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Radiation induced color centers in cerium-doped and cerium-free multicomponent silicate glasses

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Abstract: The effect of doped cerium on the radiation-resistance behavior of silicate glass was investigated in our work. The ultraviolet-visible absorption spectra and electron paramagnetic resonance (EPR) spectra were obtained after the cerium-rich and cerium-free multicomponent silicate glasses (K509 and K9) were irradiated by gamma rays with a dose range from 10 to 1000 kGy. The results showed that E' center, oxygen deficient center (ODC) and non-bridging oxygen hole center (HC1 and HC2) were induced in K9 and K509 glasses after radiation. The concentrations of all color centers presented an exponential growth with the increase of the gamma dose. Moreover, the concentration of HC1 and HC2 in cerium-doped K509 glass was much lower than that in cerium-free K9 glass at the same dose of radiation, which could be attributed to the following mechanism: Ce^{3+} ions capturing holes then forming Ce^{3++} centers inhibited the formation of hole trapped color centers (HC1 and HC2) and Ce^{4+} ions capturing electrons to form Ce^{3+} centers suppressed the formation of electron trapped color centers like E' center.

Keywords: multicomponent silicate glasses; cerium ions; gamma radiation; color center; rare earths

Multicomponent silicate glass, due to its excellent optical properties, has long been hot-cell windows, optical fiber waveguides and space optics[1–3]. However, in some harsh environment such as nuclear reactor and space environment, color centers could be induced into multicomponent silicate glass due to the high energy ionizing radiation from X-ray, gamma rays, neutrons and electrons[2,4,5], which leads to a terrible absorption in visible light range. Non-bridging oxygen hole center (NBOHC) is considered to be the most common defect in irradiated glasses related to visible absorption bands (~400 nm for HC1 and ~600 nm for HC2)[6]. Doping with cerium, based on former investigation, has been found to be an efficient way to prevent the coloration process[7]. Two UV absorption bands of cerium-doped glass exist around 240 nm for Ce^{4+} and around 330 nm for Ce^{3+} [1,3,7]. When exposed to irradiative environment, Ce^{3+} and Ce^{4+} ions in the glass would capture the irradiation-induced electrons and holes to avoid strong absorption in visible region. Till now, a lot of efforts have been dedicated to the research of radiation-hardness glasses[3,8,9], nevertheless the mechanism of anti-coloration effect of cerium is still not fully explained and the glasses that have been investigated are only limited to silica glasses[6], binary sodium-borate, sodium-phosphate[10,11], etc. So we feel obliged to make a much more detailed study on multicomponent silicate glasses.

In our work, cerium-doped and cerium-free multicomponent silicate glasses (K509 and K9) were chosen to carry out the research. The ultraviolet-visible absorption spectra and electron paramagnetic resonance (EPR) spectra were used to analyze the coloration behavior of the glasses before and after irradiation. It is also worth mentioning that we used Gaussian fitting to process the spectra results and specific color center kinetics were obtained.

1 Experimental

Both-side-polished cerium-free glasses (Type K9) and cerium-doped glasses (Type K509) with a size of 20 mm× 20 mm×0.2 mm were purchased from CDGM Glass Co., Ltd. Table 1 lists the composition of the glasses determined by inductively coupled plasma-optical emission spectrometry (ICP-OES). All the samples were irradiated by Co-60 γ-ray source with a dose rate of 3.8 kGy/h while the total dose varies from 10 to 1000 kGy. UV-Vis transmission measurement by a double beam spectrophotometer (Cary 500 type) was made before and after

Table 1 Composition of K9 and K509 determined by ICP-OES (wt.%)

Composition	SiO_2	Al_2O_3	Na_2O	K_2O	BaO	CaO	ZnO	Fe_2O_3	CeO_2
K9	76.39	0.14	10.78	10.76	1.71	0.017	0.20	0.002	/
K509	77.58	0.13	10.67	9.11	1.86	0.011	0.20	0.002	0.43

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irradiation and during the time samples were stored in liquid N_2 to inhibit thermal bleaching of color centers. EPR measurement was performed at room temperature on an X-band JEOL-FA200 spectrometer with a 100 kHz field modulation. A modulation amplitude of 2G was employed to record each spectrum and EPR data were normalized to the specimen mass of 1 mg.

2 Results

Fig. 1 shows the radiation effects on the induced absorption spectra of K9 glasses during the dosage from 10 to 1000 kGy. Induced absorption is defined as the difference between the absorption after radiation and before radiation. The overall induced absorption spectra increase progressively with increasing doses. Significant absorption was induced from 400 to 800 nm, transforming K9 glasses from transparent before irradiation to pale brown after gamma irradiation. Fig. 2 shows the induced absorption spectra of K509 glasses. It is obvious that visible absorption is much weaker compared to K9, and there are two UV bands located around 280 and 330 nm, which were attributed to oxygen deficient center (ODC)

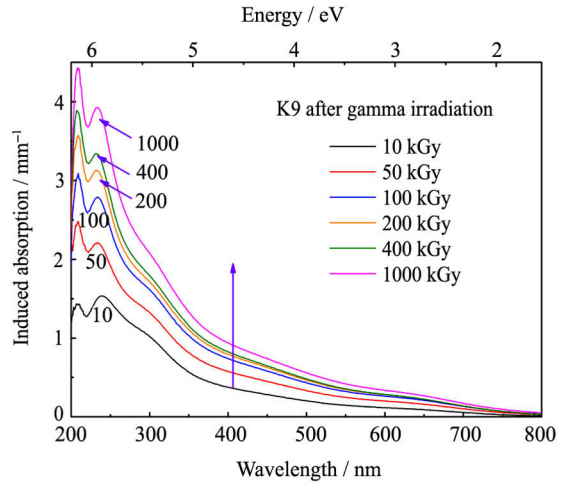

Fig. 1 Induced absorption spectra of K9 glass after being irradiated with different gamma doses

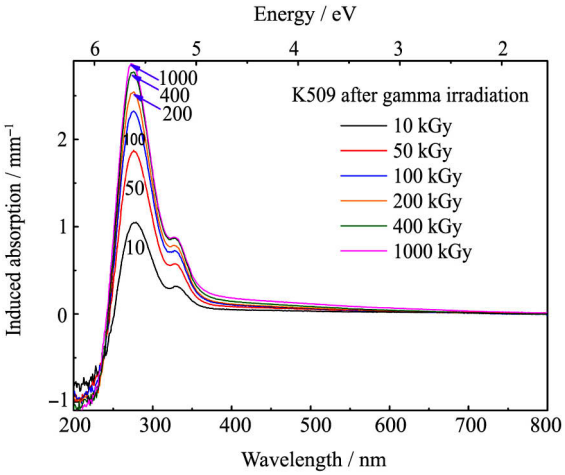

Fig. 2 Induced absorption spectra of K509 glass after being irradiated with different gamma doses

and Ce^{3+} [1,3,6]. By comparison of Figs. 1 and 2 in the UV region, we found that the value of the induced absorption from 200 to 250 nm of K509 was negative, implying the decrease of some defect.

As a direct way to identify the structural changes, optical bandgaps of K9 and K509 glasses before and after radiation have been calculated by Davis and Mott formula[12]:

$$\alpha(\omega)=B/\hbar\omega\times(\hbar\omega-E_g)^n \quad (1)$$

where B is a constant. For direct forbidden transitions, n=2. The optical band gap, E_g, can be calculated by plotting $(\alpha E)^{1/2}$ as a function of E ($E=\hbar\omega$). The value of E_g is determined from a linear extrapolation to zero ordinate as shown in Fig. 3. The bandgap of K9 decreases from 3.46 to 3.37 eV with increasing doses, while the value of K509 decreases from 4.80 to 4.38 eV. The decrease of band gap shows that the structure of glasses has been changed during radiation[13], which is most possibly due to the generation of some defects[14].

Gaussian fitting was adopted as shown in Fig. 4 in order to distinguish the overlapped bands and investigate specific defects. We fixed the center of band and FWHM to represent specific color centers as listed in Table 2, according to literature[1,6,15]. The result reveals five bands in the studied region for K9 glass irradiated to 1000 kGy, band centered at 208, 230, 285, 410 and 630 nm, correspond to the color centers of E', ODC, B1, HC1 and HC2, respectively[6]. For K509 glass, there is an additional band located at 328 nm, which is attributed to cerium ions[1]. Although the intensity of spectra goes up as

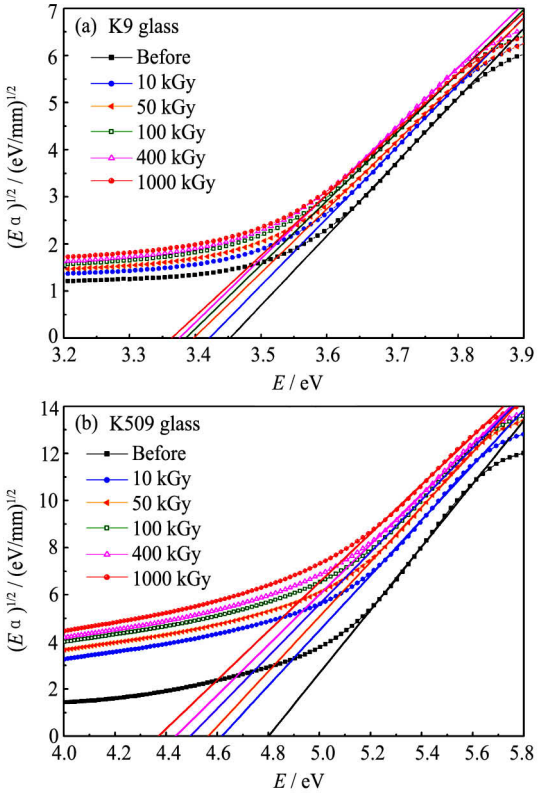

Fig. 3 Bandgap of K9 and K509 after being irradiated with different gamma doses