Electron Paramagnetic Resonance and optical absorption characterization of E'$_\gamma$ centers in silica

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Abstract: We report an experimental study of the modifications of Electron Paramagnetic Resonance (EPR) and optical spectra of the E'$_\gamma$ center in silica induced by room temperature gamma irradiation and by subsequent thermal treatment. Our data show that the EPR signal of this center changes on increasing the irradiation dose from an almost axial symmetric line shape to an orthorhombic one in all but the synthetic wet silica materials, where only the orthorhombic line shape is found. The changes in EPR signature occurs together with a red shift of the peak position of the absorption band around 5.8 eV attributed to the E'$_\gamma$ center. These features suggest the existence of two different precursors of this center. After thermal treatment the EPR orthorhombic line shape converts to the axial symmetric one together with a blue shift in the peak position of the absorption band pointing out a structural degree of freedom of the E'$_\gamma$ centers.

1. Introduction

The E'$_\gamma$ center is one of the most investigated point defects in silica due to its widespread occurrence in many applications [1]. This center is characterized by an Electron Paramagnetic Resonance (EPR) signal centered near g≈2.001 and by a correlated optical absorption band peaked at ~5.8 eV [2]. Many experimental and theoretical efforts have been done to correlate these spectral features to a specific microscopic structure [1-6]. Up until now the most accepted model contains a threefold coordinated Si atom with an unpaired electron in a non-saturated bond [3-4], even if the complete structure of the defect and the nature of its precursor are still debated [1]. Furthermore, the electronic transition related to the optical absorption band has not been fully clarified [1, 5]. In particular, it is not known if the electronic transition is confined to electronic states localized in the threefold coordinated Si group or if it involves a charge transfer process to the neighboring atoms.

To investigate the E'$_\gamma$ center precursors and to shed new light on the nature of the associated optical absorption band at 5.8 eV we have carried out optical absorption together with X-band (9.8 GHz) EPR measurements in high purity commercial silica samples of natural (from fused quartz) and synthetic type exposed to γ rays irradiation at room temperature. Samples were also thermally treated after irradiation in the temperature range 290-700 K.

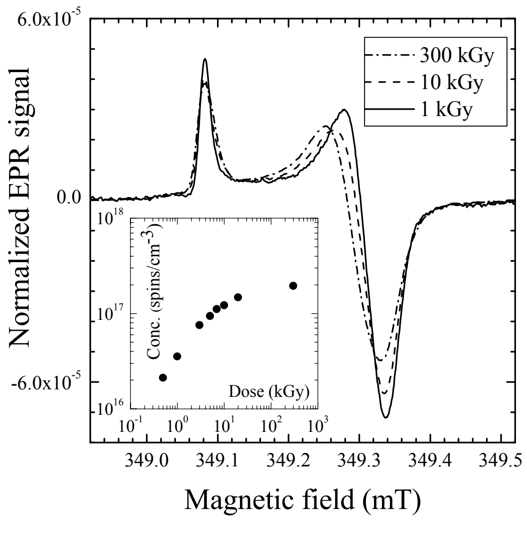

Figure 1: EPR signal of a natural dry sample irradiated at 1 kGy, 10 kGy, 300 kGy, normalized to the double integral and horizontally shifted to make the first maximum coincide. In the inset, the concentration as a function of dose is reported.

Table 1. Differences of the EPR signal principal g*-values and position of the peak of the absorption band associated with the low dose, <3kGy (L1), and high dose, >200kGy (L2), E'$_\gamma$ center.*

E'$_\gamma$ Line shape	$\Delta g_{1,2}$	$\Delta g_{1,3}$	*Energy (eV)*
L1	(1.24 ±0.01) x 10^{-3}	(1.47±0.01) x 10^{-3}	5.83±0.02
L2	(1.15 ±0.01) x 10^{-3}	(1.42 ±0.01) x 10^{-3}	5.75±0.02

2. Experimental results and discussion

As reported in Fig.1 for a natural dry sample, after irradiation the EPR signal of E'$_\gamma$ center can be detected. The concentration gradually increases with the irradiation dose and finally reaches a constant value typically of the order of 10^{17} centers/cm^3, as shown in the inset of Fig.1. Modifications of the line shape can be observed on increasing the dose as evidenced by the shift of the zero crossing point of the resonance line. For doses lower than 3 kGy and for doses higher than 200 kGy two distinguishable line shapes, L1 and L2, take place. Their features are summarized by the differences of the principal *g*-values reported in Table 1. For intermediate doses a superposition of L1 and L2 is observed. This line shape variation occurs in all natural, dry and wet, and in synthetic dry samples investigated. At variance, in the synthetic wet silica only L2 is observed for all the doses from 0.5 kGy up to 10^4 kGy.

In Fig.2a, the optical absorption band associated to the E'$_\gamma$ center is reported for the same natural dry sample of Fig.1. The peak position of this band was found at ~5.83 eV when the defect possesses the L1 EPR line shape and at ~5.75 eV when the defect possesses the L2 line shape. This red shift takes place gradually and in the same dose range where the EPR line shape modification occurs.

Isochronal (20 minutes) thermal treatments of the samples in which the E'$_\gamma$ shows the L2 line shape were carried out. The EPR measurements pointed out that in the temperature range between 370 K and 460 K the line shape gradually converts from L2 to L1. This modification takes place in all the materials including the synthetic wet in which, as above reported, only L2 was observed during the irradiation. Furthermore, for the natural dry silica, no significant concentration changes occur during the line shape conversion suggesting that the observed features are related to a structural modification. As reported in Fig.2b, the optical measurements show that in the same temperature range in which the EPR line shape change is observed, a blue shift of the absorption band peak position occurs. This result evidences a variation of the splitting of the electronic energy levels induced by the structural modification of the E'$_\gamma$ center.

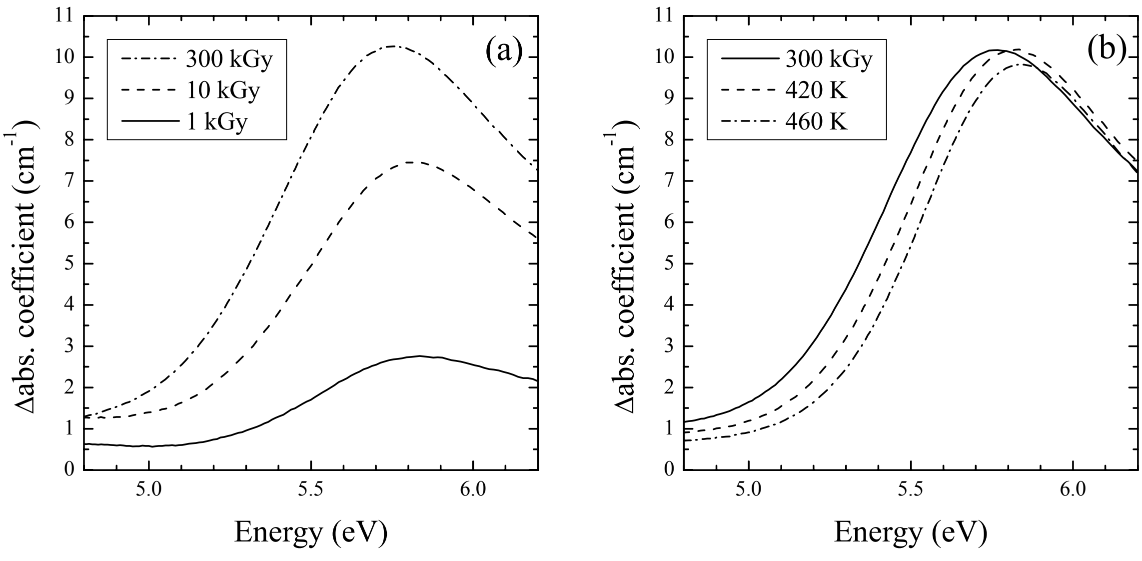

Figure 2: (a) Difference absorption spectra with respect to not irradiated material of natural dry sample irradiated at doses 1 (continuous line), 10 (dashed), 300 kGy (dash dotted); (b) difference absorption spectra with respect to not irradiated material of natural dry sample irradiated at 300 kGy (continuous line) and after thermal treatment at 420 K (dashed) and 460 K (dash dotted) for 20 minutes.

Perturbation theory calculation shows that, through the spin-orbit coupling, the g shifts can be related to the electronic energy level separation of the ground and excited states [8]. On the basis of this theory we found that the ~0.1 eV change of the peak position of the absorption band is compatible with the observed variation of Δg. This result suggests a strong localization on the threefold coordinated silicon group of the wavefunctions involved in the optical transition.

3. Conclusion

We have observed that the EPR signal of the E'_γ center changes on increasing the irradiation dose from an almost axial symmetric line shape to an orthorhombic line shape in all but the synthetic wet silica materials, where only the orthorhombic line shape is found. These features have been handled supposing the existence of two different precursors of the E'_γ center. After activation, one gives the axial and the other the orthorhombic line shape. Thermal treatments of the samples featuring the orthorhombic line shape shows a conversion to the axial line shape without concentration change suggesting that a structural change of the E'_γ center occurs. Finally, correlated changes of the optical absorption band and of the EPR line shape are observed indicating that the optical absorption could involve a localized electronic transition.

4. References

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