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Irradiation hardness in silica glass

SIJIAN GAO*, SHIXI OUYANG, TINGJI WANG
China Building Materials Academy,Guanzhuang Dongli, Chaoyang, Beijing 100024, People's Republic of China
E-mail: gaosijian@263.net

Absorption spectra of quartz glasses before and after γ-ray irradiation were discussed. It was found that the irradiation hardness is mainly dependent not only on the concentration of impurities or hydroxyl group alone but on the relative relation between them.

1. Introduction

Visible or/and ultraviolet (uv) transmittance of some silica glasses decreases, and the glasses may even blacken in the course of their operating under irradiation condition. In contrast the change of transmittance for other glasses is not so obvious. What is the difference between these silica glasses? What is the factor which influences the irradiation hardness of silica glass? The question is interesting to researchers and manufacturers relating to silica glasses. The influence of γ-ray irradiation on some silica glasses is investigated and discussed in this paper.

2. Experimental procedure

Raw materials, manufacturing methods, and impurity concentration for the samples used in experiments are listed in Table I. The symbols, q, s, and si, in the sample name represent the quartz crystal powders, silica powders from the oxidized $SiCl_4$, and natural silica sands, respectively. Diameter and thickness of the polished samples were about 30 and 6 mm respectively. Accuracy of measurement of thickness was ± 0.05 mm in calculation of absorption coefficients.

Samples were irradiated by a ^{60}Co γ-ray source. The irradiated dose was about 13 kGy $\times$ 4 h = 5.2 Mrad.

Transmittance spectra 150 to 200 mm and 200 to 2900 nm were measured by N100 VUV Spectrometer made by Chinese Academy of Sciences, and by Lambda 19 UV/VIS/NIR Spectrometer made by Perkin Elmer Co., respectively.

3. Results and discussion

The concentration of impurity and hydroxyl group in the samples in Table I is different. The absorption spectra for the pre-irradiated and irradiated samples are shown in Figs 1 and 2 respectively.

3.1. The radiation hardness

In comparison with Fig. 1, Fig. 2 shows that the silica glasses used can be classified into three categories in the radiation hardness. The first category is the colored silica glass caused by γ-ray irradiation, which is called N-type. That is the samples of q6, q1, and q7 (Figs 1a and 2). N-type of silica glass is characterized by the induced visible bands, such as the 2.3- or 2.8 eV- or other bands (Fig. 2).

The second category is called Y1-type of silica glass that uv-visible absorption is almost not influenced by γ-ray irradiation. The sample, s3, belongs to this category (Figs 2 and 1b).

The third category is between two categories mentioned above. It is called Y2-type, and it is characterized by the induced uv-bands, such as the 4.2 eV-induced band (Figs 2 and 3a), and the disappearance of bands, such as the 5.0 eV-band (Figs 1b and 3b). The absorption band change caused by irradiation is easily observed in the α_{irr}/α-plot (Fig. 3d). Where the α and α_{irr} are the absorption coefficient for the sample before and after irradiation, respectively. The region for the ratio $\alpha_{irr}/\alpha >$ or < 1 relates to the induced or disappeared band. The peaks for the ratio >1 indicate the 4.1-, 4.7-, 5.5-, 7.0 eV, and other induced bands (Fig. 3d). The valleys indicate the disappeared or decreased bands, such as the 5.0 eV-band.

The hydroxyl group (OH) concentration for Y1-type is higher than for other two types (Table I). It implies that the radiation hardness is related to the OH-concentration in silica glasses. This is in agreement with the results obtained by Boscaino *et al*. [1], i.e., the radiation hardness is higher in wet than in dry silica glasses. In addition, the radiation hardness also relates to the impurities and other defects in silica glasses [2]. Of course, it is better to investigate the inducing or vanishing of the color centers in discussion of the radiation hardness. However, it is complex and difficult. A simple statistic method will be used to discuss this problem.

The C_T in Table I is the total concentration of impurities excepting the hydroxyl group in the samples used. The C_{OH} is the OH-concentration. η in Table I is the ratio of the total impurity concentration to OH-concentration, $\eta = C_T/C_{OH}$. η has the physical

*Author to whom all correspondence should be addressed.

TABLE I Manufacturing methods and main impurities for silica glasses used. NQC: natural quartz crystal powders. SS: silica powders by the oxidation of $SiCl_4$. NSS: natural silica sands. C_T: total concentration of impurity excepting hydroxyl (ppm). C_{OH}: hydroxyl concentration (ppm) $\eta = C_T/C_{OH}$

No.	Raw materials	C_{OH} (ppm)	Main impurities (ppm)	$\eta = C_T/C_{OH}$	Manufacturing method
q1	NQC	5	Fe: 5, Al: 30, Ti: 1, Ca: 5, Mg: 5, Cu: 0.5, B: 0.3, Mn: 0.2, C_T: 47	9.4	Vacuum electrofusion in graphite vessel for about 4 h and then applied N_2-pressure
q2	NQC	200	Fe: 1, Al: 15, Ti: 1, Ca: 1.5, Mg: 1, Cu: 0.2, B: 0.2, Mn: 0.2, C_T: 20	0.1	$H_2 + O_2$ flame in air
s3	SS	1246	Fe: 0.1, Al: 0.38,Ti: 0.11, Sn: 1.0, Na: 0.4, K: 0.3. C_T: 4	0.0032	CVD soot in air
s4	SS	0.01	<0.01, C_T: 0.02	2	CVD soot in air, and then Cl_2-treated
si5	NSS	80	Fe: 3.35, Al: 15, Ti: 1.2, Mg: 8.82, Li: 2.65, Na: 8.72, K: 6.71, C_T: 45	0.56	Electrofusion in wolfram vessel in H_2-atmosphere
q6	NQC	1	Fe: 1, Al: 15, Ti: 1, Li: 0.5, Na: 1, K: 1, Ca: 2, Mg: 0.6, Cu: 0.2, B: 0.2, C_T: 23.5	23.5	Vacuum electrofusion in graphite vessel for near 300 h and then applied N_2-pressure
q7	NQC	17	Fe: 0.22, Al: 26, Ti: 2.73, Li: 0.72, Na: 0.84, K: 0.21, Mn: 0.2, C_T: 33	1.94	Air-plasma

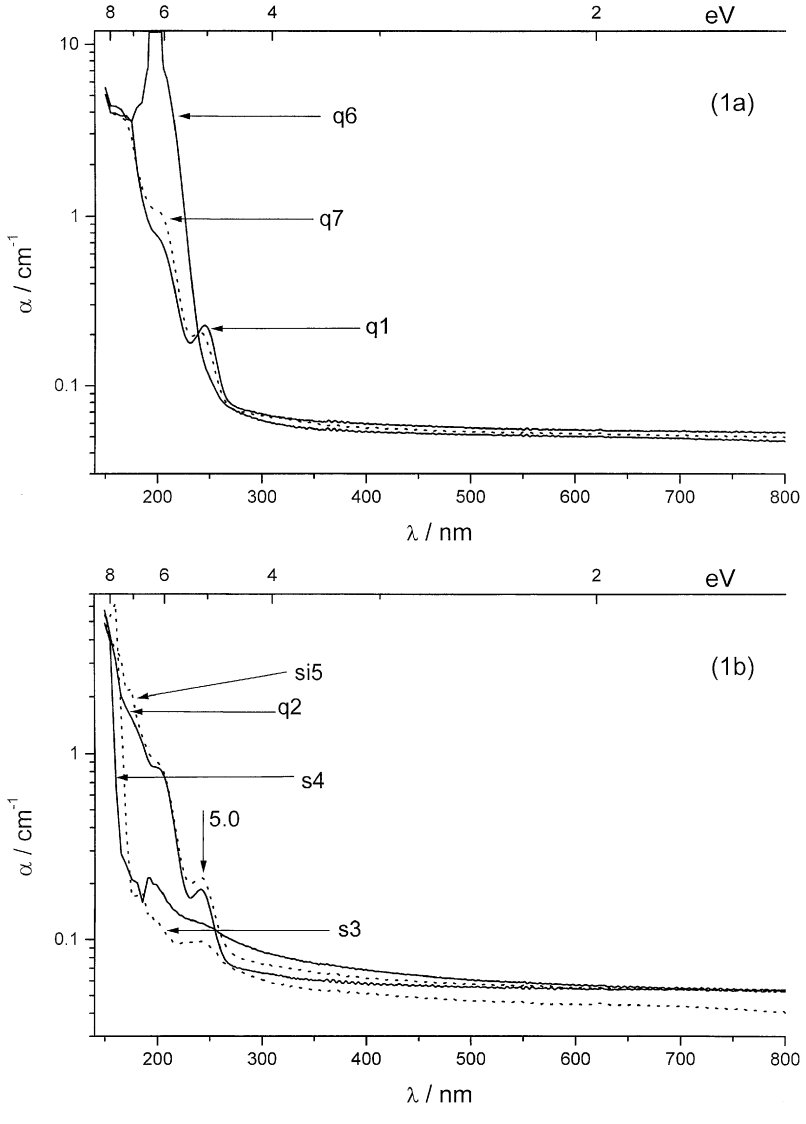

Figure 1 Absorption spectra for samples, q1, q6, and q7 (a), and q2, s3, s4, and si5 (b).

meaning of the relative concentration of impurity to hydroxyl group in the silica glasses. One can see easily in Table I that the η value for Y1- and N-type is less than 0.01 and greater than 2, respectively. The η value for Y2-type is between 0.01 and 2. It implies that the radiation hardness is determined not only by the impurity, or OH-concentration alone. It is determined by the relative relation between the concentrations of impurity

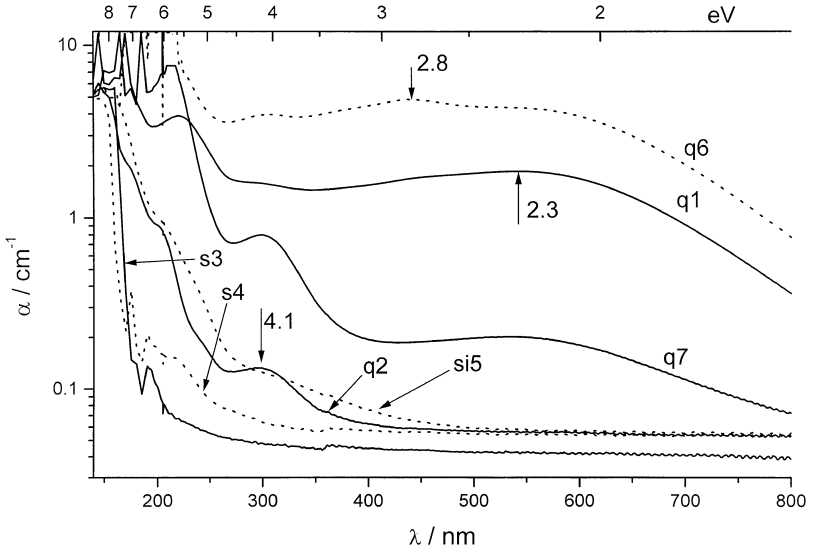

Figure 2 Absorption spectra for γ-ray irradiated samples.

and hydroxyl in silica glasses. This opinion is supported by the following argument. The impurity concentration for sample, s4, is lower than for sample, s3. However, the radiation hardness for sample, s4, is not better than for sample, s3. The reason is that the OH-concentration for sample, s4, is lower than for sample, s3. It leads to that the η value for sample, s4, being higher than for sample, s3.

3.2. Parameter, C_R

A parameter, C_R, is introduced for discussion of the radiation hardness. It is seen by all figures above that the area under the absorption curve is a response to the radiation hardness. The smaller the area, the better the radiation hardness for the silica glass. The area can be used to describe the radiation hardness for the silica glass. It is called the parameter, C_R, for characterizing the radiation hardness. The parameter, C_R, is dimensionless, and such magnitude as follows.

$$C_R = \int_{\lambda_1}^{\lambda_2} \alpha(\lambda)\mathrm{d}\lambda = \alpha(\lambda_2 - \lambda_1)$$
$$\approx 1\,\mathrm{cm}^{-1} \times 10^2\,\mathrm{nm} = 10^{-5}$$

Fig. 4a shows that a relationship between both parameters of C_R and η exists approximately. It is confirmed further that the radiation hardness depends on the ratio of impurity concentration to OH-concentration in the silica glasses.

The dependence of the radiation hardness on the OH-concentration was obtained by the E' generation efficiency by γ-ray [1]. This dependence also was obtained by the analysis of a several samples of silica glass. It implies that the dependence of the radiation hardness on the OH-concentration is the general property of silica glass. Why is the radiation hardness of silica glass dependent on the OH-concentration? It was not discussed in the reference [1]. A simple model is given here for understanding this dependence.

The parameter, C_R, in fact, is proportional to the concentration of all absorption centers, including pre-existing and induced, in the wavelength region between 140 and 800 nm [3]. $C_R = \sum C_{i,ind} + C_0$. Where the $C_{i,ind}$ and C_0 are the concentration of the ith induced center and all pre-existing center respectively.

As the concentration of the defects in the silica glass increases, the possibility of producing the induced absorption center in the silica glass also increases. It is assumed, hence, that the concentration of the induced center is proportional to the concentration of the defect, C_i, approximately, i.e., $C_{i,ind} = a_i C_i$. Where the a_i is the proportional coefficient.

$$C_R = \sum a_i C_i + C_0 \quad (1)$$

The induced center is created by the absorbing energy from the γ-ray field. The possibility of producing the induced center increases with the increase of the energy offered by the γ-ray field. It is assumed, hence, that the energy offered by the γ-ray field is proportional to the concentration of induced center, i.e., $E_i = b_i C_{i,ind} = b_i a_i C_i$. Where the b_i is the energy needed for creating the i-th center. The sum of the energy absorbed by all the induced centers should be equal to the energy absorbed, E_T, by the sample from the γ-ray field, i.e.,$\sum E_i = E_T$.

$$\sum b_i a_i C_i = E_T \quad (2)$$

The greater the dose of the γ-irradiation, the more the E_T. The E_T is assumed to be proportional to the dose of the γ-irradiation approximately. One can see from Equations 1 and 2 that the C_R-parameter is dependent on the defect concentration and the dose of the γ-irradiation.

For simplicity, it is assumed that the contribution of OH-induced centers to parameter, C_R, can be omitted. Therefore Equation 1 can be rewritten as follows.

$$C_R = \sum_{i \neq \mathrm{OH}} a_i C_i + C_0$$

For simplicity in the analysis below it is assumed that the proportional coefficient, a_i, is same one, a, for

all the induced absorption centers approximately. The equation above can be written as follows under this condition.

$$C_R = a \sum_{i \neq OH} C_i + C_0 \quad (3)$$

The proportional coefficient, a, can be obtained by Equation 2. Equation 3 can be rewritten as follows.

$$C_R = \frac{\sum_{i \neq OH} C_i}{\sum b_j C_j} E_T + C_0 \quad (4)$$

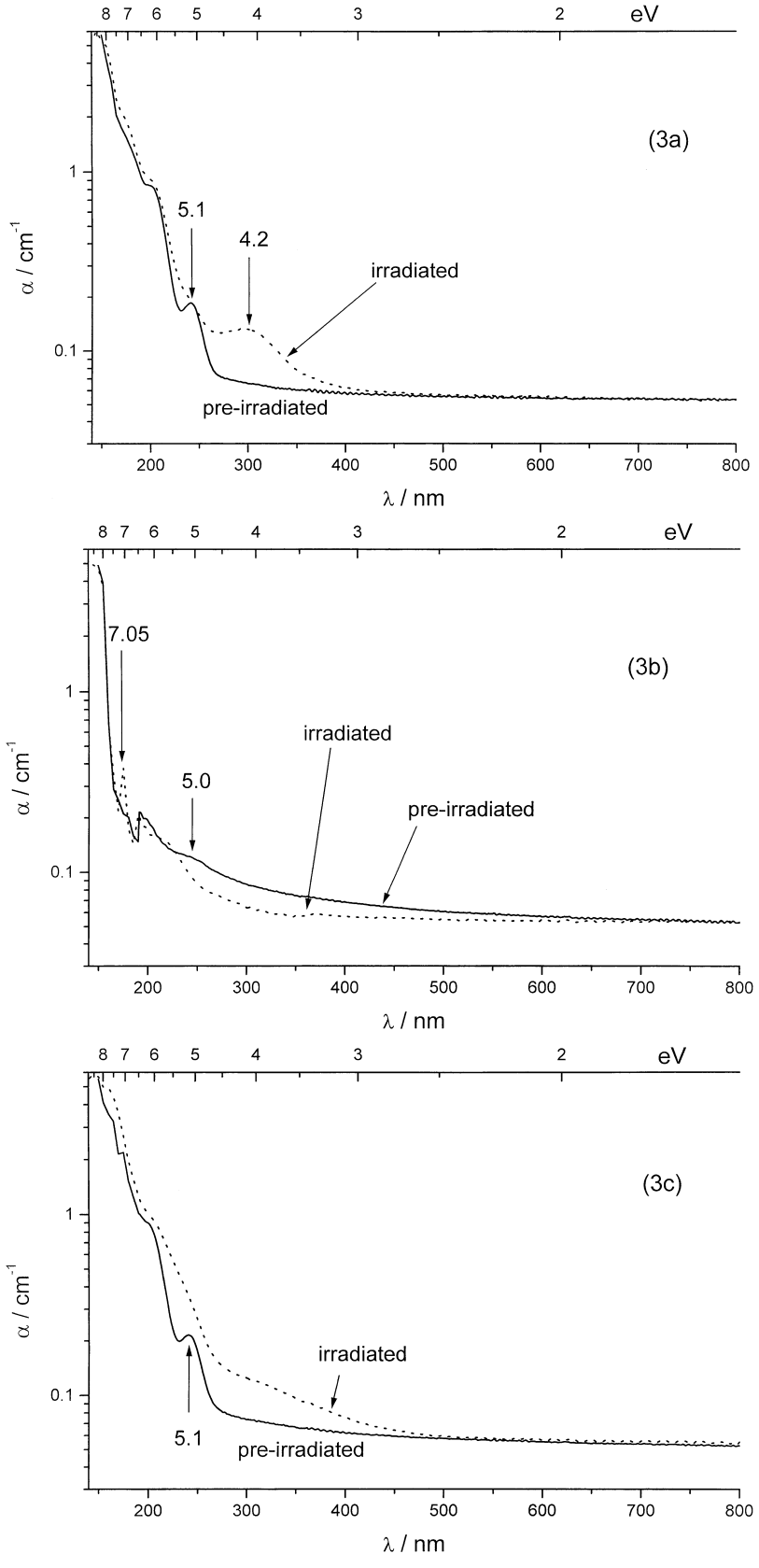

Figure 3 Absorption spectra for samples before or after irradiation, q2(a), s4(b), and q5(c). The spectra for ratio of absorption coefficient after to before irradiation (d). (*Continued*)

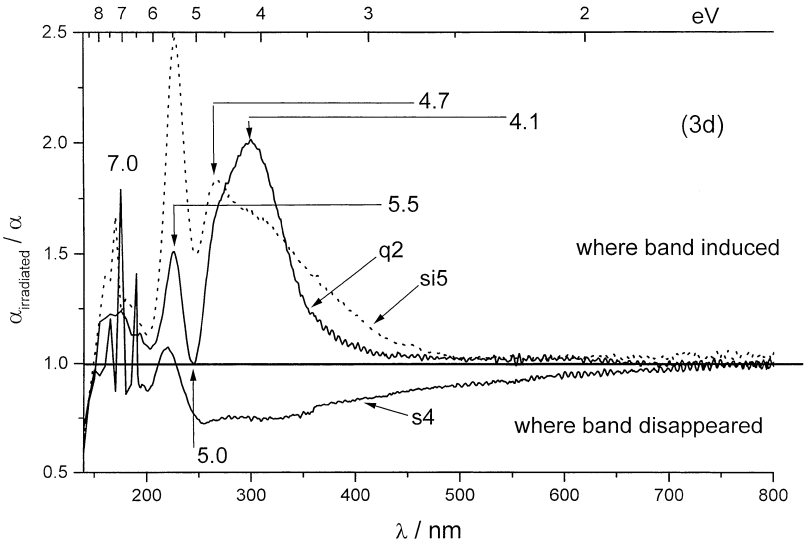

Figure 3 (*Continued*)

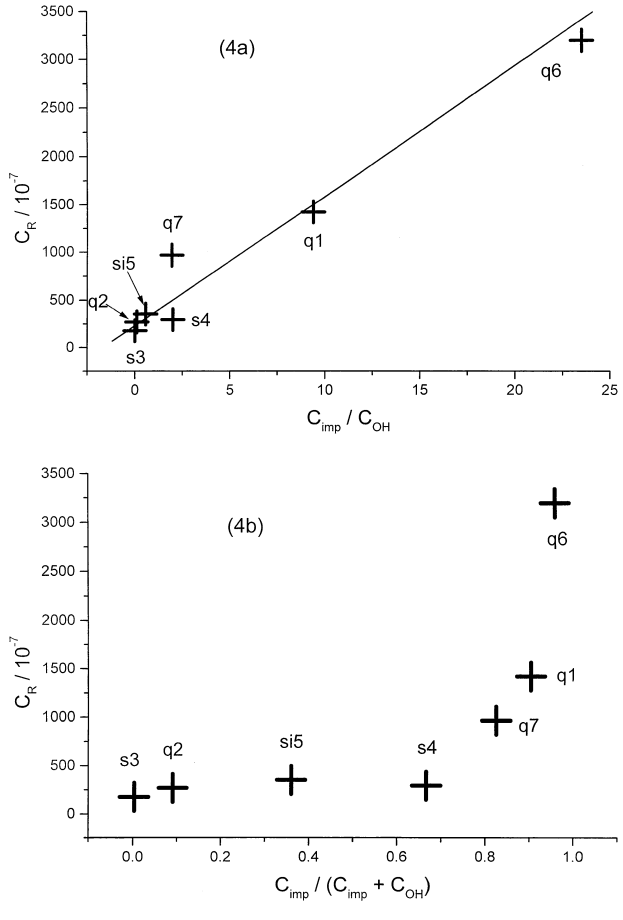

Figure 4 The parameter, C_R, as a function of the parameter, η, (a) or $C_T/(C_T + C_{OH})$ (b), respectively.

In case where the impurities and hydroxyl group are dominating defects in the samples, and other defects can be omitted, Equation 4 can be rewritten as follows.

$$C_R \approx \frac{C_{imp}}{b_{imp}C_{imp} + b_{OH}C_{OH}} E_T + C_0$$
$$\approx (1/b)\frac{C_T}{C_T + C_{OH}} E_T + C_0 \qquad (5)$$

where an assumption was used, i.e., $b_{imp} \approx b_{OH} = b$. The impurity concentration, C_{imp}, is the total concentration of impurity, C_T, mentioned above.

Equation 5 shows that the C_R-parameter is dependent on the OH-concentration. The experimental results above are explained.

Fig. 4b shows that the C_R-parameter increases with the ratio, $C_T/(C_T + C_{OH})$, increased but not a linear relation. If it is assumed that $b_{imp}C_{imp} \ll b_{OH}C_{OH}$ for $C_{OH} > 0$, Equation 5 can be rewritten as follows.

$$C_R \approx \frac{C_{imp}}{b_{imp}C_{imp} + b_{OH}C_{OH}} E_T + C_0$$
$$\approx \frac{C_T}{b_{OH}C_{OH}} E_T + C_0 \qquad (6)$$

Equation 6 is in agreement with experimental results above. The influence of hydroxyl group on the irradiation hardness is from its absorption to γ-irradiation energy. Its absorption decreases the absorption of other defects to γ-irradiation energy. Thus it also decreases the concentration of centers induced by other defects. In other word, it results in improving the irradiation hardness for the silica glass.

4. Conclusions

The irradiation hardness is mainly dependent not only on the concentration of impurities or hydroxyl group alone but on the relative relation between them.

References

1. R. BOSCAINO, M. CANNAS, F. M. GELARDI and M. LEONE, *Nucl. Instr. Meth. Phys. Res.* B **116** (1996) 373.
2. C. D. MARSHALL, J. A. SPETH and S. A. PAYNE, *J. Non-Cryst. Solids* **212** (1997) 59.
3. J. H. SCHULMAN and W. D. COMPTON, "Color Centers in Solids" (Pergamon Press, 1962) p. 56.

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