Nuclear Instruments and Methods in Physics Research B 330 (2014) 7–10

Contents lists available at ScienceDirect

Nuclear Instruments and Methods in Physics Research B

journal homepage: www.elsevier.com/locate/nimb

Radiation induced color centers in silica glasses of different OH content

Xinjie Fu [a,b], Lixin Song [a], Jiacheng Li [a,*]

[a] The Key Laboratory of Inorganic Coating Materials, Shanghai Institute of Ceramics, Chinese Academy of Sciences, 1295 Dingxi Road, Shanghai 200050, PR China
[b] University of Chinese Academy of Sciences, 19 Yuquan Road, Beijing 100049, PR China

ARTICLE INFO

Article history:
Received 5 December 2013
Received in revised form 13 February 2014
Accepted 13 March 2014

Keywords:
Silica glass
Gamma irradiation
Color center
Hydroxyl

ABSTRACT

Color centers induced by gamma radiation in high-purity silica glasses with various OH contents were investigated in this work. Several measurements, UV–Vis absorption spectra, electron paramagnetic resonance and Fourier Transform Infrared spectra were performed after the glasses being irradiated by 1000 kGy gamma rays. The results show that E′ centers (≡Si·), oxygen deficient centers (≡Si—Si≡) and B1 centers are induced in all samples, while non-bridging oxygen hole centers (≡Si—O·) and aluminum–oxygen hole centers (≡Al—O·) appear only in low-OH JGS3 and medium-OH JGS2. The concentration of each color centers in high-OH JGS1 is lower than that in JGS2 and JGS3. It is found that different type and concentration of induced color centers are closely depending on the amount of the OH in the glasses. Through the recombination with atomic hydrogen released by photolysis of hydroxyl, the color centers named E' center, non-bridging oxygen hole centers and aluminum–oxygen hole centers, could be transformed into visible colorless groups such as Si—H, H-bond Si—OH and Al—OH, which could be a good explanation for the suppressing effect of OH on the radiation coloration.

1. Introduction

For its good optical properties, silica glass has long been considered to be the ideal materials in the situations demanding high ultraviolet or infrared transparency, and especially in some harsh environmental conditions [1–4]. However, strong absorption would occur when the glass is exposed to ionizing radiation such as gamma ray, X-ray, electron, ultraviolet light etc. which would limit the application of silica glass in radiative environment (space environment and nuclear reactor) [5–8]. This optical degradation, based on the former research, is closely related to the color centers in the glass induced by radiation environment [3–5]. The main types of these color centers in silica glass are E' center, non-bridging oxygen hole center (NBOHC), oxygen deficient center (ODC), B1 center and aluminum–oxygen hole center (Al-OHC), which would induce absorption in special regions of 215 nm, 400–700 nm, 250 nm, 300 nm and 535 nm, respectively [3,9]. It also has been found that, in visible region, this color center-induced absorption would decrease drastically when the concentration of OH increased [10–12]. However, so far, the formation and bleaching mechanism of these color centers is not that clear [13]. For this reason, the investigation of color centers' behavior in silica glass will be of great importance to clarify the coloration mechanism and for the further guidance of manufacturing radiation-hard silica glass.

In this work, three type of glasses, JGS1, JGS2 and JGS3 were selected to carry out the research. JGS1 is UV grade silica glass with the highest OH content, JGS3 is IR grade silica glass with lowest OH content, and JGS2 is Optical grade, containing medium OH content compared to JGS1 and JGS3. We investigate the formation of color centers in JGS1, JGS2 and JGS3 after being irradiated by gamma-rays, and intend to explain the effect of OH on the coloration behavior after radiation.

2. Experimental details

JGS1, JGS2 and JGS3 silica glasses ($20 \times 20 \times 1$ mm) with two optically polished surfaces were irradiated by Co-60 γ-ray source with a dose rate of 3.8 kGy/h. And the total dose is 1000 kGy. The UV–Vis absorption spectra and infrared spectra of the samples were measured both before and after the irradiation, using UV–Vis spectrometer (Cary 500) and Fourier transform spectrometer (Equinox55), respectively. EPR measurements were performed at room temperature on an X band JEOL-FA200 spectrometer with a 100 kHz field modulation. The modulation amplitude of 2G was employed to record each spectrum. EPR data were normalized to the specimen weight of 1 mg. To avoid thermal bleaching of color centers, the samples were stored in liquid N_2 during the time between the measurements.

* Corresponding author. Tel.: +86 21 69906163; fax: +86 21 69906171.
E-mail address: jchli2012@mail.sic.ac.cn (J. Li).

http://dx.doi.org/10.1016/j.nimb.2014.03.011
0168-583X/© 2014 Elsevier B.V. All rights reserved.

3. Results

The UV–Vis absorption spectra of three types of silica samples after being irradiated 1000 kGy gamma rays is illustrated in Fig. 1. Characteristic induced optical absorption appears in all three specimens after exposure to gamma rays. However, only ultraviolet absorption appears in JGS1 while both UV and Vis absorption exist in JGS2 and JGS3. In the studied region from 200 nm to 800 nm, the curve of JGS3 is higher than that of JGS2 and JGS1. Specific color centers are difficult to identify directly from absorption curves for the overlapped bands.

In order to distinguish the overlapped bands of the absorption spectra, Gaussian fitting is adopt as Fig. 2 shows. We fixed bands and FWHM to represent specific color centers as Table 1 lists, according to reports in literature [1,3,5]. The fitting result reveals three bands in the studied range for JGS1, band centered at 215 nm, 250 nm, and 300 nm, corresponding to the defect type of E', ODC and B1, respectively. For JGS2 and JGS3, there are another three bands in the visible region, band centered at 400 nm, 535 nm and 670 nm, corresponding to HC1, Al-OHC and HC2, respectively.

Since most of these defects investigated in silica glasses are paramagnetic centers except for ODC and B1 center, EPR measurements were further used to estimate their presence. Fig. 3 shows the first-derivative EPR spectra of the samples after 1000 kGy gamma irradiation. There is a sharp signal around $g = 2.000$ in all of these three silica glasses, which is ascribed to E' center. The $g \sim 2.026$ resonance is identified as a superposition of Al-OHC ($g_1 = 2.0023$, $g_2 = 2.0182$, $g_3 = 2.0353$) and NBOHC ($g_1 = 2.0023$, $g_2 = 2.0088$, $g_3 = 2.0213$), according to computer lineshape simulation by Dutt [14]. These EPR results verifies the existence of E', Al-OHC, HC1 and HC2, which is correlated with the 215 nm, 535 nm, 400 nm and 670 nm Gaussian absorption band, respectively.

Fig. 4 shows the concentration difference between JGS1, JGS2 and JGS3 when these silica glasses are irradiated by the same gamma dose. The area under Gaussian absorption bands was defined as the relative concentration of color centers, according to Smakula formula [15]. It is found that all color centers in JGS3 have a larger quantity compared to the same species in JGS2, while that in JGS1 is the smallest.

4. Discussion

The Gaussian bands of absorption spectra and EPR data allow us to identify the nature of defect centers formed in the silica glass after gamma irradiation. The formation of E' center in all the three glasses can be attributed to the breaking of the regular Si—O—Si bonds due to irradiation [3]:

$$\equiv Si - O - Si\equiv + \gamma(\sim 1.25\ \text{MeV}) \rightarrow \equiv Si^{\cdot} + {}^{\cdot}O - Si\equiv \quad (1)$$

E' center ($\equiv Si^{\cdot}$) is generated together with NBOHC (${}^{\cdot}O—Si\equiv$), this is why E' center always coexist with NBOHC in irradiated glasses, just as JGS2 and JGS3. And NBOHC can be divided into two types, HC1 and HC2 [16]. The configuration of HC1 is express as ($\equiv Si—O^{-} + h^{\cdot}$), which is same to the structure in Eq. (1), while HC2 is ($h^{\cdot} + {}^{-}O—Si—O^{-} + h^{\cdot}$) [17].

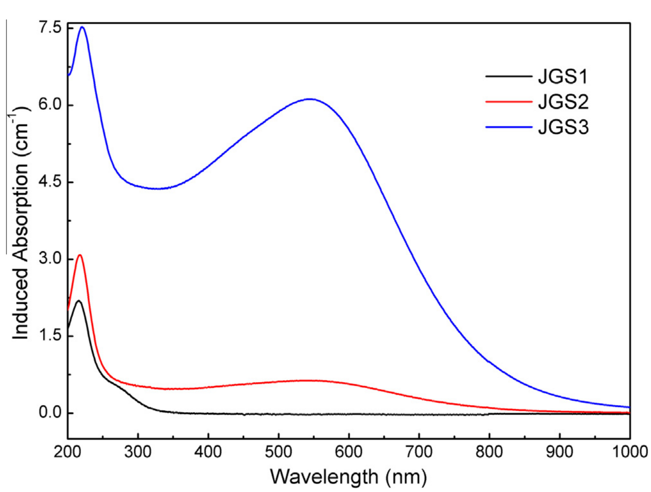

Fig. 1. Induced absorption of JGS1, JGS2 and JGS3 after 1000 kGy gamma irradiation.

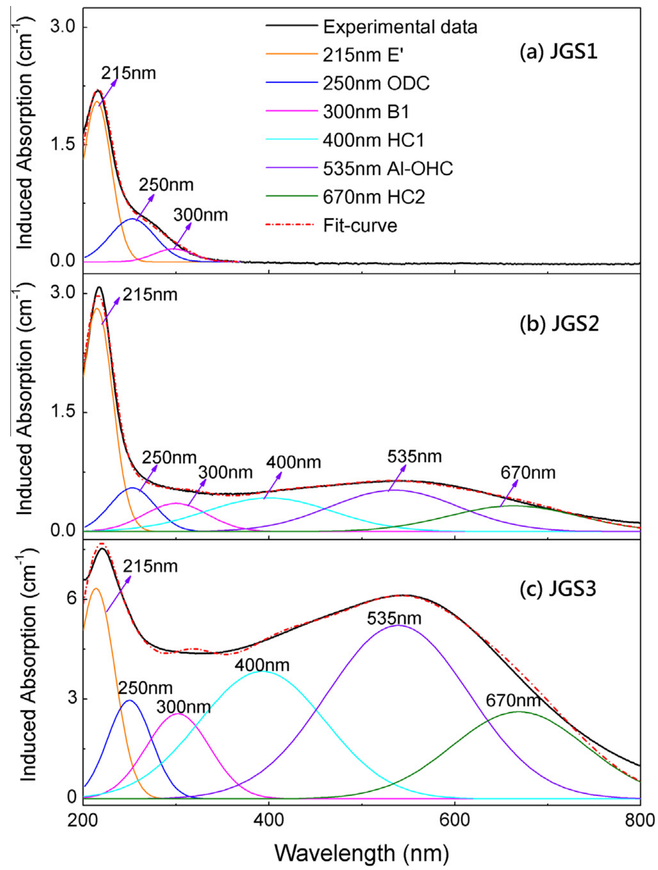

Fig. 2. Gauss resolution of induced absorption of JGS1, JGS2 and JGS3 after gamma irradiation.

Table 1
Parameters of Gaussian absorption bands of silica glasses.

Glass type	Center (nm)	FWHM (nm)	Max height (cm^{-1})	Defect type	R^2
JGS1	215	40	2.00625	E'	
	250	50	0.46942	ODC	0.9981
	300	60	0.2405	B1	
JGS2	215	40	2.83971	E'	
	250	50	0.46659	ODC	
	300	65	0.38437	B1	0.9973
	400	160	0.43827	HC1	
	535	160	0.53709	Al-OHC	
	670	160	0.32487	HC2	
JGS3	215	40	6.65832	E'	
	250	50	3.64225	ODC	
	300	65	2.81095	B1	
	400	160	4.02245	HC1	0.9954
	535	160	4.87645	Al-OHC	
	670	160	3.0041	HC2	