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Radiation processes in oxygen-deficient silica glasses: Is ODC(I) a precursor of E'-center?

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Abstract

The accumulation of radiation-induced defects under non-destructive X-ray and destructive cathodoexcitation was studied in pure silica KS-4V glasses possessing an absorption band at 7.6 eV. The correspondence between the existence of this band and the creation of the E′-center by radiation was checked. Detection of induced defects was accomplished by measurement of the luminescence during irradiation, post irradiation afterglow or phosphorescence, induced optical absorption, and thermally stimulated luminescence. In all samples, these observed phenomena associated with charge trapping and recombination on the oxygen-deficient luminescence center. Others centers of luminescence were not significant contributors. In some samples, the intensity of the 7.6 eV absorption band was deliberately increased by treatment in hydrogen at 1200 C for 100 h. The intensity of luminescence in hydrogen-treated samples was smaller because of the known quenching effect of hydrogen on the luminescence of oxygen-deficient centers. The optical absorption method does not reveal an induced absorption band for the E'-center in the hydrogen-free samples with different levels of oxygen deficiency. Therefore, we did not detect the transformation of the defect responsible for the 7.6 eV absorption band or the ODC(I) defect into the E'-center. In the hydrogen-treated sample, the absorption of the E'-center was detected. The E'-centers creation in the hydrogen-treated sample was associated with precursors created by hydrogen treatment (≡Si–O–H and ≡Si–H) in the glass network. The destructive e-beam irradiation reveals an increase with dose of the ODC luminescence intensity in the sample exhibiting a small 7.6 eV band. That means that the corresponding luminescence centers are created. Optical absorption measurements in that case reveal the presence of E'-centers and a broad band at 7.6 eV. A compaction of the irradiated volume was detected. Therefore, we conclude that the E'-center is produced by heavy damage to the glass network or by the presence of precursors.

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1. Introduction

Facilities for material irradiation, appeared in the 1950s, allow the measurement of neutron influence on crystalline quartz and silica glass. Two absorption bands, apparently belonging to radiation induced defects in the host material, were discovered. These are the so called C-band at 5.75 eV (now ascribed to E'-center) and E-band at 7.6 eV [1,2]. Later, progress in production provided more pure silica material and it was discovered that even in virgin samples there was a band at 7.6 eV, which is significantly increased when extra silicon is added to the raw material before fusion [3,4]. In such a way correspondence of this band to oxygen deficiency was discovered. This center is labelled as the ODC(I).

There is a long history of a tempts to understand the nature of the 7.6 eV absorption band in silica glass. Two luminescence bands could be excited: one at 2.7 eV another

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at 4.4 eV [4]. Sometimes, in the samples obtained or treated in oxygen-deficient conditions, an absorption band at 5 eV was observed. Two luminescence bands at 2.7 eV and at 4.4 eV could be excited at 5 eV [4]. The last absorption band with corresponding luminescence was consistently attributed to the twofold-coordinated silicon center [5]. This center is labelled as ODC(II).

Complicated phenomena accompany the existence of the 7.6 eV absorption band and this has resulted in disagreement in interpretation of the nature of this band. There is a natural assumption of a correlation to the neutral oxygen vacancy (NOV) in the tetrahedral network [6]. The NOV could be presented as $3O \equiv Si–Si \equiv 3O$. Treatment in hydrogen at 800 °C [6], results in the disappearance of the 7.6 eV band followed by the appearance of the ≡Si–H vibration band at 2255 cm^{-1}. This was interpreted as the reaction: $\equiv Si–Si \equiv +H_2 = >2 \equiv Si–H$ [6]. Another experiment [7], demonstrated that the intensity of vibration IR bands, corresponding to the ≡Si–H and ≡Si–O–H centers, that were created by treatment in hydrogen at 800 °C of silica samples with different levels of oxygen deficiency does not depend on the level of the oxygen deficiency. In addition the intensity of the ≡Si–H band is similar to that observed in [6]. The absorption band at 7.6 eV become broader after treatment in hydrogen in the case of low oxygen deficiency whereas in the case of high oxygen deficiency, this band was not affected by hydrogen treatment [7]. The luminescence of the oxygen-deficient centers is strongly affected by treatment in hydrogen, therefore all ODC defects are interacting with hydrogen. So, two main reactions of hydrogen at 800 °C in the experiment of [7] were proposed. One is a rupture of normal silicon–oxygen–silicon bonds with the creation of ≡Si–H and ≡Si–O–H. Another is the interaction of hydrogen with the defect responsible for the 7.6 eV band. The lack of correlation between the level of oxygen deficiency and the IR bands, induced by treatment in hydrogen, is the main argument supporting the interpretation that the reaction of oxygen-deficient centers with hydrogen is different from the hypothetical rupture of the silicon–silicon bond and that the center responsible for the 7.6 eV absorption band is different from the NOV in the tetrahedral structure.

Treatment in hydrogen at 1200 °C [8], provides a strong increase of the 7.6 eV band. It is assumed in the last case that structural motifs of the defect under consideration are prepared by fusion and hydrogen works as reducing condition, binding oxygen and revealing the 7.6 eV absorption band.

We have performed a study of silica samples with different intensities of the 7.6 eV absorption band achieved by preparation or by treatment. The main experiment involved the influence of irradiation on optical absorption, luminescence afterglow and thermally stimulated luminescence. All these phenomena bring information about radiation-induced defects. One irradiation approach involves the use of an X-ray source. In this case we have almost uniform irradiation of the volume of the sample and, for the case of silica, this irradiation method could be characterized as 'non-destructive' to the main network because of low energy (45 keV). The irradiation leads to the creation in silica of electronic excitations – excitons, electron–hole pairs, etc. (see e.g. [9], which are interacting with the 'perfect' lattice network, producing self-trapped excitons with corresponding luminescence [9], or with imperfections, existing in the samples, providing their excitation or recharging. The structure of those imperfections could be changed in that case. The changes can be related to defect dissociation in the excited states. Also trapping of charge could lead to changes in the structure. So, we could recharge the hypothetic neutral oxygen vacancy and detect creation of the E'-centers in the samples containing the 7.6 eV band, if the corresponding defect participates in charge trapping. We compared the same samples both treated with hydrogen and untreated. X-ray irradiation, as a non-destructive method, was compared with destructive irradiation with an electron beam. In the last case, we had checked the irradiated location by measuring induced optical absorption and we also checked for volume changes using a phase-shift interferometric microscope. Previously [10], densification due to irradiation was discovered. Another experiment [11] revealed the presence of a hollow after e-beam irradiation. This was connected with the compaction of the irradiated location. The latter can be cured by heating.

2. Experimental

The samples for investigation were pure dry silica (the level of metallic impurities is about 10^{-6} wt% and content of OH group is about 10^{-7} wt%, [3]). The samples were produced as KC-4B (or the same KS-4V) silica (see for example [3,4]). The method of preparation was based on electrofusion of cristobalitisied synthetic silicon dioxide. A high level of oxygen deficiency was provided by reaction of cristobalite with silicon vapour [3,4]. A 'normal' level of oxygen deficiency in the samples was achieved by 'washing' in oxygen of cristobalite. Some of produced samples were treated in oxygen or hydrogen at 1200 C during 100 h. Some treatments were done in shorter period of time.

The samples were previously studied in papers [4,7,8] and their optical absorption spectra are presented in Figs. 1, 2. All the samples contain the band at 7.6 eV. Different intensities of the band show on different level of oxygen deficiency.

The optical spectra were measured with different equipments. One equipment contains windowless hydrogen discharge source with 0.5 Seja–Namioka vacuum monochromator working in the range of photon energies 4–14 eV. The equipment with irradiation facilities contains a X-ray tube with W anticathode, regime 45 keV 15 mA; a vacuum monochromator with the plane grating, two mirrors and a deuterium discharge source with MgF_2 window; a grating monochromator for luminescence detection. The sample was kept in cryostat with possibility of