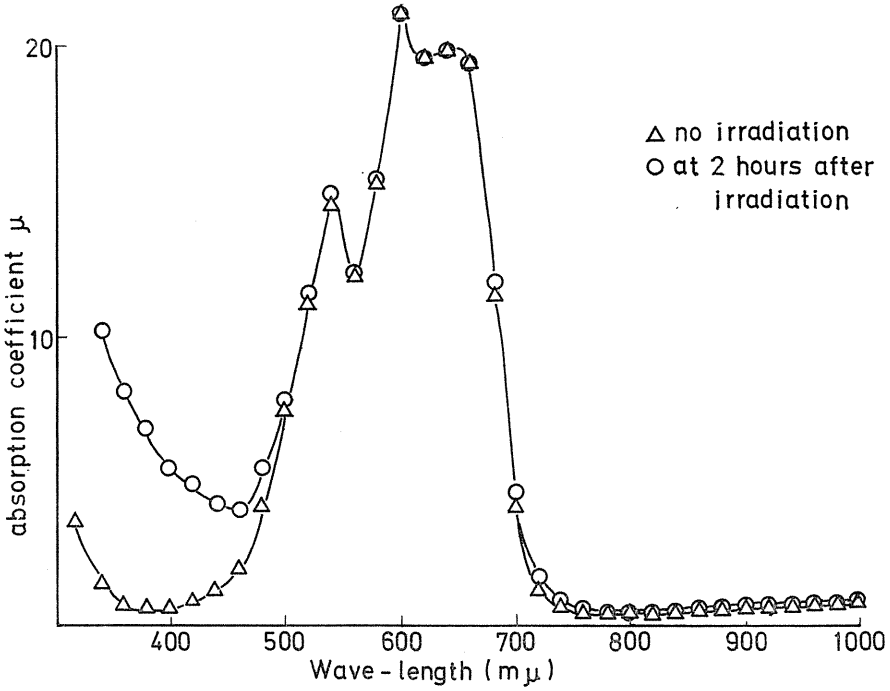

Fig. 2. The change of absorption coefficient of cobalt glass (γ-ray).

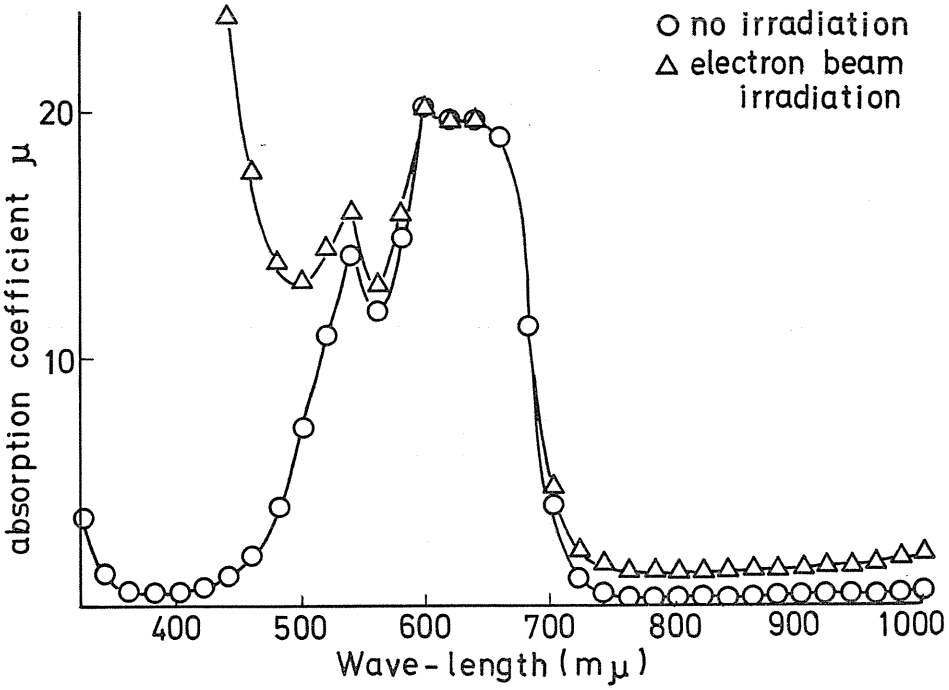

Fig. 3. The change of absorption coefficient of cobalt glass (electron beam).

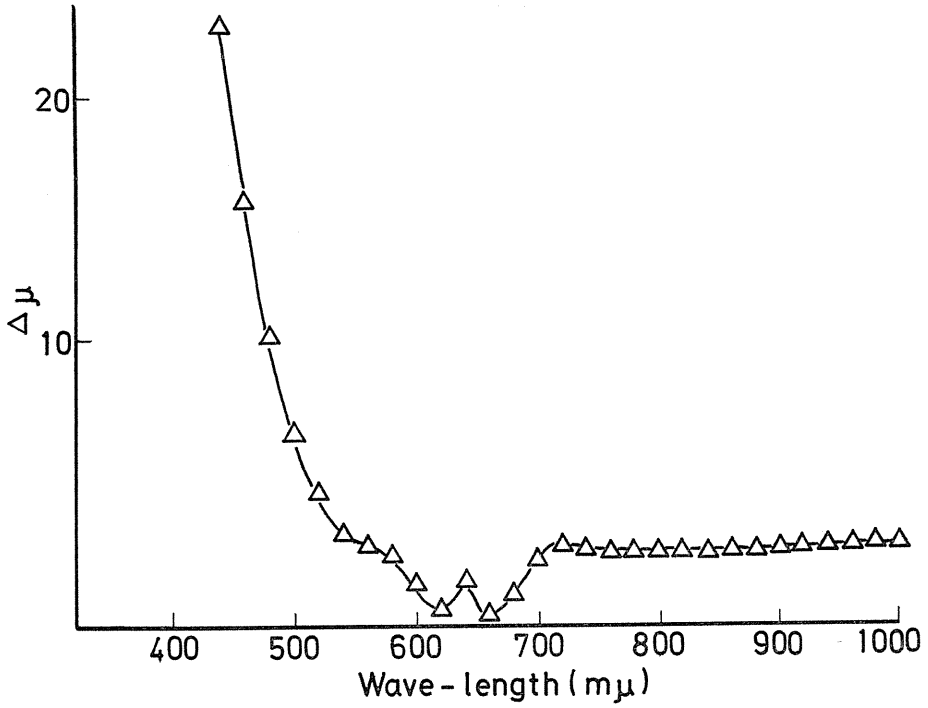

Fig. 4. The increase of absorption coefficient of cobalt glass (electron beam).

When the cobalt glass was irradiated by electron beam (4 and 6 Mev), the color changes from blue to green. This case has a variation of transmissivity as shown in Fig. 3 and 4. The electron beam spreads somewhat at 4 Mev of electron energy. By using the pile of glass pieces, we can get a maximum range of electron in glass. As shown in Fig. 5, we can estimate this range $\sim$ 1.3 cm for 6 Mev electron and $\sim$ 1.15 cm for 4 Mev electron. According to the experimental formula, we get the calculated value 1.34 cm and 0.9 cm respectively. For 6 MeV case, the agreement is good, but for 4 MeV case it is not so since the beam spread contributes this large value.

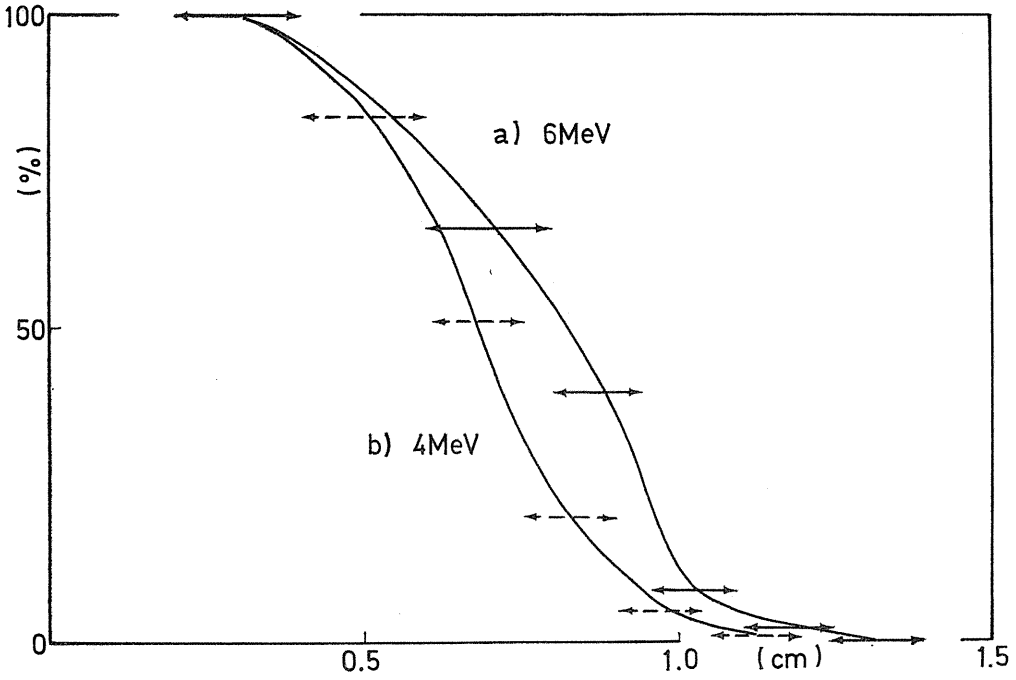

Fig. 5. The change of absorption coefficient of the piled cobalt glasses (electron beam, normalized at the first pieces).

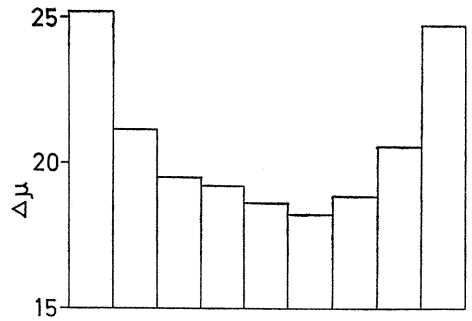

Fig. 6. The increase of absorption coefficient of the piled cobalt glasses (neutron flux).

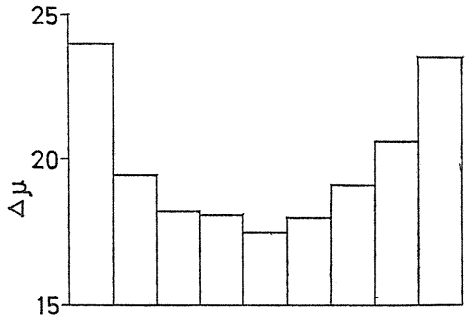

Fig. 7. The increase of absorption coefficient of the piled cobalt glasses (neutron flux).

Neutron irradiation was done in nuclear reactor. As neutron beam has a γ-ray mixture in reactor, so the obtained results is the summed effects of γ-ray and neutron. The picking up of neutron effect is very hard. We used a pile of glass pieces for this purpose. The experimental results are shown in Fig. 6 and 7. Clearly, neutron effect is not so effective. However, as γ-ray induces many free electron, so if there is no γ-ray mixture neutron effect may be more downed. This results shows this possibility, but do not give a definite answer to the neutron irradiation problem.

2. 3. Fading

According to Rabin-Price's and Kondo's results[3], we take the decrease of the absorption coefficient with time (fading) as one proportional to $t^{-\lambda}$. During irradiation, it decrease with time too, so we must correct the obtained results considering these fading phenomena. At time t-hours after τ-hours irradiation, the increase of the absorption coefficient $\Delta\mu$ is represented as

$$\Delta\mu=\Delta\mu_0(t_0,\ \tau)\left\{\left(1+\frac{t}{\tau}\right)^{1-\lambda}-\left(\frac{t}{\tau}\right)^{1-\lambda}\right\}$$

where $\Delta\mu_0$ (t_0, τ) is the absorption coefficient increase at time t_0-hours after τ-hours irradiation and it is given

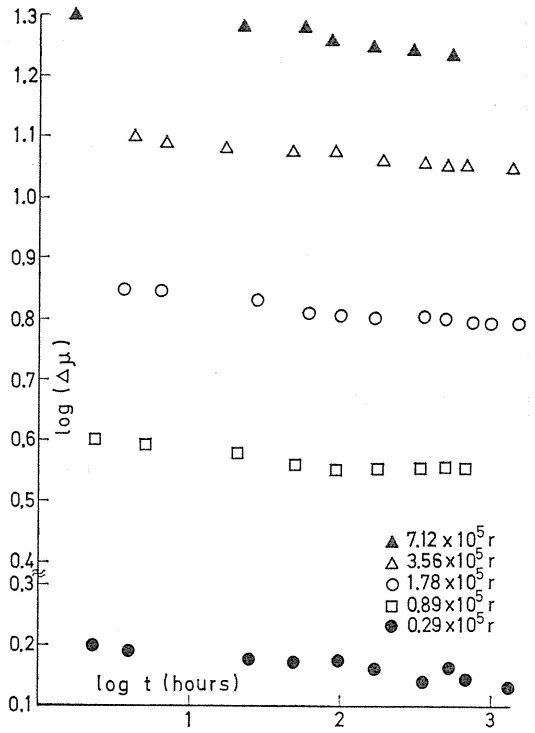

Fig. 8. The fading of cobalt glasses (radiation dose dependence).

$$\Delta\mu_0(t_0,\ \tau)=\frac{\Delta\mu_0}{\left\{\left(1+\frac{t_0}{\tau}\right)^{1-\lambda}-\left(\frac{t_0}{\tau}\right)^{1-\lambda}\right\}},$$

$\Delta\mu_0=\Delta\mu_0\ (0,\ \tau)$. In our experiment, irradiation time τ is nearly $1\sim2$ hours or smaller, and t is 20 hours or longer. So we estimate t/τ is 10 or larger. As stated following, λ is order 10^{-2}. From these values we can get an approximate formula

$$\Delta\mu=\overline{\Delta\mu}\,t^{-\lambda}$$

where $\overline{\Delta\mu}=(1-\lambda)\Delta\mu_0(t_0,\ \tau)$. This formula is valid for $\tau\ll t$.

From this consideration, we represent the fading behaviour in Fig. 8 and Fig. 9. On the measurement of fading phenomema, we used the light at three wave lengths 350 mμ, 400 mμ, and 450 mμ. Glasses are kept at constant temperatures 0 ℃, 100 ℃ and 200 ℃ between the successive measurements.

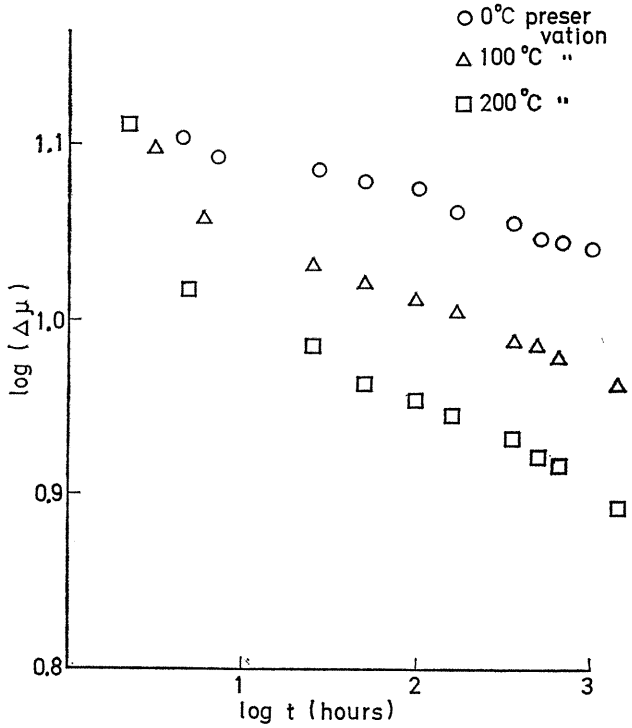

Fig. 9. The fading of cobalt glasses (temperature dependence).

The obtained λ-value are summarized in Table 2. λ-values are considered to be dependent on the temperature at which glasses are kept. According to Kondo's treatment[4], we can approximate this temperature dependence as

$$\lambda=e^{-A+BT}$$

where A and B is constant. In our case, we get

Table Ⅱ λ values

irradiation dose (r)	preserving temperature		
	0℃	100℃	200℃
1.78×10^5	0.018	0.029	0.039
1.5×10^5	0.018	...	...
1.0×10^5	0.017	...	...
0.89×10^5	0.021	0.026	0.032
0.75×10^5	0.022	...	...
0.295×10^5	0.022	0.026	0.038
average	0.020	0.027	0.036

$$A=4.74, \qquad B=3.01\times10^{-3}$$

This values can be compared with the window-glass value[4]

$$A=11, \qquad B=3\times10^{-2}$$

Nearly one order is lower in our case than the window-glass' case. Fading befaviour are similar for other radiation than γ-ray.

2. 4. Some Properties

(a) $\Delta\mu$-R relations*

On the basis of several experiments at different radiation dose (R), we can deduce $\Delta\mu$-R relation over $R=10^4\sim5\times10^6r$ range. From this figure (Fig. 10) we can say the linearity relation in log-log graph is valid for $5.10^4r\sim8.10^5r$. This relation is reptesented as

$$\Delta\mu=3.3\times10^{-4}R^{0.86} \quad (at\ 400\ m\mu)$$

($\Delta\mu$ is in cm^{-1}, R is in r). The increase of $\Delta\mu$ is slower than R for $R>8\times10^5r$, and may approach to the constant value for larger R, but it does not show the constant value yet at 10^7r. Same relation at wave length 450mμ is shown in Fig. 11.

(b) Dose rate and energy dependence.

Dose rate dependence is studied by changing the distance from glass to Co-60 source. This results coincide with each other. A small discrepancy is observed at low dose rate. However this does not make trouble since there is fading during the exposure (i. e. long exposure time is needed, see 2. 3). From these results, we can estamate dose rate dependence is smaller than $1\sim2\%$ if any.

Energy dependence is investigated by using Cs-137 source. Energies of γ-ray of Co-60 source are mainly 1.173 Mev and 1.332 Mev and of Cs-137 source is 0.66 Mev. $\Delta\mu$-R relation obtained from both sources are parallel in log-log graph. The values of $\Delta\mu$ at 10^5r are 4.175 (for CO-60 source) and 4.20 (for Cs-137 source). The difference 0.6% of total, so we can say that energy dependence does not exist for the energy range between 0.66 ~ 1.33 Mev.

*) We used the μ-value at 10h after exposure in $\Delta\mu$-R relation.
This value is obtained by assuming $t^{-\lambda}$ law (see 4.1). For other cases, we use the same $\Delta\mu$-value in $\Delta\mu$-R relation.

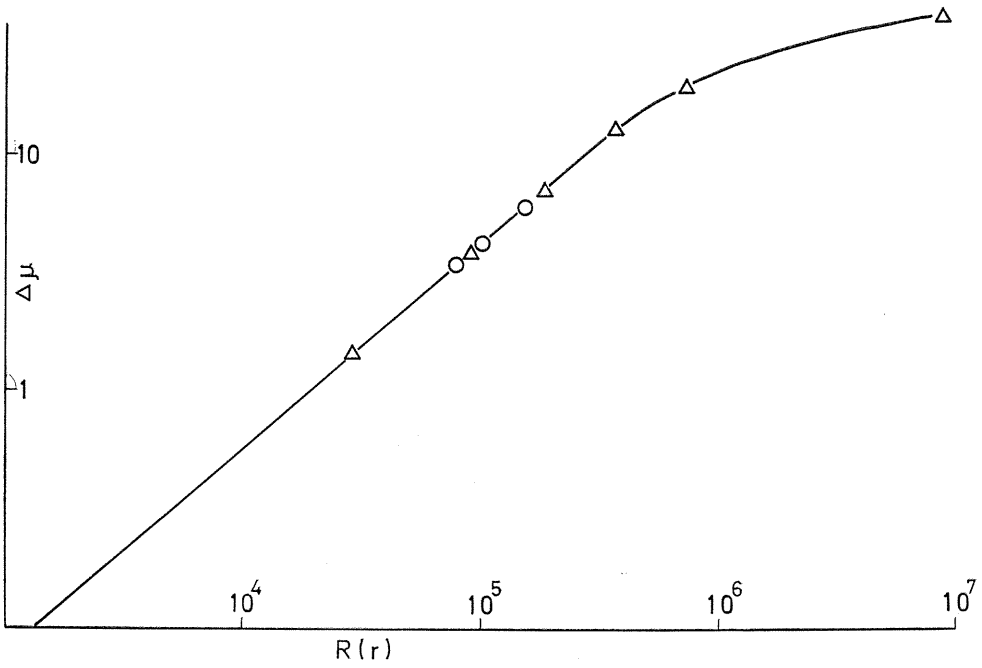

Fig. 10. $\Delta\mu$-R relation (cobalt glass, at 400 mμ).

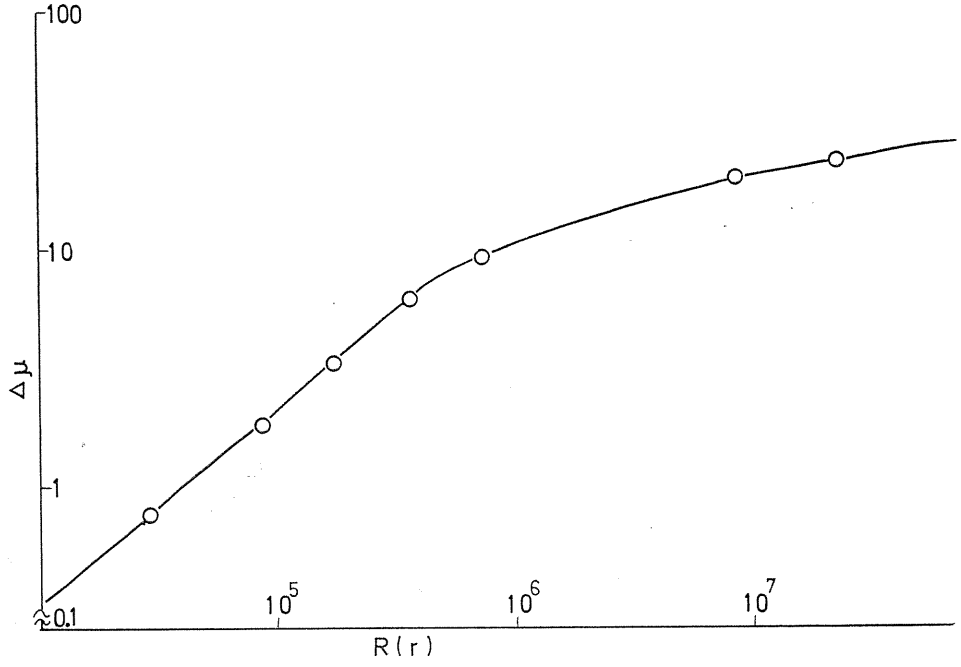

Fig. 11. $\Delta\mu$-R relation (cobalt glass, at 450 mμ).

(c) reproducibility

Re-irradiation of glass which was irradiated once before and kept at a constant temperature results a summation of effect of two exposures. That is represented as

$$\Delta\mu = at^{-\lambda} + b(t-t_0)^{-\lambda} = \Delta\mu_1 + \Delta\mu_2$$

where t is time after the first irradiation and t_0 is the time between the first and the second irradiation. For $t_0 \ll t$, $\Delta\mu_2 \approx bt^{-\lambda}$, so $\Delta\mu$ becomes the summation of the independent two irradiation.

Reproducibility repuired $\Delta\mu_1$ is smaller than $\Delta\mu_2$. If we compare the value of $\Delta\mu$ at 10 hours after irradiation, the requirement is

$$\frac{(\Delta\mu_2)_{10}}{(\Delta\mu_1)_{10}} > 100\left(1+\lambda\frac{t_0}{t}\right)$$

where $(\Delta\mu)_{10}$ is $\Delta\mu$ at 10 hours after irradiation. Then, we must take care the pre-history of glass, when we use the same glass twice.

(d) homogeneity

We always measure the transmissivity before its irradiation. From these measurements, we can conclude the used glass are nearly homogeneous. The difference of each glass is only $\sim$ 1% if exist.

(e) Change of λ-value on a long preservation[5]

Some glasses are kept 0℃ over $10^2 \sim 10^4$h. After this preservation, the temperature of presevation are changed into 100℃ suddenly. By this changes, λ-value of fading changes too. The relation of λ-value and preservation time is shown in Fig. 12. and Table 3.

For $t<10^2$ hours, λ-value after this change is nearly same as λ-value when it is preserved at 100℃, after exposure. However for 100h$<t<10^3$h, λ-value decreases to 0.02. This value is nearly same as one when it is preserved at 0℃. For $t>$

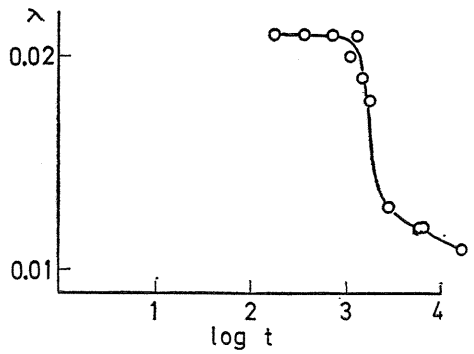

Fig. 12. The relation bwtween λ-value and preserving time at 0℃ (t).

Table Ⅲ λ values

0℃ holding hours	0	168	336	504	672	840	1008	1176	1344	1689	2712	5541	6186	15763
Values of	0.027	0.021	0.021	0.021	0.021	0.021	0.020	0.021	0.019	0.018	0.013	0.012	0.012	0.011

10^3h, λ-value dalue damps rapidly. For $t>2.5\times10^3$h, the damping of λ-value becomes show a little. We may expect λ-value becomes constant value $\sim$ 0.01 for larger time.

2. 5. Other glasses

(a) Phosphate glass with iron.

Phosphate glasses containing iron oxide 0.6%, 1.0%, and 2.5% are irradiated by Co-60 γ-ray. In Fig. 13 and 14, the absorption coefficient before and after irradiation for 0.6% and 2.5% cases are shown. The increase of the absorption coefficient for 2.5% case is larger than 0.6% case. In 1.0% case, $\Delta\mu$-R relation is obtained (Fig. 15). The linearity relation in log-log graph is hold and that region is broader than cobalt glass, nearly to 10^6r. Fading of this glass is a little faster compared to fading of cobalt glass.

(b) Artificial synthesized quartz

Synthesized quartz is difficult to be colored by irradiation. The absorption coefficient before and after 1.01×10^8r γ-ray irradiation is shown in Fig. 16. Fading is very small.

The change of the absorption cofficient by neutron irradiation is shown in Fig.

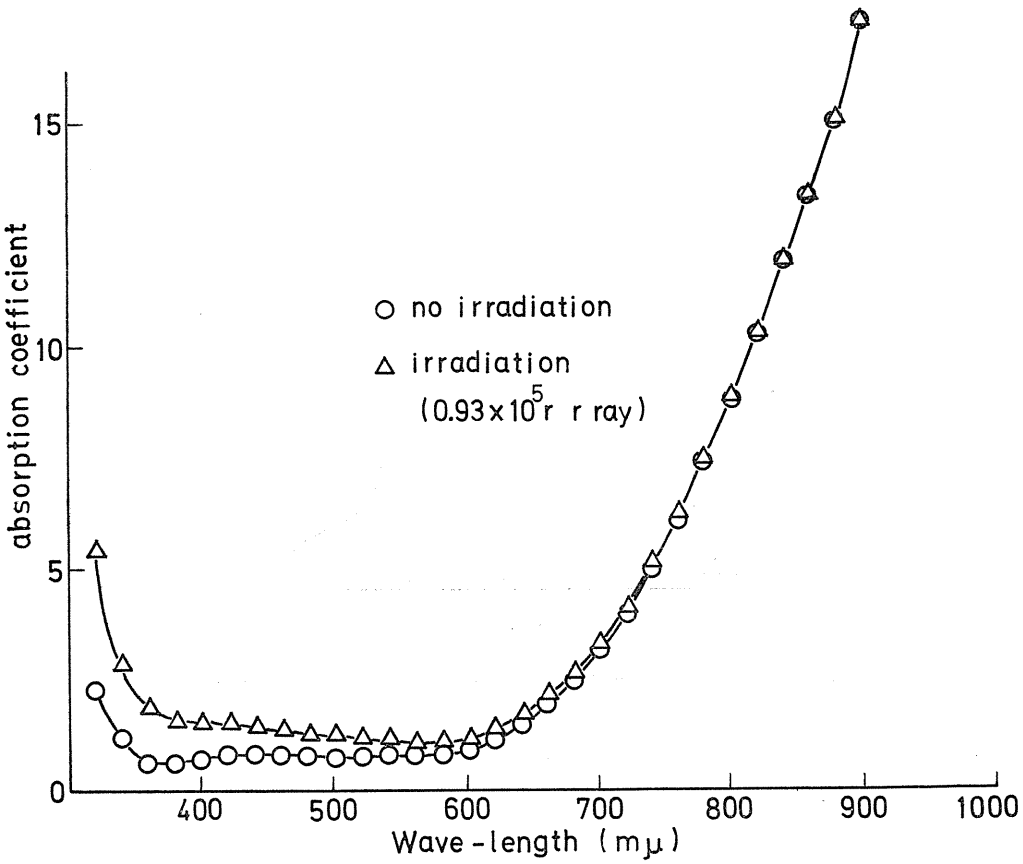

Fig. 13. The absorption coefficient of phosphate glass with iron (FeO 2.5%).

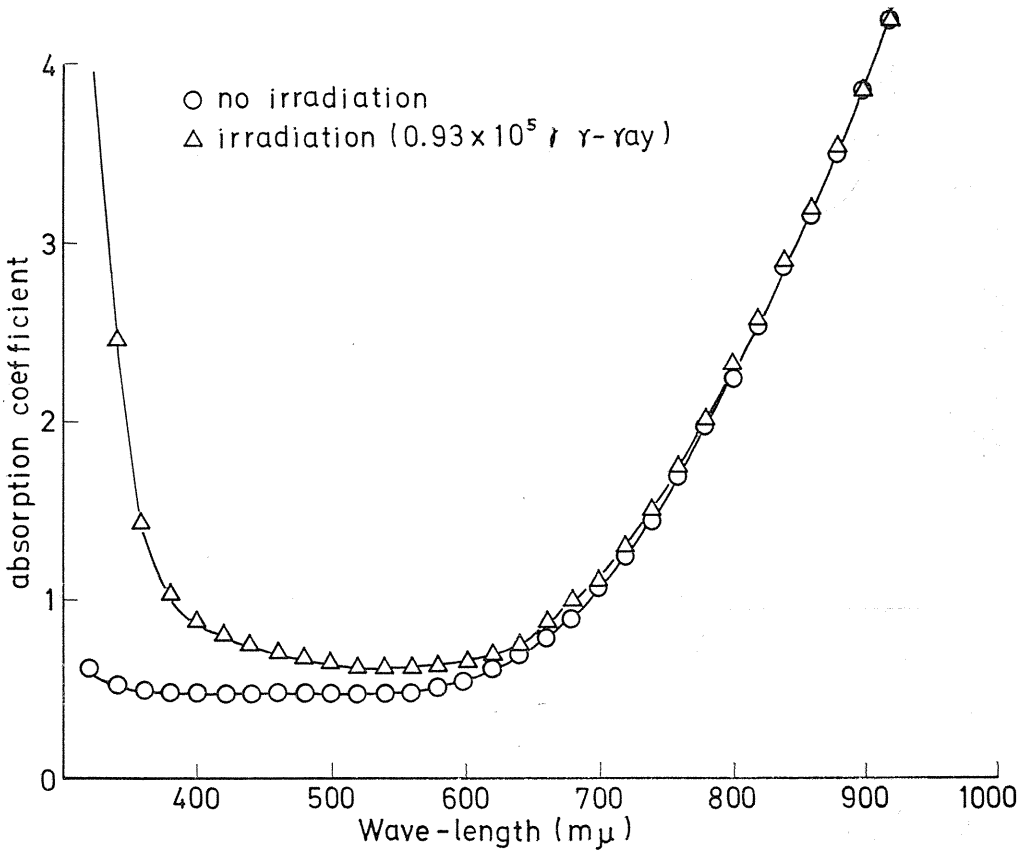

Fig. 14. The absorption coefficient of phosphate glass with iron (FeO 0.6%).

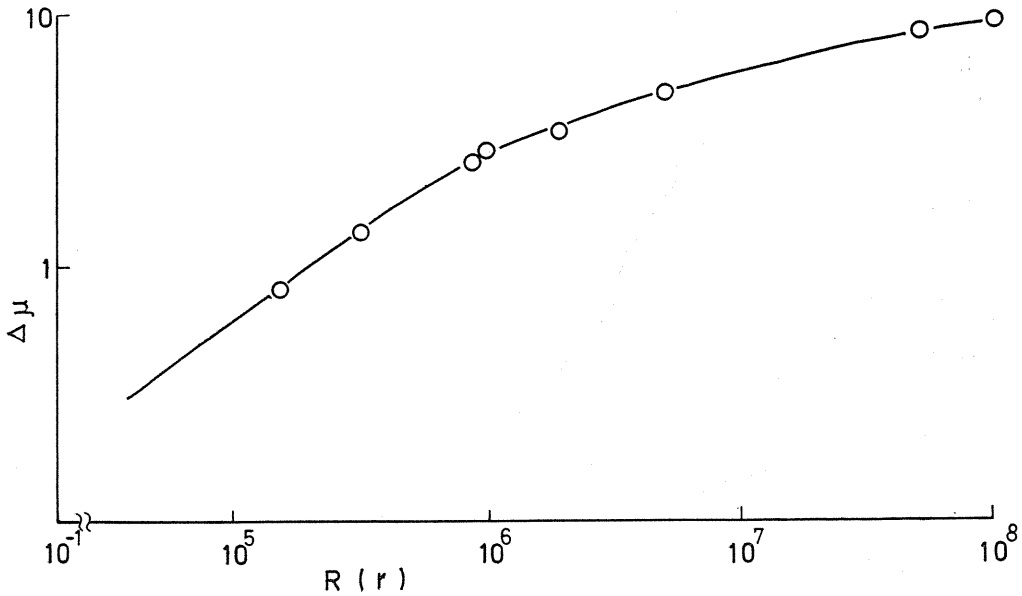

Fig. 15. $\Delta\mu$-R relation (phosphate glass, FeO 1.0% at 400mμ).

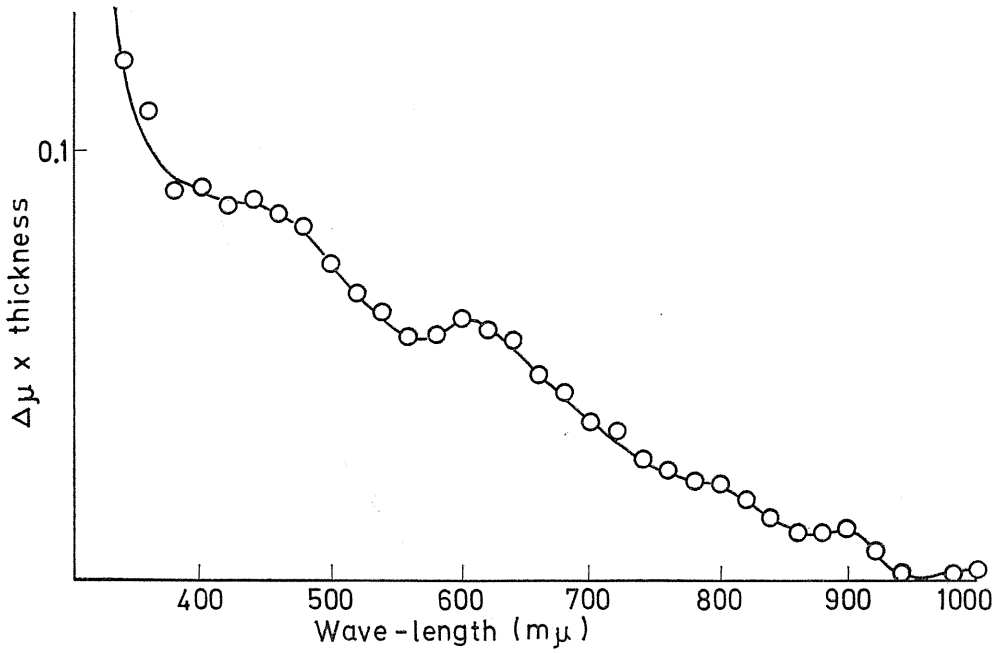

Fig. 16. The absorption coefficient of artificially synthenized quartz (γ-ray, 1.01×10^{8}r).

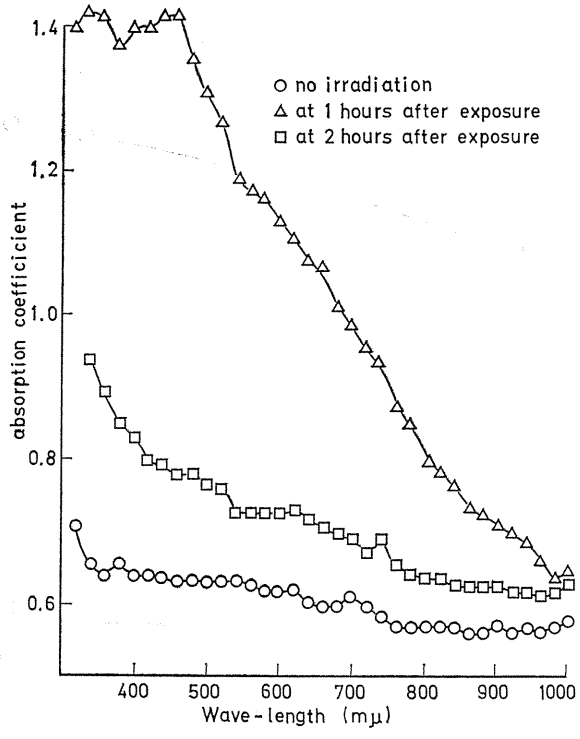

Fig. 17. The absorption coefficient of synthenized quartz (neutron flux).

17. Comparing one irradiated one hour with two hours by 3×10^{11} n/cm²sec neutron flux, the bleaching of color can be observed.

(c) Other materials.

We attempt to make the synthesized quartz with various impurity under high pressure. They are tabulated at Table 4. In this Table the condition of irradiation are show too. They are not thought to be perfectly homogeneous and may have some other impurity not mentioned here (e.g. carbon etc.).

Table Ⅳ Composition and irradiation conditions of Z-glasses

NO.	impurities	irradiation condition
Z-2	Zr 1.0%	$Co^{60}\gamma$-ray 10^5r
Z-6	Dy 1.0%	$Co^{60}\gamma$-ray 10^5r
Z-7	Mo 0.5%	$Co^{60}\gamma$-ray 10^5r
Z-4	Zr 0.5%	neutron flux (3×10n/cm²sec) 30 min.
Z-5	Co 0.5%	neutron flux (3×10n/cm²sec) 30 min.
Z-8	Dy 0.5%	neutron flux (3×10n/cm²sec) 30 min.

The change of the absoption coefficients are shown in Fig. 18 ~ Fig. 25. From these figures, the results are sumarized as follows.

1. Z-2 and Z-5 show a marked bleaching after irradiation over all wave length.

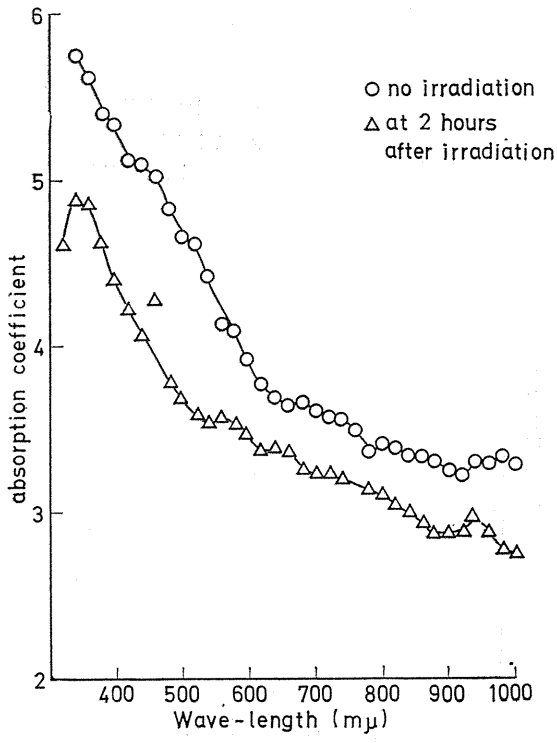

Fig. 18. The absorption coefficient of Z-2.

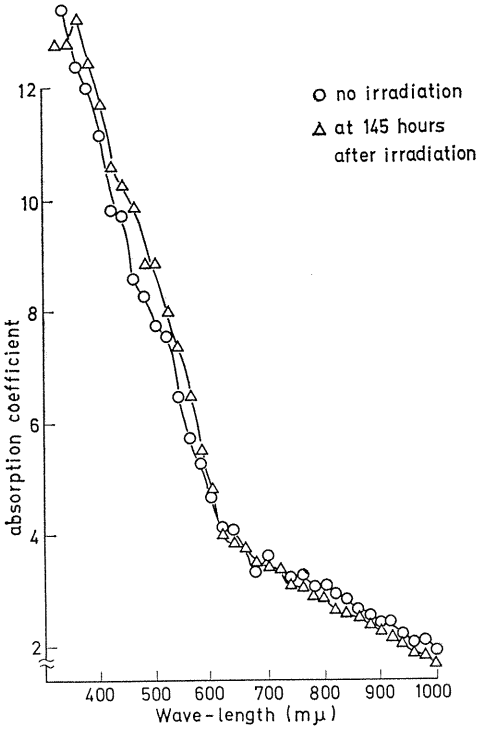

Fig. 19. The absorption coefficient of Z-4.

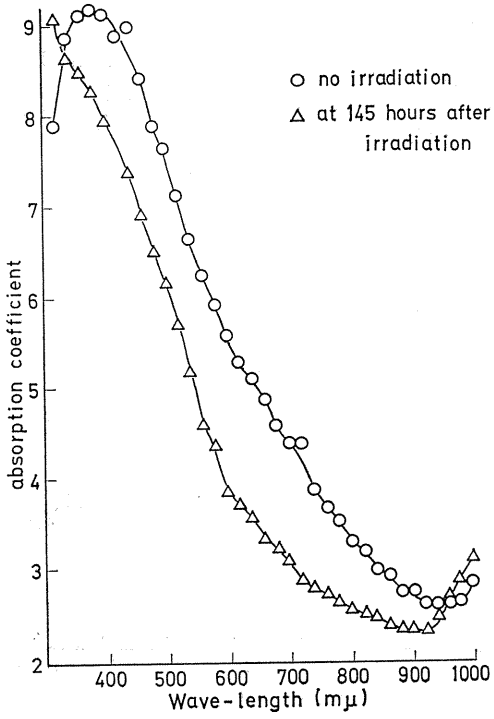

Fig. 20. The absorption coefficient of Z-5.

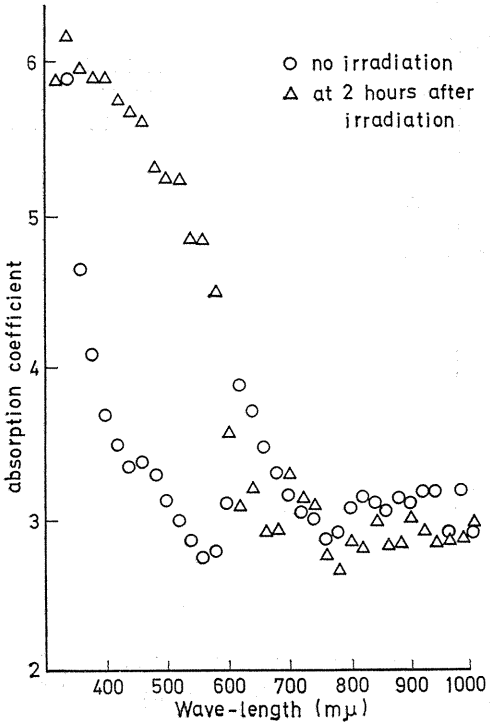

Fig. 21. The absorption coefficient of Z-6.

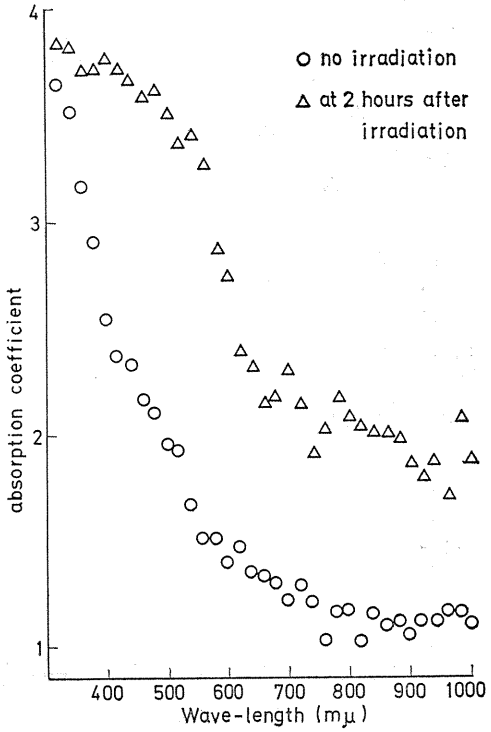

Fig. 22. The absorption coefficient of Z-7.

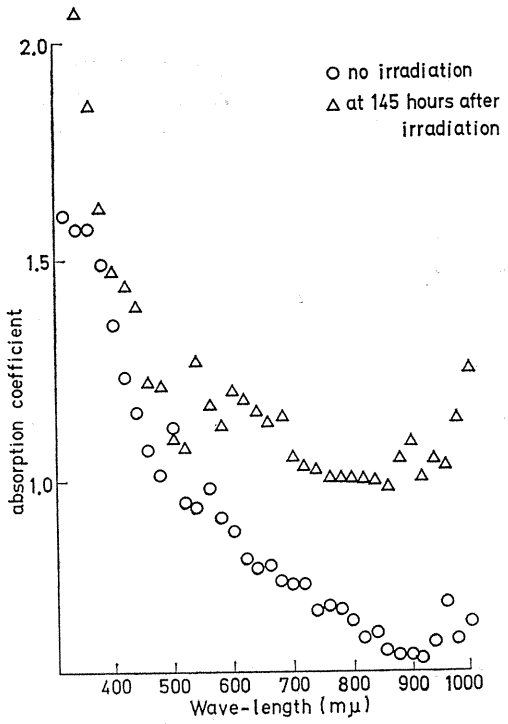

Fig. 23. The absorption coefficient of Z-8.

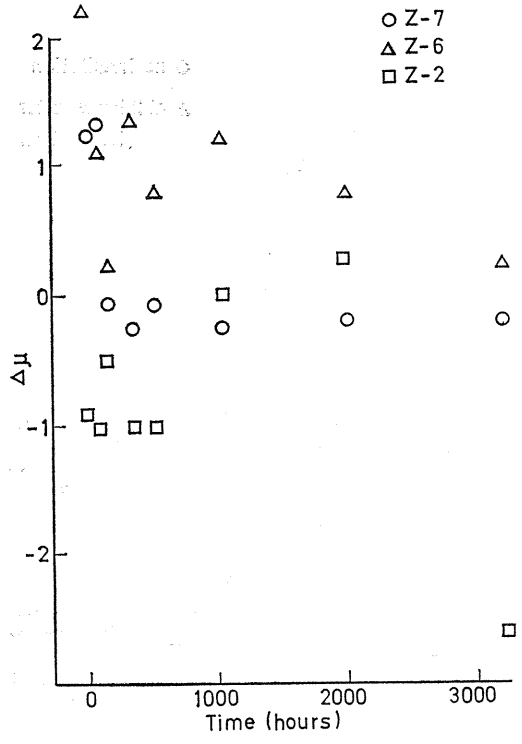

Fig. 24. The fading of Z-2, Z-6 and Z-7.

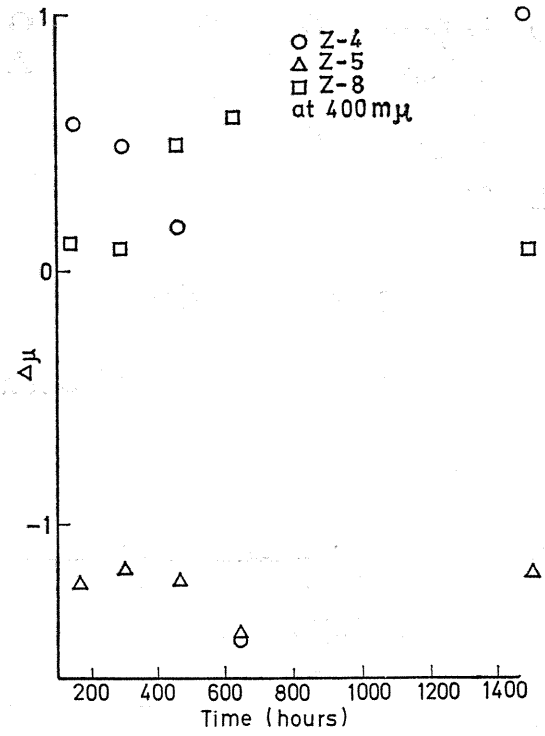

Fig. 25. The fading of Z-4, Z-5 and Z-8.

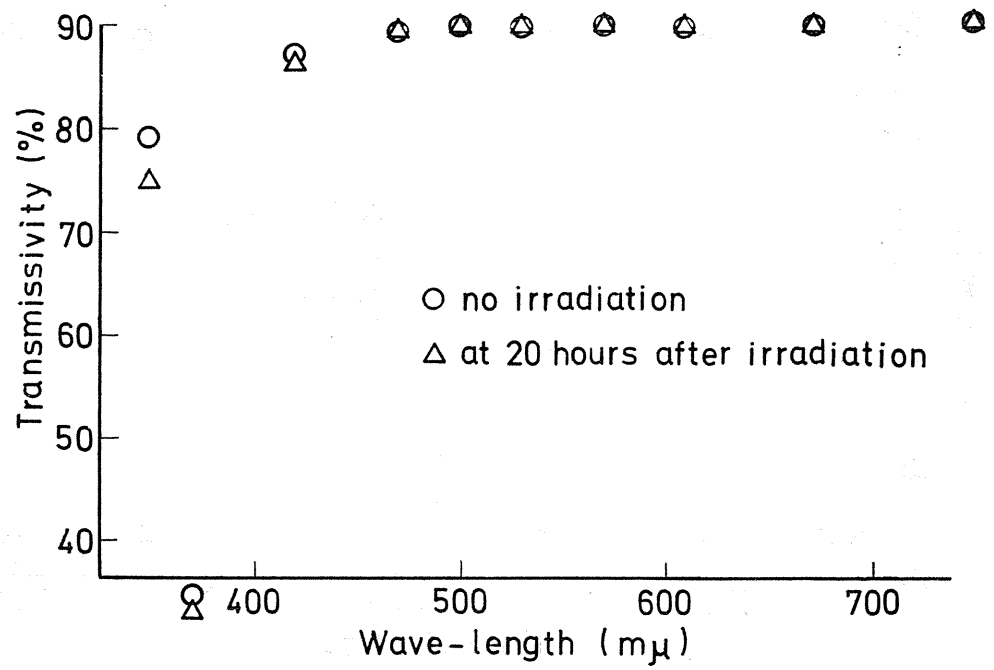

Fig. 26. The transmissiAity of A-glass.

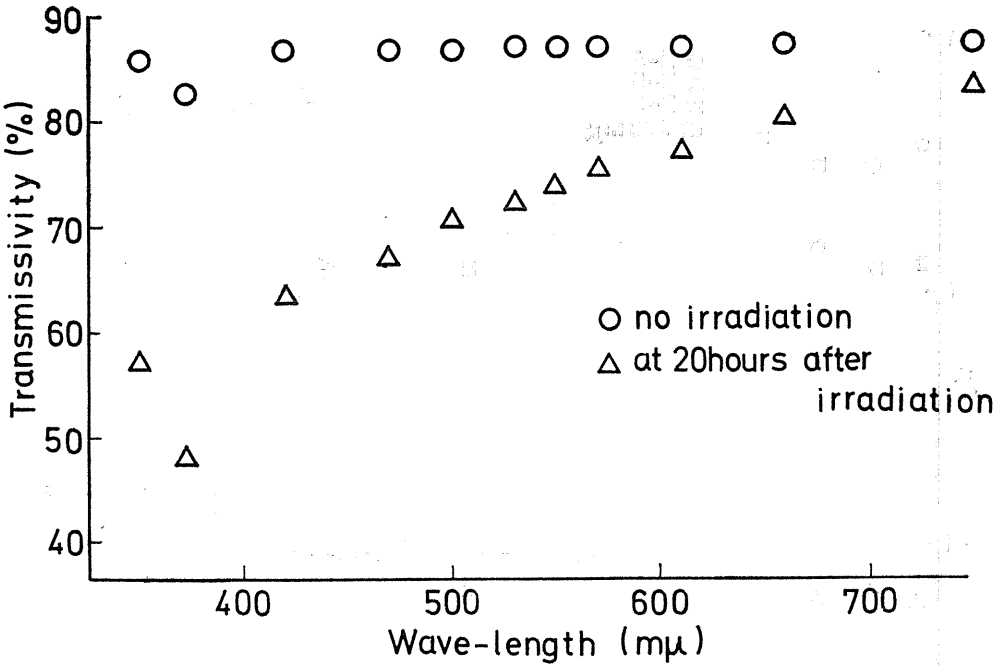

Fig. 27. The transmissivity of B-glass.

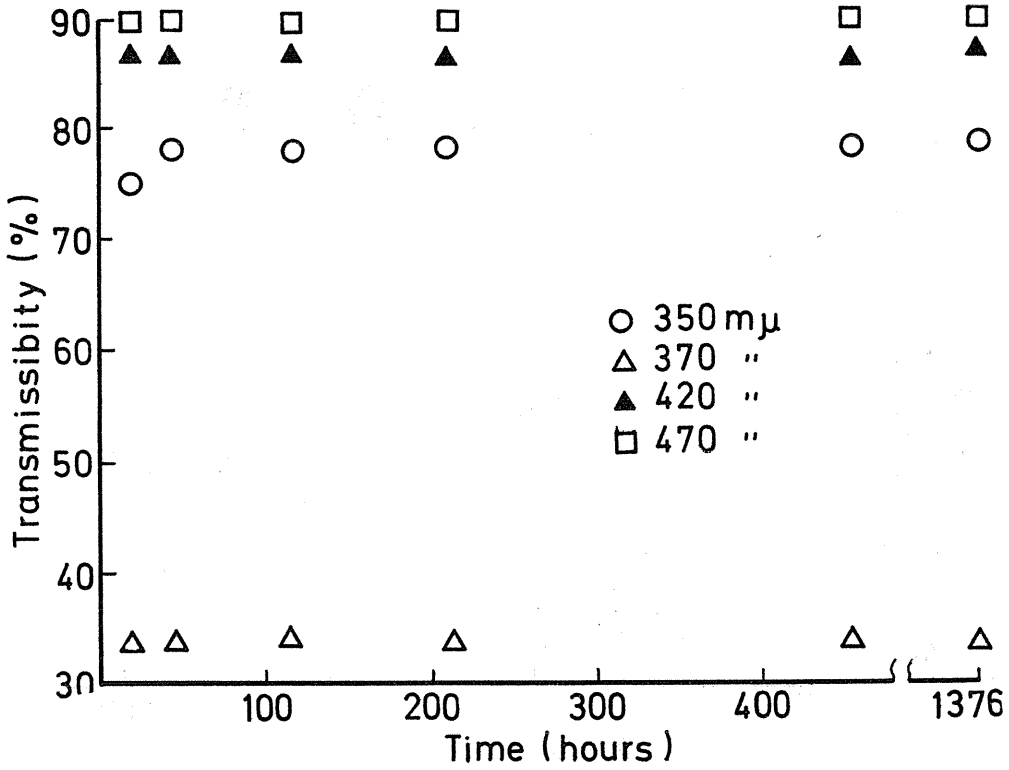

Fig. 28. The fading of A-glass.

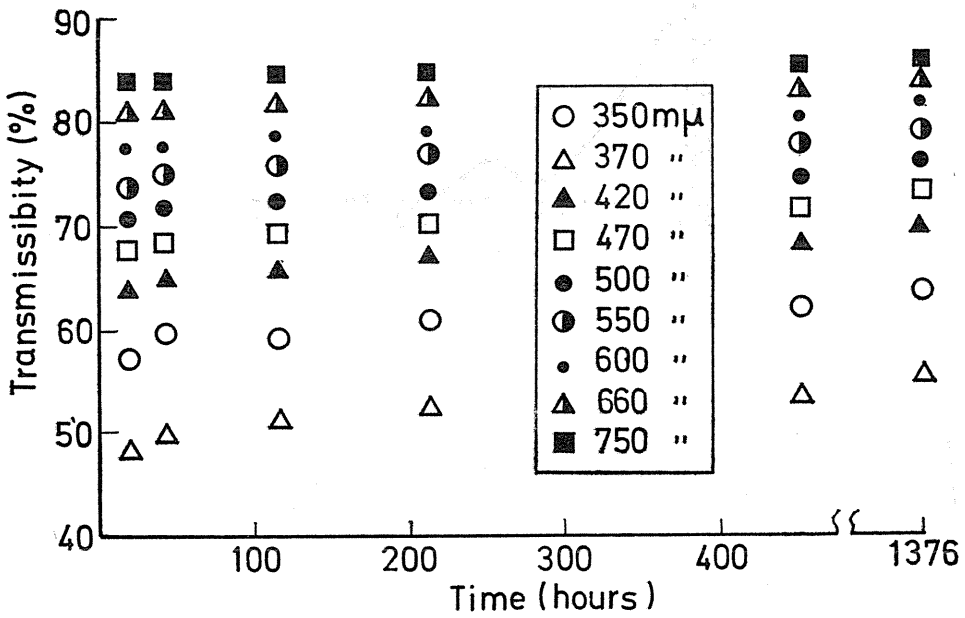

Fig. 29. The fading of B-glass.

2. Z-6 and Z-4 show a weak bleaching for a long wave length than 600 mμ.

3. In general, the increase of the absorption coefficients is larger for γ-ray irradiation than neutron irradiation.

4. The behaviour of the absorption coefficients of Z-2 and Z-4, Z-6 and Z-8 before irradiation show the similar characteristics.

5. The fading of Z-7 (at 400 mμ) is very small.

(d) Other glasses

Another silicate glasses are irradiated with γ-ray. They, A glass, have a composition indicated in Table 4. The transmissivity is shown in Fig. 26 and 27 respectively. Fading behaviour are shown in Fig. 28 and 29, too.

3. Analysis and Discussion

We will discuss the possible origin and behaviour of the coloration on the basis of experimental results in 2. In this section we start with the analysis of cobalt glass and examine the extension to other glasses.

3. 1. Absorption band

From Fig. 2 we can separate the absorption band. The obtained bands are shown in Fig. 30 schematically. We shall call these bands A, B, C and D from high wavelength to low. A band locates at 580 mμ, B band at 530 mμ, C band at 440 mμ, and D band at 305 mμ. The characteristics of these bands are tabulated in Table 5. Band D is excited most strongly but has a small fading. Band A and B have nearly same characters, —— small band width, weak excitation and relatively flarge ading. The strong excitation of D-band can mask B-and C-bands. Owing to this fact, the

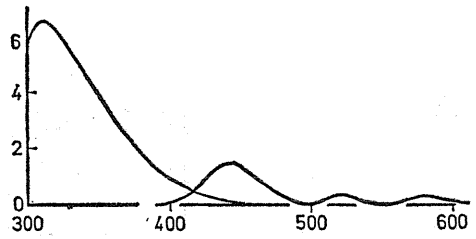

Fig. 30. The band structure of irradiated cobalt glass.

location of B-and C-bands can not be determined definitely. Probably they may have the error of ± 10mμ. At 10^3 hours after irradiation, A-, B-and C-bands fade out and D-band becomes only detectable one in all cases.

3. 2. Centers[6]

These bands can be ascribed to the existence of centers considering to our experimental results and other analysis.

(1) D-band

Strong excitation of this band and no strong signal of ESR indicate this center is not electron trapping. And the original excitation at this short wave length suggests this center is due to a defect in original network. So we can regard this as center composed from positive ion trapping at non bridging oxygen. Scematically we can take this model as Fig. 31. This may include a interstitial positive ion. This center may be thought to be stable relatively, and exists in original glass network too. The number of original defects in glass is very large, so it is produced easily.

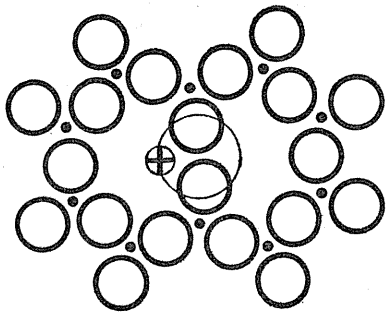

Fig. 31. An exampleof the model of D-center.

(2) C-band

The excitation of C-band is the second strength. Relative large signal of ESR probably owes to this band. This possibility suggests this band is the electron trapping one. Comparing cobalt glasses containing various cobalt contaminent, it is seen that the maximun position of the excitation curve displaces according to the variation of contaminent. And the fading of ESR signal is similar to the fading of this band. So we may assign this center to be electron-trapping interstitial positive ion. The interstitial positive ion is not so stable as D-center, so it will decay into the stable state. Thus this band fades away more faster than D-band. As the positive ion we can mention Na^+, Ca^{++}, Mg^{++} etc. in cobalt glass. An example of the possible structure of this center is shown in Fig. 32.

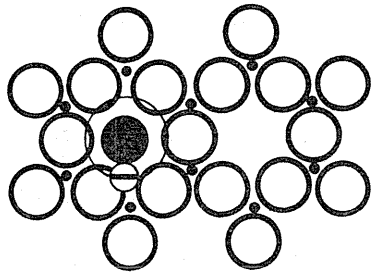

Fig. 32. An example of the model of C-center.

(3) B-band

This band does not show the displacenent of the maximum position of excitation with its positive ion density. By the help of another analysis, we can guess this center may be oxygen vacancy. When the nonbriding oxygens are knocked out from the original network, the produced vacancy of oxygen become to trap the free electrons. If so, this center will show ESR-signal. However, this band is weak compared with C-band, since C-center owes to the original positive ion, but this center depends on numbers of knocked out oxygen by irradiation. So the intensity of ESR of this center will be weaker than one of C-center. In Fig. 33, the possible structure of this center are sketched.

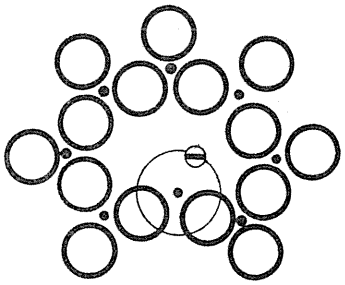

Fig. 33. An example of the model of B-center.

Fig. 34. An example of the model of A-center.

(4) A-band

We can not infer the definite structure for this center owing to the relative weak excitation. From the probable case of the defects in glass, we may be able to asign this center as (oxygen vocancy) + (positive ion). Accepting this idea, this center can trap electrons too. However as described in B-band case, the contribution of this center to ESR signal is smaller than C-center. We attempt to sketch this model in Fig. 34.

Finally, we summarize the characte-

Table V The characterist ics of centers.

Band	Position (eV)	Half-width (eV)			Remarks	Symbols
A	2.14 (580 mμ)	0.07	0.7	>0.2	Definitely unknown, probably electron capture by the oxygen vacancy and/or interstitial positive ion. ESR yes.	$_{Me}T_{2-}$ $_{Me}T_{2-}$ $_{2Me}T_{3-}$
B	2.34 (530 mμ)	0.12	0.7	<0.2	Electron trap by oxygen vacancy, does not depend on the density of positive ion. ESR yes.	B_{2-} B_{-}
C	2.83 (440 mμ)	0.48	3.0	<0.2	Electron trap by the interstitial positive ion, dependent on the density of positive ion. ESR yes.	$_{Na}P_{-}$ $_{Ca}P_{-}$ $_{Mg}P_{-}$
D	4.05 (305 mμ)	~1.8	13.2	≲0.02	Positive ion trapping by oxygen (nonbridging), (include interstitial positiveion). relatively stable. ESR no.	Q_{+} Q_{+} Q_{2+} $_{Me}D_{+}$

Table Ⅵ Symbols in Table Ⅴ

	B	D	P	Q	T
Oxygen vacancy	●				●
Nonbridging Oxygen		●		●	
Interstitial position		●	●		●
Charge	+2	−2		−2	+2

ristics of these centers in Table 5 (In Table 6, we interprete symboles used in Table 5). We can separate four bands, but there may be still some other bands, not separated or very low excited. Then we can not say these centers is only one possibility. However, these centers is only possible one till now.

3. 3. *Production mechanism*

Irradiation of γ-ray and other radiation produces many free electrons and positive holes, so there occured the new defects, e. g. the getting in interstial position or the knocking out an ion. Both of the original and the new defects contribute the coloration too. Mainly D-band, basing on the existence of nonbridging oxygen, contributes on the optical behaviour. The incident γ-rays set free the electrons and cut down the bridge of oxygen in the original network. So D-band is produced from this nonbridging oxygen. This interpretes the original excitation and the induced excitation by irradiation. In this case, positive ion, mainly Si plays a role to produce D-center. Free electrons contribute to produce C, B and A conters, with the help of the defects and the rearrangement of defects formed through thermal treatment of glass. After production of those centers, they disappear gradually through their thermal motion.

The production processes are due to the original defects and the produced defects. At the first sight, this makes the coloration, for the production of band to be dependent on the original defects are very larg in number, so the formed excitation may be thought to depend seriously on the original state.

Stevels and Kats[7] cited the eight theoretical possible imperfections in glass-network. From their theory, we induce our model and the production mechanism described above. However, another interpretation may be possible.

Just after exposure, incident radiation remains a large thermal energies in local. So the production fo these centers fluctates and the fading of transmissivity does not follow the approximate formula and fluctuates on a few hours after irradiation.

C-band are excited more by high dose radiation, e. g. electron irradiation, so the yellow component of light increases and glass is looked like green.

3. 4. *Fading*

Fading phenomena are recognized on this model of these centers. A and B bands fade out relatively fast, i. e. these centers are unstable. These centers are considered that they are produced from oxygen vacancy. The oxygen vacancy is recoverd relatively fast into the original network. Especially the temperature of glass increases as the result of irradiation, so the available thermal energy after irradiation will be large. This thermal energy makes electrons and ions to more freely. So the produced vacancies can be filled easily. The A- and B- centers disappear on

this recombination, and electrons are set to be free. The reason of the metastability of C-center is due to the stability of the interstitial position. The glass network has a local regularity, but the regularity allows the inclusion of impurities. The distortion due to the existence of impurities is absorbed by the surround network. Probably this distortion is compensated by trapping electrons too. The trapped electrons are knocked out by free electrons, so the interstitial ion goes to be unstable. This mechanism is one of model of C-band's fading. D-band consists of original defects, so this center is thought to be the most stable. Accordingly, the fading of D-center depends on a character of the positive ion. However, these positive ions take the relative stable position as seen in original network. Only the small distortion and the effect of the fading of other centers produce the fading of D-center.

The existence of Co-ion may contribute to the fading phenomena (especially C-centers). The large ion-radius and divalent nature of cobalt ion will contribute the metastability of C-band.

The dependence of λ-value on preserving temperature is interpreted as the effect of themal motion of electrons. After sometimes preserving at 0℃, λ-value at 100℃ decreases. This is thought that the number of defects decrease and the probability of the recombination goes to be low after the elapsed long time, so A-, B- and C-centers becames almost scant. Thus the λ-value goes to nearly one of D-centers. As we can not measure transmissivity on a short wave length, so we can not conclude the fading characteristics of D-band definitely. However it may be not so in error to think the fading mechanism as one described above.

3. 5. Other glasses

(1) Phosphateglass

We can count four bands at least on this glass. Of course, we can not definitely mention the number of bands, because the excitation is small especially on the long wave length range. The maximum positions of the four bands at ~300 mμ, 470~480 mμ, 560 mμ and 670 mμ respectively. In these bands, the band at 470~480 mμ has a slight different position for its iron contaminent. The glass with 0.6% iron oxide shows the maximum at 470 mμ, on the other hand one with 2.5% iron oxide shows the maximum at 480 mμ. The position has an error, but the difference is observed clearly. So we may consider this center as similar as C-center in cobalt glass. The maximum at ~300 mμ will be due to the Alkal ion defect which is the original or the induced one by irradiation. This assignment based on the similar consideration about D-center in cobalt glass. Other two bands are broad and their fading are fast. These centers are recognized on the same model of cobalt glass. Thus, the centers of phosphate glass are similar structure but their energy levels are different owing to the difference of the eriginal network.

(2) Artificial synthesized quartz.

This has many small excitations. These may be due to some impurities contained. In the production process, the possibility of the mixture of various impurities exists. The background network is nearly pure, so the defect due to this impurities occur easily. Accordingly we can not assign definitely on this case.

(3) Other materials

Z-glasses have a remarked properties. However we have not sufficient materials and data. In this case, they may have impurities (e.g. carbon). From these circumstance, we can't get definite results. Only one mentioned is the bleaching phenomena. This phenomena are seen in symthesized quartz and glass manufactured on

the base of symthesized quartz. These show the possibility of the destruction of centers by irradiation.

(4) Other glasses

These glasses show the excitation at 370 mμ, and other excitations can not be separated each other. The excitatiln at 370 mμ may be overlapped by a stronger excitation at shorter wave length. And it is known that this excitation does not show ESR signal. So we will consider this center is due to the defects in the original uetwork. Other small excitations which is not separated well, are probably two or three maximum. They are especially small for A-glass. The situation is similar to cobalt glass. However, there is not the second strong excitation (correspond to C-band in cobalt glass). This reason probably may be due to the difference of the role of positive ion. B-glass has the second maximum at 470mμ. These will be due to the positive ion. The ESR signal does not become a remarkable notice, so we can't say definitely about this center.

4. Glass as a radiation dosimeter[8)]

Many attempts to use glass as a radiation dosimeter have been done[9)]. They showed the stability and applicability over wide dose range. It is also valid in our case shown in 2. Especially glass is useful for a high dose. For the dosimetry of high dose, the chemical dosimeter (e. g. ferrous compound solution) is used. However, this method is tedeous and not so convenient. Glass dosimeter is convenient and easy. In this section we summarize the characteristics of glass as dosimeter and add a needed notice.

4. 1. Characteristics as dosimeter

The increase of the absorption coefficient $\Delta\mu$ increases with the radiation dose R. From $\Delta\mu$-R relation, we obtained the efficiency $d(\Delta\mu)/dR$. When the linearity in log-log scale is valid, $\Delta\mu$ is given (see 2. 4)

$$\Delta\mu = aR^b$$

so

$$\frac{d(\Delta\mu)}{dR} = abR^{b-1} = \frac{b}{R}\Delta\mu$$

If we want the large efficiency, it is necessary to take a large b value. (In our case, $b<1$, so $\Delta\mu/R$ decreases with R). When the linearity in log-log scale is not good and $\Delta\mu<aR^b$, it gets smaller than linearity case. At 400 mμ case, this value is $2.8\times10^{-4}r$, for $R=10^4r$, 4.3×10^{-4} for $R=10^5r$ and 3.1×10^{-4} for $R=10^6r$. Accordingly, the use of glass dosimeter is effective over this linearity range. ($10^4\sim10^6r$). This effective range can be enlarged into $10^3\sim10^7r$ with some uncertainty.

The fading of cobalt glass is small. By considering this fading behaviour, the measurement of dose can get more exactness. The measurement of transmissivity is done at the time 10~20 hours after the end of exposure. The obtained value is extraporated at some time (we use 10 hours) using the approximate relation $\Delta\mu\propto t^{-\lambda}$ This inclusion of the fading effect increases the exactness. This procedure may be somewhat tedious and need some times too. If needed, no corrected values are used,

so that value will be the order estimete only.

4. 2. Some notice on measurement

As stated in 2, there are some fluctuations of transmissivity on some times after irradiation. The time is nearly same or twice of the exposure time. This behaviour is due to the local heating by irradiation. The radiation heat up the glass, so the produced centers decay and new centers are produced. This process is a complex process and can not be described easily. On the use as dosimeter, the measurements during this period do not offer a good data, so we must avoid that.

If possible, one or two measurements at the time of few or more times of exposure time after irradiation must be done. These obtained values are extraporated to a some determined time (we use 10 hours after irradiation as above) assuming $\Delta\mu \propto t^{-\lambda}$ relation. So the results is compared to $\Delta\mu$-R relation.

The original transmissivity is not so different each other. However to obtain an accuracy, the original transmissivity before irradiation must be measured.

4. 3. Some considerations on error

We consider some sources of the error and estimate their order briefly.

(a) Measurements of transmissivity

The error is due to the scale of a measuring apparatus. This error is nearly 1% or smaller.

(b) The change of preservation temperature

During the successive two or three measurements, material is kept at a constant preserving temperature. In the case of change of this temperature, the effect on the measurement appeared through the change of λ-value.

Assuming the formula of λ-value on temperature (2. 3), we get

$$\frac{d(\Delta\mu)}{dT}=\Delta\mu lnt\cdot\frac{d\lambda}{dT}=\Delta\mu B\lambda lnt$$

By our experimental value $B=3\times10^{-3}$, $\lambda=0.020$, it goes to

$$\frac{d(\Delta\mu)}{dT}=4\times10^{-4}\Delta\mu$$

Following this formula, $d(\Delta\mu)/dt$ is smaller than 4×10^{-3}.

(c) Fading

As stated in a previous section, we may estimate the error to be smaller than 1% by adapting the mentioned procedure.

(d) Fluctuation of centers

The number of the produced centers depend on the original status and the situation after irradiation. However, the measurements before irradiation indicate the homogeneity of this glass. After irradiation, we avoid the measurement at nearly same time as exposure time, so the thermal fluctuation will be lowered.

Summary we can say the error will not exceed a few percent of the measured value.

5. Summary

The optical phenomena of the irradiated glass show many characteristics. In the case of cobalt glass, there are four bands at least. These bands are due to the centers produced by irradiation. In original glass, there are some defects of its network structure. That defects are the one of the origin of these centers. And the produced defects can make a furthur centers. The former is the main part of the coloration of glass. The production of the defect is so-called the secondary process, so the contribution of this defects is relatively small.

The produced coloration of irradiated glass fades out gradually. Heretofer, it has been frequently said that the fading is small. In this work, we studied this fading phenomena carefully over large time after exposure. So we can estimate the used figure is mainly due to the behaviour of D-band. This band is a nature of original defect. So this ought to be relatibely stable.

From our discussion, we can deduce the method for the exact measurement of radiation dose. The convenience of the treatment and the easiness of the measurement are the excellent nature of glass dosimeter. Especially, for the high rose rediation, glass dosimeter can play the important role.

On the other hand, the study of irradiated cobalt glass and other glass is useful for the study of structure of glass. In particular, the bleaching seen in some substances is interesting, and this will be used for the study of transformation between centers.

We wish to thank many people for their hospitality.

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