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Thermal stability of neutron irradiation effects on KU1 fused silica

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Abstract

Optical absorption spectra of neutron irradiated (10^{21} n/m^2 and 10^{22} n/m^2) KU1 quartz glass samples have been measured. The effects of post-irradiation isochronal thermal annealing, up to 850 °C, have been investigated. The general effect of the isochronal annealing is a decrease in the optical absorption bands as the temperature increases. Optical absorption bands have been identified with known defects from the literature, and their concentration temperature dependence has been analyzed. While the annealing curves of the E' and non-bridging oxygen hole centres (NBOHC) are similar, that corresponding to oxygen deficiency centres (ODC(II)) is quite different suggesting that the recombination of E' and NBOHC is part of the same process whereas the recombination of ODC is controlled by the presence of another undetected defect.

1. Introduction

KU1 quartz glass, developed by the Russian Federation, is a candidate material for ITER optical components in the UV and visible range [1,2] for both remote handling and diagnostics applications. For remote handling, the optical components are required to maintain their transmission properties under high levels of ionizing radiation (1–10 Gy/s) during many hundreds of hours. Here radiation induced optical absorption imposes the main limitation. In the case of diagnostics, in addition to a higher level of ionizing radiation (tens to hundreds Gy/s), the material will be subjected to atomic displacements of the order of 10^{-10} dpa/s. In this case both radiation induced absorption and light emission (radioluminescence) impose severe limitations on the use of silica. In addition the components are expected to operate at temperatures between about 100 and 200 °C.

Recent gamma and neutron irradiation tests on KU1 [3–7] show that this silica is a suitable window material in the visible range. KU1 was also studied for gamma and electron irradiation [8,9], indicating that the dose dependence of the optical absorption bands is strongly dependent on irradiation temperature in the range from 15 to 250 °C.

It is well known that in silica, radiation gives rise to optical absorption bands in the ultraviolet, associated with the radiation induced intrinsic point defects. Their study is important to understand the behaviour of the material under radiation. The main defects in fused silica are [10]: the family of paramagnetic 'E'-type' centres (threefold coordinated silicon $\equiv$Si$^\bullet$), the non-bridging oxygen hole centre (NBOHC, a dangling oxygen bond $\equiv$Si–O$^\bullet$), the peroxy radical (POR $\equiv$Si–O–O$^\bullet$), and the oxygen deficiency centres ODC(I) (oxygen vacancy $\equiv$Si–Si$\equiv$) and ODC(II) (twofold coordinated silicon $=$Si$^{\bullet\bullet}$). Although defects in silica have been studied extensively for many years [10–12], some aspects of their structure, formation, and conversion mechanisms are still not thoroughly understood. A more complete knowledge of how radiation affects these induced defects can help to understand their

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possible role as precursors for other point and extended defects [13], as well as to explain other aspects in the behaviour of the material when exposed to radiation. Earlier thermal annealing experiments (optical absorption measurements) in gamma, neutron, and ultraviolet irradiated silica have been performed by Marshall et al. [14], and electron spin resonance (ESR) measurements in vitreous silica irradiated to low neutron doses were carried out by Moritani et al. [15]. Recently Agnello et al. [16] have studied the thermal stability of the point defects induced by gamma irradiation in four different types of silica. However no studies of KU1 irradiated to high neutron doses have been published.

In this work, optical absorption measurements of neutron irradiated KU1 as a function of post-irradiation isochronal annealing in air have been carried out, to study the thermal stability of the different defects induced by high dose irradiation.

2. Experimental

KU1 is a pure silica glass (type III: wet synthetic) with high OH content (800 ppm), and metallic impurities (Al, Fe, Ti, Ca, Cr, Li, Na, K) content less than 1.5 ppm [3]. Samples of this material were irradiated at 50 °C with a neutron flux of 4×10^{15} n/m^2 s ($E > 0.1$ MeV) at the GKSS reactor, Geesthacht, Germany. Total doses were 10^{21} n/m^2 (γ dose ≈ 2 MGy), and 10^{22} n/m^2 (γ dose ≈ 20 MGy).

Optical absorption spectra for as-received and neutron irradiated samples were measured at room temperature from 0.4 eV (3000 nm) to 6.5 eV (190 nm) using a Varian Cary 5E spectrometer. It must be noted that the absorption measurements were carried out ten years after the irradiation, hence only highly stable defects remain. The absorption spectra have been analysed in terms of a sum of simple Gaussian bands. After initial optical characterisation, the irradiated samples were heated in air in 50 °C steps up to 850 °C. Heating was at 10 °C/min and at each step (50, 100 °C etc.) the temperature was held constant for 15 min, then the samples were allowed to cool down to room temperature and the optical absorption spectra were measured.

3. Results and discussion

3.1. Irradiation effects

Fig. 1 shows the optical absorption spectrum for unirradiated KU1, and spectra for irradiation to two different neutron doses. A large increase of the UV optical absorption with neutron dose in the range 3.5–6.5 eV is observed, and a much smaller increase in the visible and IR regions. Three radiation induced absorption bands, increasing with dose, are clearly observed at about 2, 4.7, and 5.7 eV.

The optical absorption spectra have been analysed as a sum of simple Gaussian bands. Fig. 2 shows the decomposition of the spectrum for the highest neutron dose (10^{22} n/m^2).

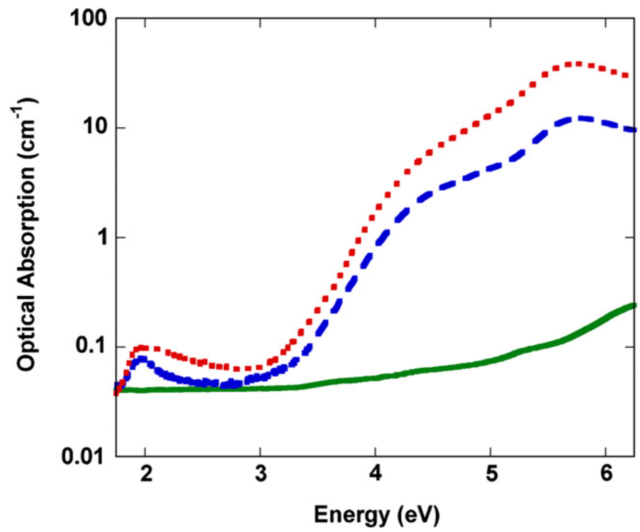

Fig. 1. Optical absorption bands of KU1, as received (continous line) and exposed to different radiation doses: 10^{21} n/m^2 (dotted line) and 10^{22} n/m^2 (points line).

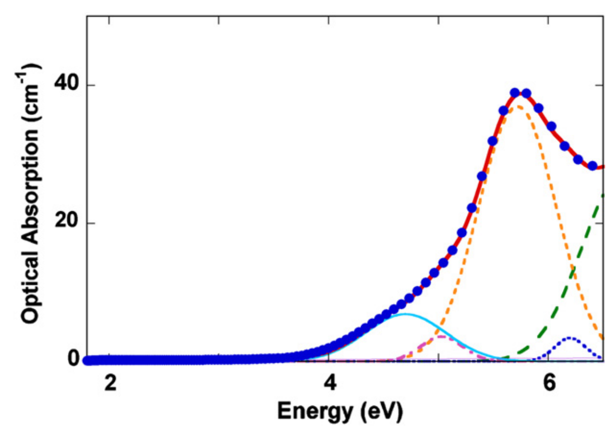

Fig. 2. Decomposition into Gaussian bands of the optical absorption spectrum of KU1 neutron irradiated up to 10^{22} n/m^2. Measured spectrum (●), fitted curve (continuous line). Band position and width of the main components: 4.7 eV (FWHH = 0.87 eV), 5.03 eV (FWHH = 0.45 eV), 6.2 eV (FWHH = 0.33 eV), 5.72 eV (FWHH = 0.78 eV) and out of detection range of the spectrophotometer 6.7 eV (FWHH = 0.92 eV).

Three main bands are identified, the most intense one is centred at 5.72 eV (FWHH = 0.78 eV), probably due to E' centres [10]. The wide band near 4.7 eV observed in Fig. 1 is the composition of two Gaussians: one at 4.7 eV (FWHH = 0.87 eV), due to NBOHC defects, and another of lower intensity at 5.03 eV (FWHH = 0.45 eV), due to ODC(II) defects [10]. The asymmetric band at 2 eV (Fig. 1) has also been associated to NBOHC defects [10], however it is not Gaussian and has not been fitted. Two additional Gaussian bands, a weak one at 6.2 eV, and a stronger band at 6.7 eV beyond the spectrometer UV range, are necessary in order to reproduce the complete optical absorption spectra. At about 6.8 eV in laser irradiated glasses a strong absorption band assigned to NBOHC defects has been reported [17].

The observed dose dependence is not the same for each band. The 5.72 eV band increases 3.5 times for a tenfold increase in dose (10^{21} n/m^2 to 10^{22} n/m^2), while for the 4.7 eV band the increase is 2.5 and for the 2 eV band the increase is less than 2. The different increasing intensity ratios must be related to different production rates for the E' and NBOHC defects with dose. A similar behaviour was reported for silica samples irradiated to lower doses [15].

3.2. Isochronal thermal annealing effects

Fig. 3 shows optical absorption spectra as a function of the post-irradiation annealing temperature for KU1 irradiated to 10^{22} n/m^2. The general effect is a decrease of the optical absorption bands with temperature, more marked in the range from 400 to 600 °C. Similar results were obtained for the low dose irradiation. However the rate of decrease is different for the different bands. The 5.72 eV band remains prominent up to 500 °C, but is strongly reduced at higher temperature. The band at 5.03 eV however is very stable, and can still be detected even after annealing at 600 °C.

This different temperature dependence for each band suggests that the ODC(II) and E' centres are not related. From 500 °C to approximately 600 °C, the band near 5.72 eV decreases at a higher rate than the band at 5.03 eV. This last band, that could not be properly seen in the spectra before this annealing temperature, begins to appear as a prominent shoulder (see 550 °C spectrum Fig. 3). For temperatures higher than 650 °C the bands intensity evolution is again comparable. It should be noticed that for annealing temperatures between 550 °C and 700 °C a new band at 5.3 eV (FWHM = 1.47 eV) is observed in the Gaussian decomposition. This band has a maximum intensity at 550 °C and disappears after annealing at 700 °C or higher and may be associated to POR centres [10]. A shift of 5.72 eV band, to higher energies, has been detected on increasing temperature. This shift is not observed for the other bands.

To calculate the concentration of defects associated with the different bands at each temperature we have used the Smakula equation with the appropriated parameters for fused silica. The heights and widths of these bands, needed for this equation, were obtained from the decomposition into Gaussian components of each spectrum. The different oscillator strengths have been taken from the literature [11]: $f = 0.3$ for E' centres, $f = 0.05$ for NBOHCs, and $f = 0.135$ for ODC(II). Fig. 4 illustrates the normalized defect concentration evolution with annealing temperature for both radiation doses.

The concentration decrease rates of the E' (5.72 eV band) and NBOHC (4.7 eV band) centres are identical between them and for the two radiation doses, while the defect concentration evolution of ODC(II) (5.03 eV band) is different. The concentration of ODC(II) is constant or even increasing up to 300 °C and only for higher temperatures a decrease of its concentration is observed. The ODC(II) concentration decreases slower than the concentration of the other defects. The similar behaviour of the E' and NBOHC defects suggests that the recombination mechanism involves both defect types in a unique reaction. It is well known that radiation induces pairs of NBOHC and E' centres by excitation of heavily strained Si–O–Si bonds [18]. It is reasonable to think that the inverse process is also favourable. The recombination of one NBOHC and one E' centre during the annealing treatments could lead to the simultaneous disappearance of both defects explaining the parallel evolution of the concentration of these two kinds of defects. Hosono et al. [17] also obtained a parallel concentration decrease rates for these two defects in glassy SiO_2 irradiated by F2 laser pulses, after thermal annealing

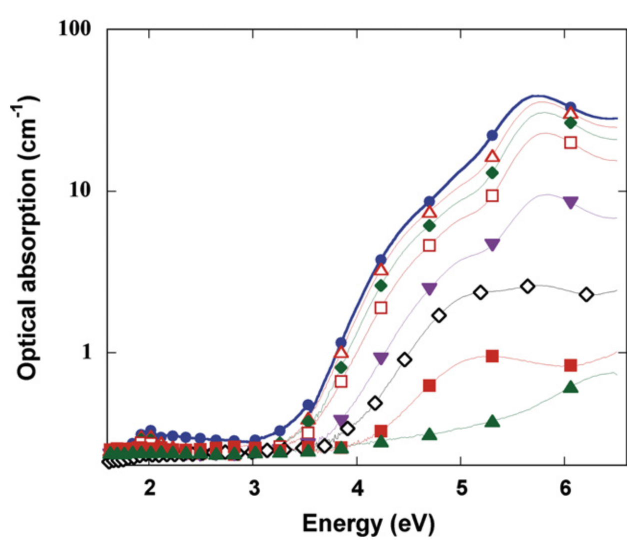

Fig. 3. Optical absorption bands of KU1 irradiated up to 10^{22} n/m^2 after different isochronal thermal treatments: (●) before thermal treatment (as irradiated) and at the maximum temperature of each isochronal cycle: (△)200 °C, (◆) 325 °C, (□) 400 °C, (▼) 500 °C, (◇) 550 °C, (■) 600 °C and (▲) 700 °C.

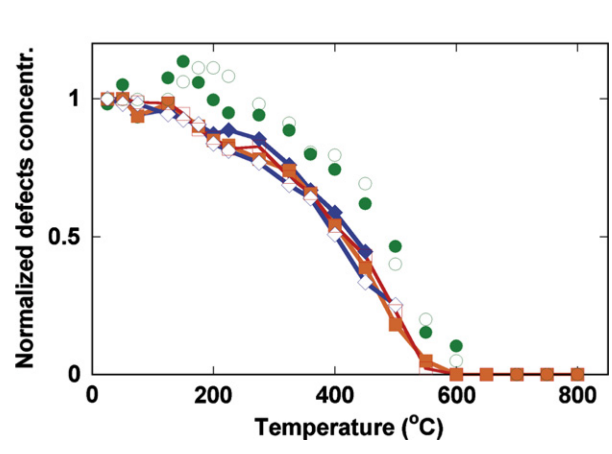

Fig. 4. Normalized defect concentration evolution with annealing temperature for the E' centres (5.72 eV) (■), NBOHCs (4.7 eV) (◆) and ODCs (5.03 eV) (●) produced in KU1 by neutron irradiation up to 10^{22} n/m^2 and 10^{21} n/m^2 (hollow symbols).

at lower temperatures than 300 K (the measurements were carried out at 77 K and the annealing temperature range was 100–300 K).

Similar studies in vitreous silica (OH content 200 ppm) irradiated with neutrons at lower dose (10^{20} n/m^2) have been carried out by electron paramagnetic resonance (EPR) giving quite different behaviour with temperature [15]. E' centres and NBOHC measured by EPR disappear at the same temperature but its concentration decrease rates are different. The E' centre concentration measured by EPR decrease faster and the decrease begins at lower annealing temperatures (lower than 100 °C) than the observed ones in this work. However, the temperature at which this defect fully disappears is higher for EPR measurements (about 800 °C). Other studies also showed different thermal stability for these defects. So, for example, the effects of isochronal thermal treatments of E' and ODC(II) centres in γ irradiated commercial samples with the same OH content [16] shows lower thermal stability, defects are completely removed by about 400 °C.

These differences need a more detailed analysis but may be related to the different material characteristics (impurity content or intrinsic defects). Well known defects in fused silica are those related to impurities like H (both as OH or molecular H_2), as well as O both as isolated ion or in molecular form. From the results shown by Moritani et al. [15] it seems that the defects in the samples with higher OH concentration are more stable. The results obtained in this work, for a material with even higher OH concentration, follows a similar tendency, suggesting that the OH concentration can play a role in the thermal stability of these defects. Anyhow O or other impurities can not be excluded. It is interesting to note that the decrease of the ODC(II) concentration starts near 200 °C. Above this temperature O_2, O, O^- and O_2^- become mobile and the reaction of these ions with the defects can lead to their annihilation. The different thermal stability of the ODC(II) defect seems to indicate that its recombination is controlled by a different reaction, involving the presence of another undetected defect.

4. Conclusions

In this work the effects of neutron irradiation on a fused silica grade with high OH content are analysed, including the thermal stability of the observed defects. Optical absorption bands associated with E' centers, ODC(II) and NOBCH defects are identified, as well as additional bands not clearly related to other defects. The results of the thermal annealing experiments suggest that these defects disappear in a wide thermal range between 100 and 600 °C. The thermal evolution of the E' centres and NOBCH is similar, indicating that their annealing behaviour is linked, whereas the thermal stability of the ODC(II) defects is higher. The thermal stability observed in this work shows some differences from those measured in other works. It is proposed that these differences are related to the impurity contents (mainly OH) in the material and the different radiation source.

Acknowledgments

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