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Gamma irradiation induced defects in different types of fused silica

M. León *, P. Martín, A. Ibarra, E.R. Hodgson

Fusion Materials Research Unit, Euratom/CIEMAT Fusion Association, Avda, Complutense 22, 28040 Madrid, Spain

A B S T R A C T

In this work, KU1 and KS-4V silica glasses, considered as the main candidate materials for optical diagnostic and remote handling components in ITER, have been gamma irradiated at doses from 10 kGy up to 12 MGy together with five commercial types of silica. After each irradiation the optical absorption of the different grades has been obtained, and the concentration evolution of each defect has been compared for the different silica types. This comparison allowed us to determine which defects are intrinsic and which depend on the impurity level or fabrication method. The results allow one a better understanding of the relevance of the precursors present in the different silica grades.

1. Introduction

Fused silica is a key element for optical diagnostic and remote handling components to be used in fusion devices. All these components will suffer significant neutron and gamma irradiation. The radiation induced optical absorption and light emission radioluminescence, will affect their optical properties, and hence the component lifetime. In the case of ITER, KU1 and KS-4V silica, are being considered as the main candidate materials [1–4]. Hence a detailed knowledge of the effect of ionizing radiation and dose accumulation in these grades under irradiation is required. Previous studies for gamma irradiated silica have been reported [5–9] and different results have been obtained in some of them. These differences suggest that the material origin must be an important factor in the type and concentration of gamma induced defects. As none of the studies include a complete comparison of the defect evolution with dose in several types of silica for high gamma irradiation doses, the role of the material origin still needs to be clarified. The aim of this work is to understand the relevance of the manufacturing process and precursors (defects and impurities) present in the material before irradiation. For this purpose, KU1 and KS-4V have been gamma irradiated under identical conditions together with five commercial types of silica with different OH and impurity contents depending on their manufacturing process. The effect of gamma irradiation at doses from 10 kGy up to 12 MGy on the optical properties of these different silica has been studied. These results also help to complete the database on materials properties required to predict the behaviour of the transmission properties for different types of silica from the onset of operation of ITER.

* Corresponding author.
E-mail address: monica.leon@ciemat.es (M. León).

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2. Experimental procedure

The seven silica grades studied were classified in four standard types according to the *Hetherington* classification [10]: *type I* natural dry silica, obtained by fusion of natural quartz crystal in vacuum or inert gas atmosphere; *type II natural wet,* prepared by flame fusion of quartz crystal in a water–vapor atmosphere; *type III* synthetic wet, made by the vapor–phase hydrolysis of pure silicon compounds such as $SiCl_4$ and *type IV* synthetic dry, obtained by the reaction of O_2 with $SiCl_4$ in a water–vapor–free plasma. Table 1 shows the name, origin, OH content, typical trace impurities [1,11] and classification [10] of the seven types of silica studied.

In order to investigate the optical absorption evolution of these different silicas with gamma dose, several consecutive irradiations were made at doses from 10 kGy up to 12 MGy. All the samples were irradiated under identical conditions in flowing dry nitrogen gas at 27 °C, 4.8 Gy/s (CIEMAT NAYADE ^{60}Co gamma pool installation).

Optical absorption spectra from 0.4 to 6.5 eV using a Varian Cary 5E spectrometer, were obtained at room temperature immediately after each irradiation. The measured absorption was corrected for sample thickness and the spectra given in optical density (OD) per cm. The spectra were analysed in terms of a sum of simple Gaussian bands.

3. Results and discussion

3.1. Before irradiation

The optical absorption spectra of the samples before irradiation are shown in Fig. 1. No absorption is observed in any sample in the visible region (1.6–3.1 eV). However, in the ultraviolet region (3.1–6.2 eV) some silica grades show appreciable absorption

Table 1
Name, origin, OH content, typical trace impurities [1,11] and *Hetherington* classification [10] of the seven types of silica studied.

Sample name	OH (ppm)	Trace impurities (ppm)		Type
		Al	Ca, Cr, Cu, Fe, K, Li, Mg, Na, Ti	
Infrasil 301 (I301)[a]	8	20	<1	Natural dry (I)
HOQ310[a]	30	20	<1	
Herasil 102 (H102)[a]	150	10	<1	Natural wet (II)
Suprasil 312 (S312)[a]	200	<0.010	<0.015	Synthetic wet (III)
KU1[b]	820	1.4	<0.8	
Suprasil 300 (S300)[a]	<1	<0.010	<0.015	Synthetic dry (IV)
KS-4V 5-155 (KS-4V)[b]	<0.1	<0.08	<0.1	

[a] From Heraeus [11].
[b] From Russian Federation [1].

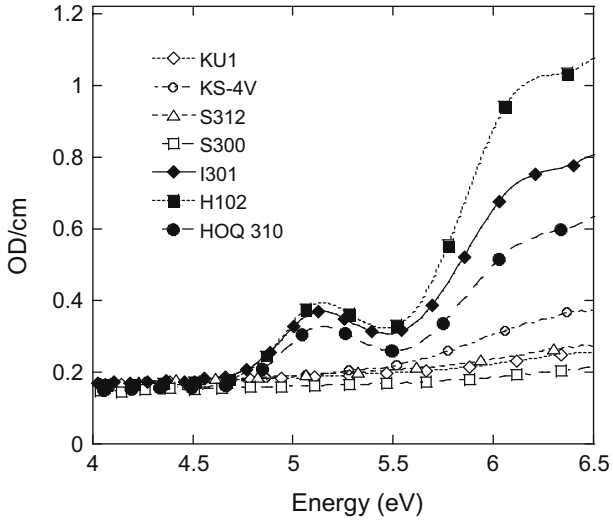

Fig. 1. Room temperature optical absorption of as received samples: natural origin samples (filled symbols) and synthetic origin samples (hollow symbols).

bands. Two bands at 5.1 eV (FWHM = 0.45 eV) and 6 eV (FWHM = 0.8 eV) can be observed in the spectra of natural origin samples although the height of each band varies depending on the sample. These bands are not detected in the spectra for the synthetic samples, which suggest that they may be related to impurities typically present in fused silica based on raw materials of natural origin. The 5.1 eV band has been related to GeODC, a two-fold coordinated Ge impurity [12–15].

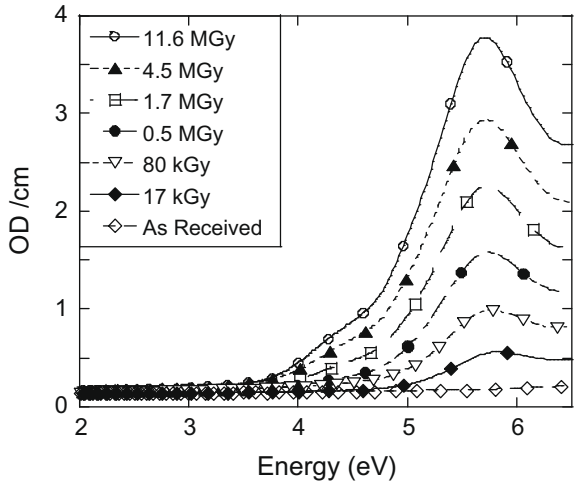

Fig. 2. Room temperature optical absorption spectra of the S300 grade irradiated at 27 °C up to different gamma doses.

3.2. After irradiation

The general effect of gamma irradiation is to increase the optical absorption with dose mainly in the UV region. The spectra of S300 silica glass at different irradiation doses is shown in Fig. 2 as an example. This figure shows how new optical absorption bands induced by gamma irradiation, increase monotically with dose. This behaviour is general although the presence of different bands marks a clear distinction between the spectra of natural and synthetic samples, as can be seen in the spectra of the samples irradiated to about 12 MGy (Fig. 3(a) and (b)).

The main optical absorption band, common to all silica grades, is centered around 5.8 eV (FWHM ≈ 0.9 eV) and has been assigned to the E′ center (≡Si·) [16]. The evolution of this band height with dose for the different silica types is shown in Fig. 4. The rate of increase is high for low doses (less than 100 kGy) because the concentration of precursors and hence the probability to trap the

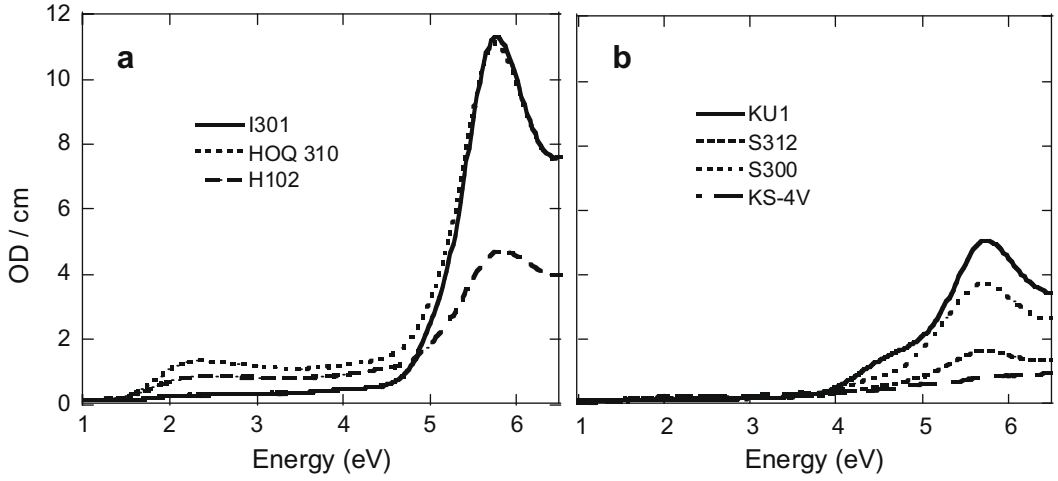

Fig. 3. Room temperature optical absorption spectra of the different silica grades irradiated at 27 °C up to a gamma dose of 11.6 MGy: (a) natural origin grades and (b) synthetic origin grades.

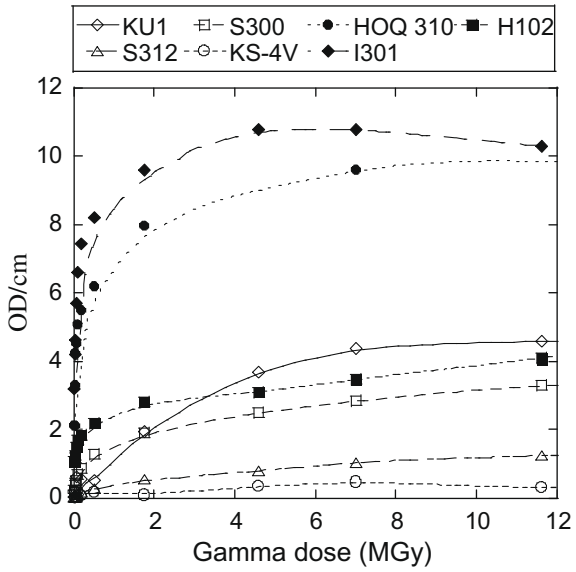

Fig. 4. Evolution with gamma dose of the 5.8 eV band height: natural origin samples (filled symbols) and synthetic origin samples (hollow symbols).

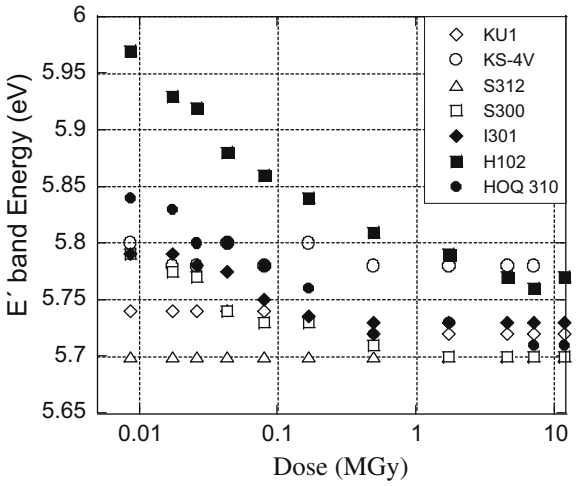

Fig. 5. Position of the 5.8 eV band maximum with dose in the different silica grades: natural origin samples (filled symbols) and synthetic origin samples (hollow symbols).

carriers produced during the gamma irradiation process is high. However, the general tendency is to reach saturation together with a very gentle positive slope.

Some notable differences between the evolution curves with dose must be pointed out:

- The saturation level reached by the 5.8 eV band is different for each silica type. In general, the optical density at this energy is higher in natural samples (with higher number of precursors to be converted into defects). No correlation between the OH content and this optical density is appreciated.
- The slope of the saturation curve is different for each silica type which suggests the existence of different precursors for this defect.
- The 5.8 eV band evolution shows a quite different behaviour in KU1 grade. The slop of this curve is gentler for low doses than the slope of other curves, but while the optical density for the other type of silica continues increasing, this curve reaches a maximum and completely stabilizes at a dose lower than the maximum studied.
- The 5.8 eV band is practically undistinguishable in KS-4V silica for the studied doses.

A shift to lower energies with increasing dose has been detected, as is shown in Fig. 5 in natural wet, natural dry, and synthetic dry silica. The magnitude of this shift varies depending on the grade, and is higher for natural grades. A similar shift has been recently reported by Agnello et al. [7]. They suggest the existence of two well differentiated precursors of the E′ center. However, we have observed a continuous shift of the bands without an appreciable variation of shape which suggests a gradual change of the E′ environment with the irradiation dose. This change could be induced by charge redistributions due to the trapping processes occurred during gamma irradiation. Several types of E′ centers have been reported and the exact next nearest neighbour environment of many of them is still under discussion [16].

A broad structure of lower intensity bands between 1.5 and 4.5 eV is present in the spectra of all the natural samples studied (Fig. 3a), although only the bands centered at 2.2 eV (FWHM = 0.9 eV), and at 4.1 eV (FWHM = 0.8 eV) can be distinguished. The band at 4.1 eV is clearly observed for doses less than 100 kGy but, for higher doses is hidden by other bands. Its origin is still unclear [14–17]. The band at 2.2 eV has been previously attributed to aluminium impurities [14,18]. The presence of these bands only in natural samples is probably a consequence of their higher concentration of impurities.

Another band at 4.7 eV (FWHM = 1 eV), assigned to the non-bridging oxygen hole centers (NBOHC) (≡Si–O·) [16], is observed only in synthetic samples spectra (Fig. 3(b)) probably due to a more favourable generation of NBOHC precursors, as peroxy linkage (≡Si–O–O–Si≡), in synthetic wet samples and the absence of higher superimposed bands.

The shape of the optical absorption evolution curve with gamma dose for the 4.7, 2.2 and 4.1 eV bands is similar to that observed for the 5.8 eV band, with no clear correlation between the OH content and optical absorption. However, no shift of the maximum has been detected for these bands.

4. Conclusions

The results obtained confirm that precursors (impurities and defects), produced during the manufacturing process of the silica samples, determine the type and concentration of defects after gamma irradiation, at least up to 12 MGy doses; hence radiation induced optical absorption depends on the material grade. This means that, during the initial period of operation in ITER, the optical degradation of the silica will be determined by the grade.

E′ centers are present in all the silica types after irradiation, although its concentration is different for each one. The type and concentration of the E′ center precursors also depend on the silica grade. The shift observed in the maximum of the band can be explained by a continuous change in the E′ environment with irradiation.

The bands related to extrinsic defects (impurities) are present only in natural samples, which are known to contain much higher concentrations of metallic impurities while the NBOHCs (4.7 eV band) has mainly been detected in synthetic wet samples, where the manufacturing process is known to favour the presence of oxygen excess in the form of peroxy linkage.

No correlation was found between the optical absorption and the OH content.

Among the different silica grades those with fewer impurities (synthetic samples) clearly show lower optical absorption. KS-4V shows the lowest optical absorption at room temperature at the studied gamma doses.

Acknowledgments

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