Charge transfer absorption of Fe^{3+} and Fe^{2+} complexes and UV radiation induced defects in different glasses

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Charge transfer absorption bands of Fe^{3+} and Fe^{2+} complexes in fluoride, phosphate and silicate glasses of ultrahigh purity were determined and the influence of Fe^{3+} and Fe^{2+} on UV lamp and laser radiation induced defects was studied. The intrinsic absorption edge of all glasses investigated is in the vacuum ultraviolet region. The position and intensity of the charge transfer absorption bands are strongly influenced by the glass matrix. Photo-oxidation of Fe^{2+} to $(Fe^{2+})^+$ hole centers (HC) and glass matrix related electron centers (EC) were found in all glasses investigated. These centers increase the UV absorption drastically which depends strongly on the glass matrix. The radiation induced defects were detected by optical absorption and EPR spectroscopy. The kinetics of defect formation were measured and simulated depending on the glass matrix.

The experiments have shown that only in silicate glass samples Fe^{3+} complexes participate in radiation induced processes and are able to form $(Fe^{3+})^-$ electron center defects which decrease the charge transfer absorption of Fe^{3+} complexes near 220 nm but increase the absorption of hole center defects with the maximum a 280 nm. So, the defect generation in the ultraviolet region increases drastically with increasing Fe content in the range 10-200 ppm. In contrast to silicate glasses Fe^{3+} complexes do not participate in the UV radiation induced processes in fluoride and phosphate glasses. Their glass matrix is not able to trap an electron and stabilize a $(Fe^{3+})^-$ defect electron center. So, fluoride glasses having only Fe^{3+} complexes by melting under oxidizing conditions are very stable against UV lamp and laser radiation.

Introduction

The role of glasses as ultraviolet transmitting material for special applications has increased in recent years. Fluoride single crystals, mainly CaF_2, and high purity vitreous silica are well known materials used for deep UV optics, especially in microlithography. Moreover, for various applications, a variety of glasses with different properties is required. It was found that special fluoroaluminate, phosphate and borosilicate glasses melted with starting materials of high purity have also high transmission in the deep UV range due to their high intrinsic band gap. But their extrinsic absorption is limited by trace impurities, mainly due to the charge transfer transitions of Fe^{3+} and Fe^{2+} complexes which are introduced through the raw materials and melting technique[1-5]. The redox ratio Fe^{3+}/Fe^{2+} in the ppm range in glasses has a large effect on UV absorption and radiation induced defects and can be shifted by melting conditions. This should be considered in different glasses.

Experimentals

Samples of multicomponent fluoride, phosphate and silicate glasses of ultrahigh purity were doped with Fe' in the ppm range and melted under oxidizing and reducing conditions (Table 1). The resulting glass samples had a good optical quality without striae or bubbles. Samples for the different measurements were prepared. Plates were irradiated at room temperature with strong UV lamps (performance density 1500 W/m^2 in the range 230-280 nm with the XeHg and 190-280 nm with the HOK Hg lamp). For laser radiation induced defects, ArF (193 nm), KrF (248 nm) and XeCl (308 nm) excimer lasers (pulse energy 50-500 mJ/cm^2, performance density to 10^{11} W/m^2, pulse length ~30 ns, repetition rate 1-20 Hz) were used. The absorbance, $E_\lambda = \log T_0/T$, was recorded with a commercial spectrometer before and after irradiation. The induced absorbance was expressed as an absorption coefficient, $\Delta E/d$ in cm^{-1}. All spectra were fitted by Gaussian bands using the commercial PeakFit software (Jandel Scientific). More details are described in Refs.[1-3]

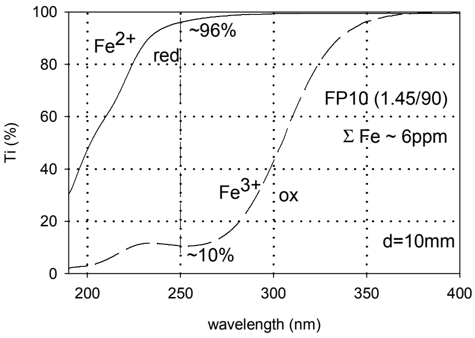
Results and discussion

Batch compositions and some properties of undoped glass samples used in our experiments are given in Table 1. All the three glass types investigated have very large intrinsic UV transmission. But their structure is very different and so their charge transfer absorption bands of Fe^{3+} and Fe^{2+} complexes are also different. The bands of Fe^{3+} complexes dominates in all cases. The measured spectra could be well fitted with Gaussian shape bands. In fluoride glasses, FP, with the highest ionic bonding the band maximum, λ=260 nm, has the lowest energy (38 500 cm^{-1}= 4.8 eV), the smallest band width (8 000 cm^{-1}) and the lowest specific absorption coefficient, ε_{260nm}=0.18 cm^{-1} ppm^{-1}. The charge transfer should occur from the surrounding ligands to the central Fe^{3+} ion. In the case of FP 4, ligands are mainly fluorine in sixfold coordination. The influence of oxygen ligands increases with the phosphate content, FP 4< FP 10 < FP 20 << P 100, and causes shifts to higher energy (240 nm, 41 700 cm^{-1}, 5,2 eV), intensity (0.20 cm^{-1} ppm^{-1}) and larger band width (10 000 cm^{-1}). Silicate and borosilicate glasses show another behaviour for the Fe^{3+} charge transfer bands. In Duran a very strong and broad band with a maximum at 222 nm (45 000 cm^{-1}= 5.6 eV) was found in good agreement with the data in high purity soda-silica glass[4]. A very high specific absorption coefficient, 0.30 cm^{-1} ppm^{-1}, was determined. But a second smaller band with a maximum at 255 nm with lower intensity (0.06 cm^{-1} ppm^{-1}) was necessary for well fitting of all measured spectra of iron doped Duran glass samples. These Fe^{3+} charge transfer bands could be determined in all glasses investigated with high accuracy. Further transitions are assumed near the intrinsic UV edge[3].

Exact determination of the Fe^{2+} charge transfer bands is more probable. Only in FP glasses was it possible to shift the redox ratio completely to the Fe^{2+} state (Figure 1) and to determine the bands with high accuracy (maximum at 220 nm; 45 500 cm^{-1}; 5.6 eV; ε = 0.006 cm^{-1} ppm^{-1}; W~ 4000 cm^{-1}). In phosphate and silicate glasses, the values for Fe^{2+} ct bands determined have a larger error. The main band maximum is between 215 and 220 nm, with ε_{λ} between 0.006 and 0.03 cm^{-1} ppm^{-1}, also with much lower intensity than those for Fe^{3+}. The large effect of the Fe^{3+}/Fe^{2+} ratio on UV transmission and solarisation is shown in the Figures 1- 6. FP glass samples with low iron content, ~ 6 ppm, have very different UV transmission depending on oxidizing or reducing melting conditions (Fig. 1). But FP glass samples with mainly Fe^{3+} are very stable against UV lamp irradiation[1]. However, FP glass samples with mainly Fe^{2+} show photooxidation forming $(Fe^{2+})^{+}$-hole centre defects (HC) which absorb near 260 nm, and a phosphorus-related electron precursor gains the electron lost from Fe^{2+} to form electron centre defects (EC) absorbing in the UV region, mainly at ~210 nm, without recovery. The measured kinetic curves (Fig. 2) could be well fitted with the function

$$f(t) = A[1 - \exp(-Bt^{1/2})] \quad (1)$$

where t is the exposure time, A is a constant and directly proportional to the initial Fe^{2+} content, the constant B correlates with the performance of the irradiation source. This process is single photon, whose rate depends on the phosphate content[2].



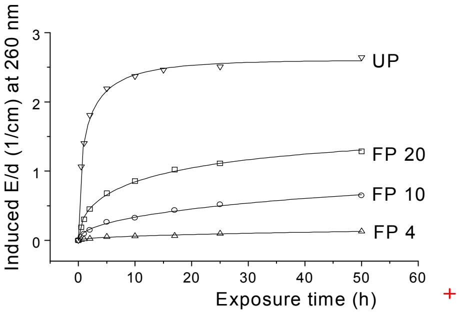


Fig. 1: Deep UV transmission of a FP glass sample with an impurity level of 6 ppm in the completely oxidized and reduced state.

Fig. 2 (right)**:** Photo oxidation of Fe^{2+} as a function of UV lamp exposure time and phosphate content. The initial Fe^{2+} content in all glasses was the same, ~15 ppm.

Table 1: Batch compositions and some properties measured on basic glass samples considered

Glass	Composition (mol%)	Tg (°C)	Refr. index	Disp. coeff.	VUV edge (nm)
FP4	4 $Sr(PO_3)_2$ – 96 (AlF_3, MgF_2, CaF_2, SrF_2)	410	1.435	95	155
FP10	10 $Sr(PO_3)_2$ –90 ((AlF_3, MgF_2, CaF_2, SrF_2)	440	1.460	90	160
FP20	20 $Sr(PO_3)_2$ –80 ((AlF_3, MgF_2, CaF_2, SrF_2)	460	1.504	80	165
MP	55 P_2O_5 – 45 (ZnO, CaO, BaO, MgO, Al_2O_3)	480	1.550	64	190
UP	65 P_2O_5 –35 (ZnO, CaO, BaO, MgO, Al_2O_3)	460	1.540	67	185
Duran	82 SiO_2, 13 B_2O_3/Al_2O_3, 5 Na_2O/K_2O	530	1.473	66	175

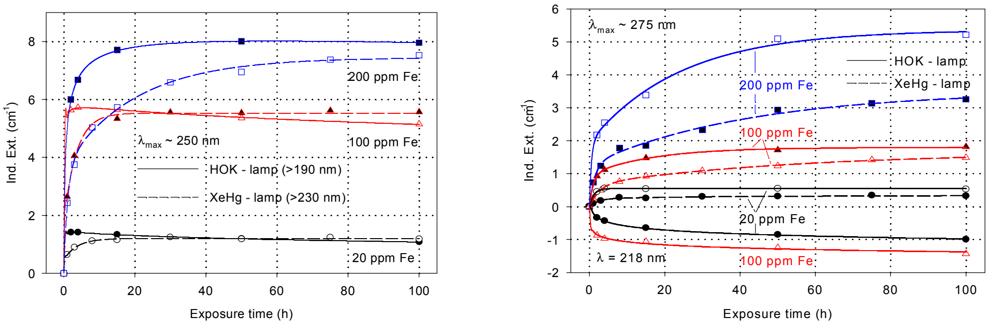


Fig. 3: Kinetic curves for maximal defect generation by different UV lamp irradiation of iron doped Duran glass samples: a) melted under reducing and b) under oxidizing conditions.

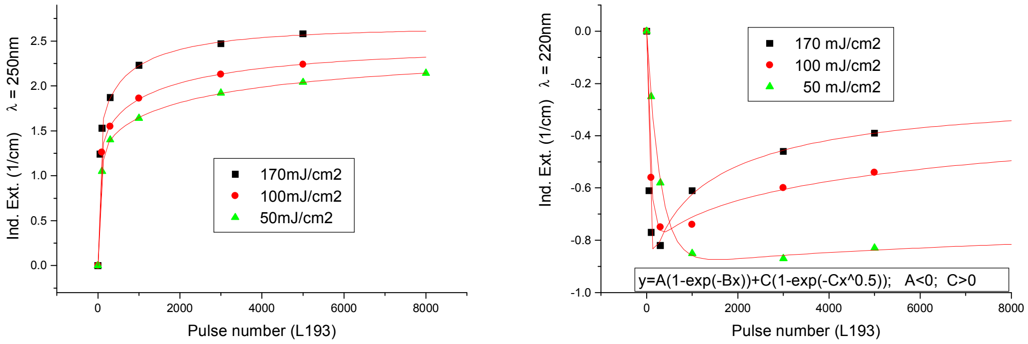


Fig. 4: Kinetics for defect generation by laser irradiation (193 nm) depending on energy density of Duran samples with 20 ppm Fe: a) melted under reducing conditions; b) melted under oxidizing conditions.

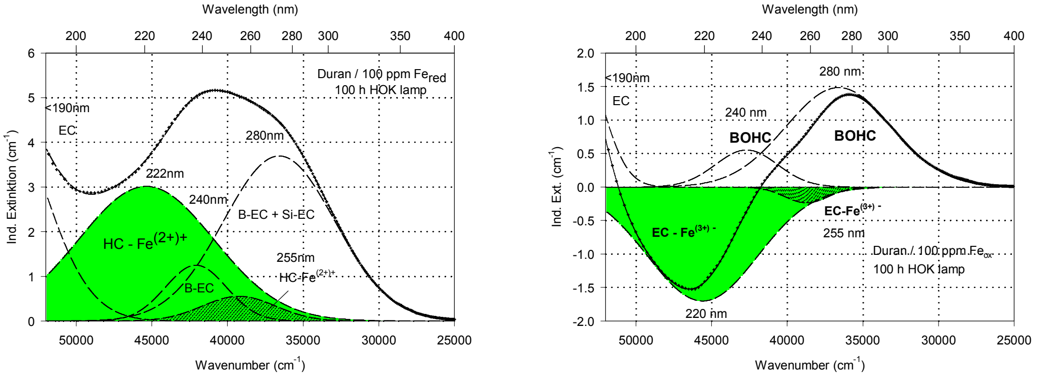


Fig. 5: Peak simulation and designation of defect bands (with EPR) in Duran samples with 100 ppm Fe after 100 h UV lamp irradiation: a) melted under reducing and b) under oxidizing conditions.

High purity borosilicate glass samples, Fe<10 ppm, are very stable against UV lamp and 248 nm laser irradiation. But the generation of defects increases drastically with increasing Fe content especially in samples melted under reducing conditions (Fig. 3-5)[2]. The kinetics at λ_{max} ~ 250 nm, Fig. 3a, could be well fitted with the following functions (x=time) for the strong HOK lamp irradiation

$$y = y_0 + a \ln x + b (\ln x)^2 \qquad (2)$$

and for XeHg lamp irradiation $y = y_0 + a [1-\exp(-b x)] + c [1-\exp(-d x)]$ (3).

In the case of samples melted under oxidizing conditions, Fig. 3b, the maximal positive defect generation at λ_{max} ~ 275 nm could be fitted for both lamps with the same function (3) and for the negative defect generation at λ_{max} ~ 218 nm with a simpler function

$$y = y_0 + a \ln x \qquad (4)$$

That means the mechanisms for radiation induced processes are very difficult to recognize because they are very complex. Kinetic curves can pass a maximum or minimum which is strongly dependent on the irradiation wavelength and energy density (Fig. 3 and 4) and makes the extrapolation of the defect generation for long time irradiation very difficult. The designation of the generated defect was assumed by correlation of the induced optical bands, EPR analysis combined with thermal annealing experiments.

Conclusions

The intrinsic VUV edge of glasses with low optical basicity is shifted to longer wavelength in the range FP < P~ Duran. Charge transfer transitions of Fe^{3+} complexes are dependent on the glass matrix, that means the local glass structure. The maximum of the dominating Fe^{3+} band has the lowest intensity and energy in the FP glass with the lowest optical basicity and the most ionic bonding. In the phosphate glasses, the energy and intensity are a little higher. The highest energy and intensity were found in the borosilicate glass, Duran. The charge transfer bands for the Fe^{2+} complexes have much lower specific absorption coefficients than those for Fe^{3+} complexes in all glasses investigated. Photooxidation of Fe^{2+} to $(Fe^{2+})^+$- hole centre and electron centre defects depending on the glass matrix was detected by UV lamp and laser irradiation with a single photon mechanism. Fe^{3+} species participate in the radiation induced processes only in silicate or borosilicate glasses. In FP and P glasses they are not able to trap an electron and stabilize a $(Fe^{3+})^-$ defect electron centre.[1]

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