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Vacuum ultraviolet excitation spectra of the 1.9 eV luminescence in neutron irradiated KU1 and KS-4V quartz glasses and Infrasil 301

M León, P Martín, R Vila, J Molla and A Ibarra

Fusion Materials Research Unit, Euratom/CIEMAT Fusion Association,
National Laboratory for Magnetic Fusion
CIEMAT. Avda. Complutense 22. (28040) Madrid . Spain

E-mail: piedad.martin@ciemat.es

Abstract. The photoluminescence emission around 1.9 eV, excited from the ultraviolet to vacuum ultraviolet was investigated in neutron irradiated silica (at 10^{21} and 10^{22} n/m^2 fluences) with different OH and impurity content: KU1 and KS-4V high purity silica and Infrasil 301. The measurements were made at different temperatures from 300K to 10K. The three irradiated silica grades show similar excitation spectra shape, although the band intensities are different depending on silica grade and temperature. Neutron irradiated KU1, with the highest OH content, shows the highest red emission attributed to nonbridging oxygen hole centers (NBOHCs). The excitation profile, from 4.0 to 8.8 eV, has two bands, which are centered around 4.85 eV and 6.5 eV. The band intensities increase with decreasing temperature from 300 to 10K for the three types of silica.

1. Introduction

It is known that fused silica is an important material due to its use in many different technology fields like optics, electronic, nuclear or space, because of their excellent optical, insulating and mechanical properties. Optical absorption and photoluminescence spectroscopy are techniques commonly used to characterize the radiation induced defects present in silica [1 ,2, 3]. The defects are introduced during the manufacturing process or induced by exposure to ionization radiation and/or particles (ions, electrons or neutrons). Irradiation effect on optical properties is an important issue, since optical absorption and light emission impose severe limitations on the use of optical material within a radiation field. KU1 and KS-4V high purity quartz glasses, are considered as reference materials for optical components (windows, lenses and optical fibers) in fusion devices as ITER [4, 5, 6] since these silica grades are highly radiation resistant with respect to their optical properties [7, 8, 9].

Defects produced in glassy SiO_2 by neutrons, beta, gamma or ultraviolet radiation lead to a luminescence band around 1.9 eV. The origin of this intrinsic luminescence band was investigated earlier by Skuja et al. [10,11,12]. More recently measurements of the ultraviolet and vacuum ultraviolet excitation spectra of this red emission band in γ irradiated silica have been carried out by Cannas and Gelardi [13]; in this work, a band at 6.4 eV excitation energy was correlated with the known 4.8 eV excitation component. Emission properties at 1.9eV, associated with the generation of nonbridging oxygen hole centers (NBOHCs), were reported by Cannas et al. [14] in wet synthetic silica samples exposed to different kinds of radiation (γ, β, neutron). On the other hand optical

absorption at 2.0 and 4.8eV and luminescence at 1.9 eV in γ and β irradiated synthetic wet silica [15] seem to be consistent with a three level energetic scheme [10, 16]. Time-resolved luminescence at 1.9eV was measured using excimer laser excitation by Hosono et al. [17] to assign the 6.8eV absorption band to NBOHC and a work on luminescence properties of NBOHCs at the silica surface was recently made by L.Vaccaro et al. [18] obtaining that the different local structure influences the emission line shape, the quantum yield and the decay lifetime.

In previous works there is a general agreement that this well known red luminescence band is attributed to the oxygen dangling bond or nonbridging oxygen hole center (NBOHC) one of the most common defects in silica. The structure of this defect is denoted by ≡Si-O•, where ≡ indicates bonds with three oxygen atoms and • indicates an unpaired electron. In the present work, the photoluminescence (PL) emission around 1.9 eV, excited from ultraviolet (UV) to vacuum ultraviolet (VUV), was investigated in neutron irradiated silica with different OH content, at different temperatures. Data on photoluminescence emission, around 4.4 and 2.7 eV, for the same neutron irradiated silica specimens induced by vacuum ultraviolet excitation were reported elsewhere [19, 20].

2. Experimental

Three silica grades with different OH content were measured: KU1 (820 ppm OH) and KS-4V (<0.1 ppm OH), high purity silica from the Russian Federation, and a commercial silica Infrasil 301 (< 8ppm OH, named I301) from Heraeus, with higher nominal impurity content (20 ppm Al and 5.9 ppm other metallic traces). Neutron irradiation of samples took place in the GKSS reactor (Geesthacht, Germany) at 50ºC with a neutron flux of 4 x 10^{15} n/m^{2}s (E > 0.1 MeV). Total fluences were 10^{21} n/m^2 (γ dose around 2 MGy) and 10^{22} n/m^2 (γ dose around 20 MGy).

Photoluminescence (PL) was investigated at the SUPERLUMI station on the I-beamline of HASYLAB at DESY (Hamburg) where the synchrotron radiation (SR) source produced the pulsed excitation light, ranging from 4.0 to 8.8 eV in our measurements. The exciting light from the primary monochromator was focused onto the sample. The emitted light was analysed by a 0.3m ARC Spectra Pro 308 monochromator (300 grooves/mm grating) equipped with a Hamamatsu R6358P photomultiplier (excitation spectra) or with a liquid nitrogen cooled CCD camera (emission spectra). The excitation spectra were corrected by using a sodium salicylate sample as a reference, to take into account the spectral efficiency of the whole optical system. The emission spectra were corrected by using an efficiency calibration curve. The intensity of the SR was also taken into account to normalize the measured intensity of the light. The temperature was varied from 10K to 300K using a sample chamber with a continuous helium-flow.

3. Results

3.1. Emission spectra

PL emission measurements in the range of 1.5 to 3.5 eV at different excitation photon energies from the UV to the VUV were performed in unirradiated and irradiated samples. As it is well known a characteristic red PL band around 1.9 eV (650nm) was observed in all the irradiated samples at excitation energies lower than 8.0 eV. The most intense emission was measured exciting at 4.8eV. By exciting at this energy at 300K, a blue emission about 2.7 eV related to oxygen deficiency centers (ODCs) was also observed. The UV and VUV excitation spectrum of this blue emission was previously studied in an earlier work [20]. At low temperature (10K) no blue emission was observed. An example of the emission spectra of KS-4V irradiated up to 10^{21} n/m^2 fluence measured at different temperatures is shown in figure 1. A shift to higher energies of the red emission is observed with increasing temperature (see detail in figure 1).

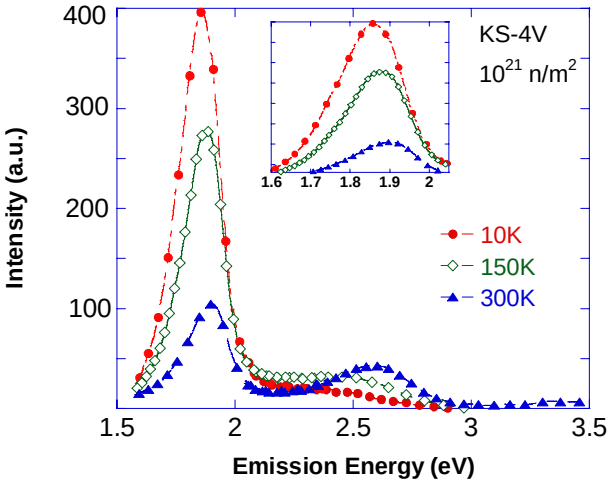

Figure 1. Emission spectra of neutron irradiated (10^{21} n/m^2 fluence) KS-4V high purity quartz glass, measured at 4.85eV excitation energy and temperature: 10K(●), 150K (**O**) and 300K (**▲**). Inside: Detail around 1.9eV

At 300K and 1.9 eV emission energy, the three unirradiated silica grades (KU1, KS-4V and I301) show undetectable PL in the UV and VUV excitation range. At 10K only KU1 high purity wet silica shows very low 1.9 eV emission.

3.2. Excitation spectra

NBOHCs are produced by γ and neutron irradiation due to the important amount of strained bonds generated by these radiations and mainly by neutrons

≡Si-O-Si≡ → ≡Si-O$^\bullet$ + ≡Si$^\bullet$

The excitation spectra of red luminescence for neutron irradiated (at 10^{21} and 10^{22} n/m^2 fluences) KU1, KS-4V and I301 grades, have been studied at different temperature. The three irradiated silica grades show similar excitation spectra shape, although the band intensities are different depending on silica grade and temperature. The PL excitation profile has two bands extending in the UV and VUV range, which are centered around 4.85 eV with full width at half maximum (FWHM) of 1.1 eV and around 6.5 eV (FWHM 1.7 eV) Excitation spectra measured at 300K for the three grades irradiated at the lowest neutron fluence (10^{21} n/m^2) are shown in figure 2. KU1 grade presents the most intense red emission of the three irradiated silica. This could be justify by the higher hydroxyl groups content of this grade, which by irradiation can be converted into NBOHCs [3]

≡Si-OH →≡Si-O$^\bullet$ + H$^\bullet$

However the NBOHC generation is affected by the reaction with mobile species as H, O and their compounds. It is known that, if atomic or molecular hydrogen is available, NBOHCs can be converted to hydroxyl groups [3] through the reverse reaction

≡Si-O$^\bullet$ + H$^\bullet$ →≡Si-OH

So the low concentration of NBOHCs observed for gamma irradiated I301 and the increase of the band associated to Si-OH (3650 cm^{-1}) during gamma and neutron irradiation [22] could be due to the presence of hydrogen. Changes in the shape of the OH band in KU1 high purity silica were observed as consequence of the process in which the restored silanol groups have different environment than the original one

The minor difference shape observed around 5.1eV in the shape of the excitation spectra of I301 irradiated at 10^{21} n/m^2 fluence could be attributed to the presence of an absorption band at 5.15eV energy which may be distorting the excitation spectra. Such absorption band in I301 is attributed to germanium oxygen deficient centers GeODC(II) [21] and is not present in KU1 [22].

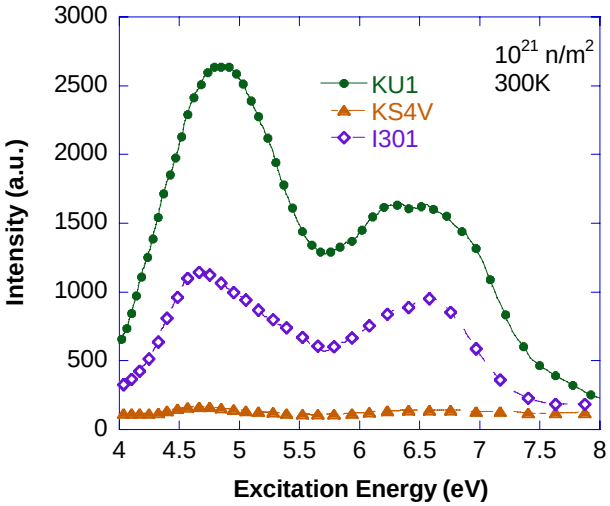

Figure 2. PL excitation spectra measured at 300K of neutron irradiated (10^{21} n/m^2 fluence): KU1 (•), KS-4V (▲) quartz glasses and infrasil I301 (◊).

The normalized excitation spectra are similar for the three types of silica. The relative intensity of the VUV band related to UV band is greater for lower fluence. This effect could be due to the high optical absorption at energies higher than 5eV [22] that could make VUV radiation to excite only the superficial defects in samples irradiated at 10^{22} n/m^2 fluence. Figure 3 shows the normalized excitation spectra for KU1 irradiated samples at the two neutron fluences measured at 10K. For all the grades with increasing neutron fluence, the maximum at 4.85eV is shifted to lower energies. This could suggest that NBOHC defect is influenced by its environment which changes with irradiation. Also a shift to lower energies as the fluence is increased was observed in the maximum of the excitation spectra of the 4.4 [19] and 2.7 eV [20] emission bands related to ODC defects.

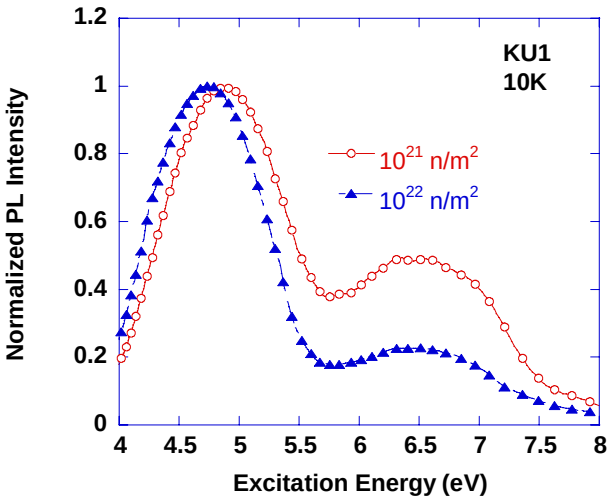

Figure 3. Normalized PL excitation spectra measured at 10K in neutron irradiated KU1 quartz glass, up to 10^{21} n/m^2 fluence (**O**) and up to 10^{22} n/m^2 fluence (▲)

The band intensities increase with decreasing temperature from 300 to 10K, for the three types of silica. An example of the temperature dependence for KU1 irradiated at 10^{21} n/m^2 fluence, is shown in figure 4. The thermal quenching suggests that NBOHCs are rapidly converted back to hydroxyl groups when the temperature increase, since H and H_2 are mobile in silica above 80 and 200K respectively [3].

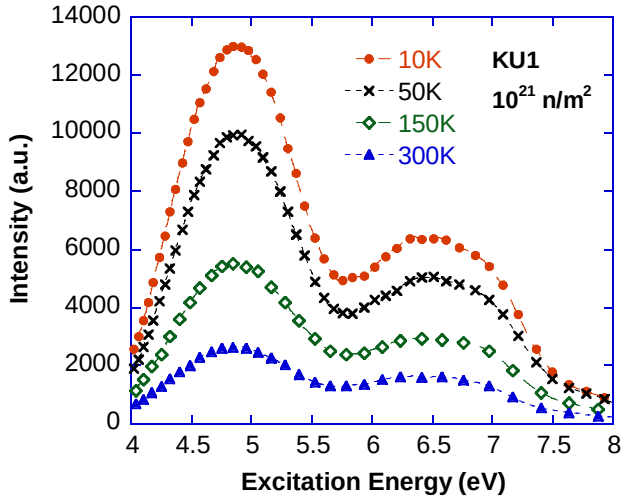

Figure 4. PL excitation spectra at 1.9 eV emission, in KU1 neutron irradiated silica up to 10^{21} n/m^2 fluence, measured at temperatures: 10K(●), 50K(x), 150K (◊) and 300K(▲).

In a previous work, measurements of the vacuum ultraviolet excitation spectra of the 1.9 eV emission band in gamma irradiated (at a dose of 10 MGy) synthetic wet silica Suprasil 311 (200ppm OH content) were carried out at different temperatures by Cannas and Gelardi [13]. They concluded that the band centered at 6.35eV is correlated to the band centered at 4.85eV, as in the measurements of neutron irradiated wet and dry silica reported in this paper.

4. Conclusions

The PL excitation spectra of the 1.9eV emission for the three neutron irradiated silica grades show similar shape. The excitation profile has two bands, which are centered around 4.85 eV and 6.5 eV. The band intensities are different depending on silica grade and temperature. The PL intensity correlates with OH content; KU1 (with the highest OH content) shows the highest luminescence around 1.9eV emission due to NBOHCs. The intensity of the bands increases on decreasing temperature. Excitation spectra for irradiated materials are modulated by the radiation induced high optical absorption in this spectral region.

Emission band at 1.9eV was practically undetectable for the three unirradiated silica grades at any temperature. Only the unirradiated high purity wet silica KU1 at 10K showed a very low 1.9eV emission.

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