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Radiation induced absorption and luminescence of selected alternative radiation resistant glasses

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ABSTRACT

Two types of multicomponent glasses, 75% SiO_2: Na, Ca, one 0.05% Ce doped, have been studied in terms of radioluminescence, radiation induced optical absorption, and photoluminescence. The samples were irradiated with 1.8 MeV electrons at different temperatures and dose rates. During irradiation radioluminescence and optical absorption measurements were performed at different doses. The results show that both types of glasses are highly sensitive to radiation damage. For irradiation at 200 °C, some improvement is observed, but the behaviour of these glasses is worse than for KU1 quartz glass.

1. Introduction

For diagnostic and remote handling systems in ITER, high purity KU1 and KS-4V quartz glasses are main candidates for use as windows and optical components (lenses, optical fibres), due to their radiation resistance, particularly in terms of radioluminescence and radiation induced optical absorption [1–4]. Recently multicomponent silicate glasses are also being considered, as they would provide optical materials with a range of refractive indices required for achromatic components [5]. In general such glasses appear to be more susceptible to radiation induced luminescence and absorption than the pure silicas, however, most of the available data is for room temperature irradiation, whereas operation in ITER will be at elevated temperatures.

To examine the possibility of improved behaviour at high temperature, a study of the radioluminescence, photoluminescence, and radiation induced optical absorption of two types of alternative multicomponent silicate glasses has been carried out. The results show that both types of glasses are highly sensitive to radiation. Some improvement is observed when these glasses are irradiated at 200 °C. However, the material behaviour is considerably worse than for KU1 even at this temperature.

2. Experimental procedure

Samples of two types of multicomponent glass, cut to about $20 \times 20 \times 1.5\ mm^3$ with the two large faces polished to standard optical quality, were provided by SCK–CEN Mol, Belgium. The glass was fabricated at CREOL, University of Central Florida (Courtesy of L.B. Glebov). The nominal composition in wt% was 75% SiO_2, 22% Na, 3% CaO. One of the types was 0.05% Ce doped while the other was undoped. High purity raw materials with heavy metal concentration less than few parts per million (ppm) were melted in an electrical resistive furnace in fused silica crucibles. Stirring was applied to homogenize the melt. The applied method allows production of glasses with a concentration of impurities of the order of 5 ppm [5,6].

Irradiation experiments were performed in a sample chamber mounted in the beam line of a Van de Graaff electron accelerator. The chamber permits irradiation in high vacuum at controlled temperatures, and in situ optical absorption and emission spectra from 200 to 800 nm, to be measured during or following irradiation. Irradiations have been carried out at 15, 100, and 200 °C, with 1.8 MeV electrons at 10 Gy/s, to study the radiation induced optical absorption and radioluminescence. Radioluminescence was measured as a function of irradiation time (dose) and temperature, and the intensity compared with that found earlier for KU1 quartz glass [2]. The optical absorption was measured in situ before and after irradiation. In addition before and after electron irradiation, optical absorption measurements were made for all the samples at room temperature, from 200 nm to 3000 nm, using a Varian Cary 5E double beam spectrometer. Absorption values are given in optical density (OD) per cm.

To examine impurity and defect related emission, photoluminescence excitation and emission spectra for the two types of glass were measured at room temperature with a Perkin Elmer LS 5 luminescence spectrometer, sensitive in the range 200–800 nm. The excitation was produced with a Xenon lamp. The bandwidth for excitation and emission was 10 nm. The $20 \times 20\ mm^2$ face of the samples was placed at 45° with respect to the ultraviolet excitation light and the emission observed at 45°.

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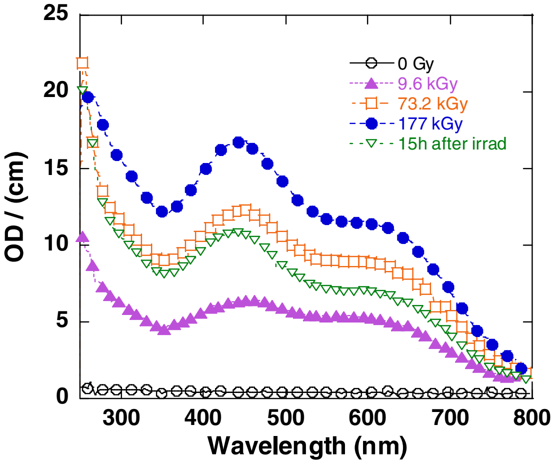

Fig. 1. Optical absorption spectra at 15 °C, for unirradiated (○) and electron irradiated undoped glass at different doses (immediately after irradiation): 9.6 kGy (▲), 73.2 kGy (□), 177 kGy (●) and 15 h after irradiation at 177 kGy (▽).

Additional samples were provided, previously gamma irradiated in the Brigitte irradiation facility at SCK•CEN at 70, 200, and 350 °C (7 Gy/s), up to total doses of between 112 and 625 kGy [5]. These allowed one to compare gamma and electron irradiation effects.

3. Results and discussion

3.1. Optical absorption at 15 °C

The initial (unirradiated), and radiation induced optical absorption spectra for the undoped glass up to 177 kGy at 15 °C, are shown in Fig. 1. The unirradiated material shows very low absorption over the whole range. On irradiation high optical absorption is observed from the UV to the visible range ($\approx$5 OD/cm), even for doses below 10 kGy. The main absorption bands at about 440 and 620 nm are due to hole centres [5,7], i.e. electronic defects caused by ionization induced charge transfer processes. Following irradiation the induced optical absorption notably decreases with time, indicating that the defects are unstable even at 15 °C. Fig. 2 shows the behaviour of the Ce doped glass irradiated up to 214 kGy at 15 °C. Even before irradiation the Ce doped glass has high absorption below 350 nm, the 315 nm absorption band is due to Ce^{3+}, and the further increase towards 250 nm due to Ce^{4+} [5,8]. On irradiation high induced absorption again occurs from the UV to the visible range. For this Ce doped glass, absorption in the visible range again decreases with time after irradiation as seen in the figure, however, in the UV range the behaviour is more complex, with absorption increasing below about 300 nm. The radiation induced optical absorption increase with dose for Ce doped and undoped glasses irradiated at 15 °C, is very similar above 350 nm, as may be seen at 445 nm in Fig. 3. Although above 10 kGy the coloration rate for the Ce doped glass is slightly less than for the undoped glass, already below 10 kGy both glasses suffer extremely high radiation induced absorption, with no advantage from Ce doping in terms of radiation hardening. In terms of optical absorption both KU1 and KS-4V are far superior, even by 200 kGy their maximum absorption, at 215 nm, is less than 0.2 OD/cm [3].

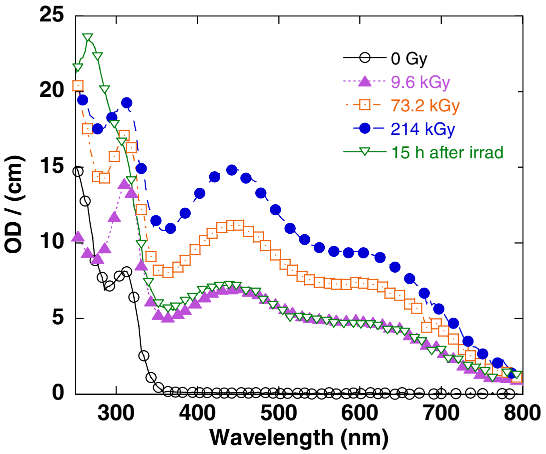

Fig. 2. Optical absorption spectra at 15 °C, for unirradiated (○) and electron irradiated Ce doped glass at different doses (immediately after irradiation): 9.6 kGy (▲), 73.2 kGy (□), 214 kGy (●) and 15 h after irradiation at 214 kGy (▽).

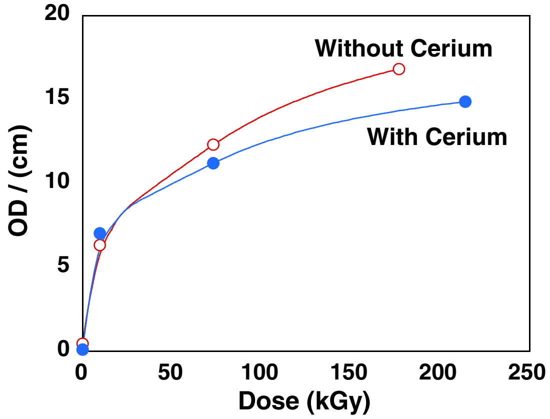

Fig. 3. Evolution with dose of the optical absorption at 445 nm for both doped and undoped glasses.

3.2. Radioluminescence (RL) at 15 °C

RL spectra at 10 Gy/s 15 °C, for the undoped and Ce doped glasses are shown in Fig. 4. An intense broad band at about 350 nm is observed for the undoped material which decreases with dose as may be seen by 145 kGy. A similar emission is observed for the Ce doped glass with an apparent shift to about 380 nm. This

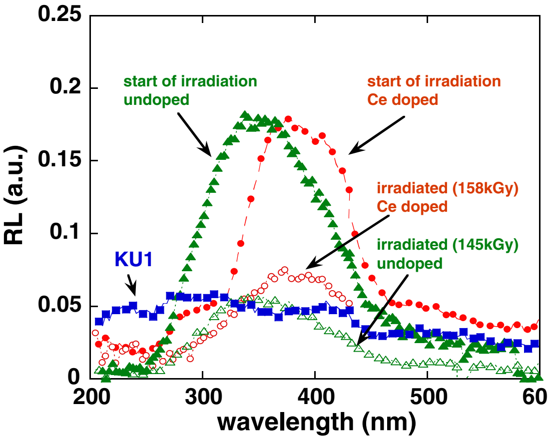

Fig. 4. Radioluminescence spectra, measured at 15 °C, for unirradiated Ce doped (●) and undoped (▲) glasses, and KU1 quartz glass (■) and for irradiated up to 158.4 kGy Ce doped (○) and irradiated up to 145.2 kGy undoped (△) glasses.

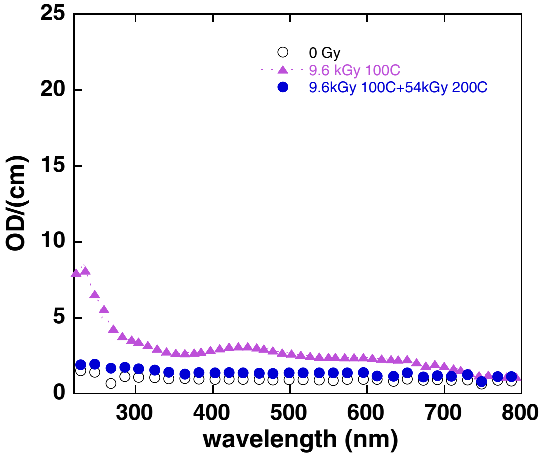

Fig. 5. Optical absorption spectra for undoped glass unirradiated (○) and irradiated at different temperature: 9.6 kGy at 100 °C (▲) and 9.6 kGy at 100 °C + 54 kGy at 200 °C (●).

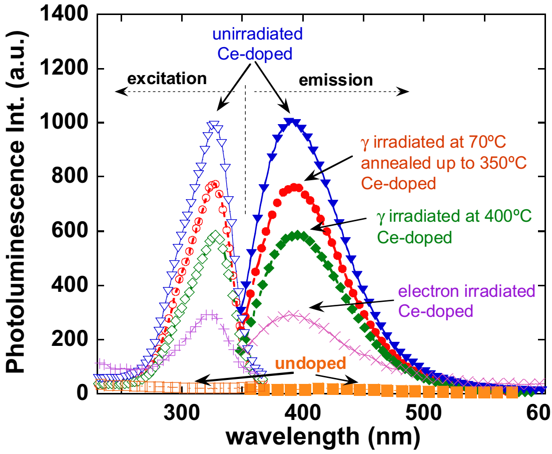

Fig. 7. Photoluminescence excitation and emission spectra, measured at room temperature, for undoped and Ce doped glasses unirradiated, gamma and electron irradiated and gamma irradiated and annealed up to 350 °C.

band also decreases with dose as may be seen by 158 kGy. Absorption in the sample itself will cause a decrease in intensity with dose. As may be seen in Figs. 1–3, by about 150 kGy the undoped sample has higher absorption in the 350–400 nm region consistent with the larger decrease observed in the emission. The shift in the observed luminescence band to about 380 nm for the Ce doped sample is caused partly by self absorption below 350 nm due to the Ce^{3+} absorption band (Fig. 2), together with an additional emission band at 390 nm again due to Ce^{3+} (see below in *Photoluminescence* and Fig. 7). For comparison the RL spectrum for KU1 quartz glass measured under identical conditions is also shown. For KU1 the RL is only Cerenkov emission, and due to the very low radiation induced absorption the intensity does not change with dose [2].

3.3. Optical absorption at different temperatures

Optical absorption spectra for the undoped glass irradiated first at 100 °C to 9.6 kGy, and then at 200 °C to 54 kGy are shown in Fig. 5. At 100 °C the induced absorption although similar to that observed at 15 °C (Fig. 1), is considerably less, and for irradiation at 200 °C the absorption is suppressed. A very similar behaviour is observed for the Ce doped glass (Fig. 6). These results are consistent with the formation of thermally unstable defects, as already noted at 15 °C. Further evidence for unstable defects is seen in the optical absorption spectrum for Ce doped glass during and just after irradiation at 200 °C (Fig. 6 inset). It is clear that the absorption is higher during irradiation, short lifetime defects only observable during irradiation give rise to measurable optical absorption.

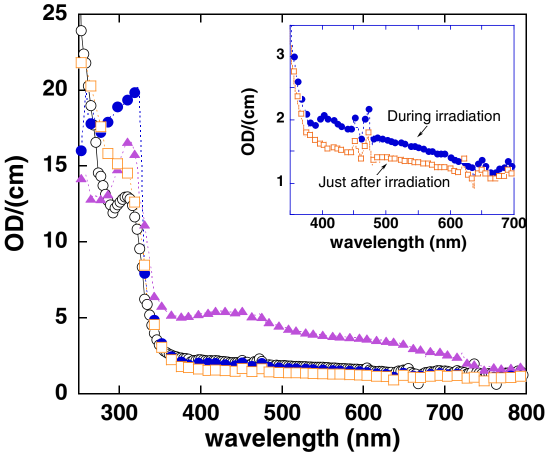

Fig. 6. Optical absorption spectra for Ce doped glass unirradiated (○) and irradiated at different temperature: 9.6 kGy at 100 °C (▲) and 27.6 kGy at 100 °C + 54 kGy at 200 °C: during irradiation (●) and just after irradiation (□). Detail during and just after irradiation in the inset.

The absorption spectra induced by the electron irradiations at different temperatures, are very similar (absorption bands and intensities, thermal stabilities) to those observed for gamma irradiations [5], consistent with electronic defects caused by purely ionizing radiation.

3.4. Photoluminescence (PL) at room temperature

PL was used to try to identify possible defect or impurity related luminescent centres responsible for the observed RL. PL excitation and emission spectra, measured at room temperature, for undoped and Ce doped glasses, unirradiated, gamma irradiated up to 500 kGy at 400 °C and electron irradiated up to 209 kGy, at 15 °C, are shown in Fig. 7. For the undoped samples (unirradiated, and gamma and electron irradiated) no PL could be detected at room temperature. However, for all the Ce doped samples a single intense broad emission band at 390 nm was observed due to the f → d transition of Ce^{3+}. These emission spectra were obtained for excitation at 325 nm, and the corresponding excitation spectra were measured for emission at 390 nm. The observed PL intensity decreases for all the irradiated samples, consistent with the increased absorption. No other emissions were detected.

4. Conclusions

The two multicomponent glass materials studied exhibit very high sensitivity to radiation in terms of optical absorption. The radiation induced optical absorption reaches values of the order of 5 OD/cm in optical density after only 10 kGy at 15 °C, with no advantage gained from Ce doping. Furthermore, in addition to introducing high absorption in the UV region, the Ce doped glass exhibits high photoluminescence. In order to anneal the coloration during irradiation, the glass temperature has to be increased up to 200 °C. However, even at this temperature, measurements during irradiation show higher absorption due to short lifetime defects. Not only the absorption, but also the radioluminescence for both types of glasses is higher than for KU1 quartz glass, limiting their potential use in ITER. The close similarity between these electron irradiation results and those obtained for gamma irradiation indicates that the same type of electronic defects are induced, and highlights the sensitivity of the glasses to purely ionizing radiation.

Acknowledgments

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