Chapter 1

The Nature of the Defects in Phosphate-Based Glasses Induced by Gamma Radiation

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Additional information is available at the end of the chapter

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Abstract

Final optics assembly is one of the most important parts in high energy and large-scale laser systems like US National Ignition Facility and SG III in China. Those final optics assembly are facing some severe tests, like the laser-induced damage caused by 3ω (351 nm) laser irradiation. Meanwhile, the irradiation of gamma ray and X-rays, will also cause the changes of optical properties in the investigated multi-component phosphate glasses that have potential use in novel color separation optics in high power laser facilities. These changes of optical properties are associated with the defects induced by gamma radiation. In details, some defects contribute to the absorption in the UV region, which will deteriorate their UV performance. However, some of the induced defects can be eliminated by thermal treatment due to the release and capture of the electrons in conduction band. Besides, the doped Fe, Co, B, Ce and Sb will also affect the defect-state in phosphate-based glasses. In details, gamma radiation resistances of the phosphate glass can be greatly improved by CeO_2 and Sb_2O_3 co-doping, and the introduction of B_2O_3 reduces the connectivity of phosphate chains and thus increases the concentration of PO_3-EC and PO_4-EC defects.

Keywords: defects, phosphate-based glass, gamma radiation, radiation resistance, absorption

1. Introduction

Fluoride-containing phosphate-based glass is considered to be a special case of optical laser glasses that have potential use in color separation optics in high power laser facilities. Thus glasses have received a great deal of interest due to their excellent properties, such as tunable melt viscosity and glass forming ability, high transparency from the ultraviolet to the infrared region of the optical spectra, relatively lower refractive together with low non-linear refractive indices, etc., which endow them with applications as an attractive candidate for high-performance UV optics and high power laser technology, such as lens system in excimer laser systems, UV microlithography equipment and other special UV optics [1–4]. In this case, the investigations on the glass's micro-structure and micro-defects as well as the corresponding optical and physical properties of various phosphate-based glasses have never stopped in the improvement of their optical properties for developing high performance UV laser glasses.

Absorptive ions-doped phosphate-based laser glasses have exhibited great potential in the area of optical filters in high-energy and large-scale laser facilities like SG III in China and US National Ignition Facility (NIF) [5–8], in which the unconverted fundamental (1ω) and second harmonic frequency (2ω) laser lights should be separated or filtered from the main third harmonic frequency (3ω) laser light as entered into fusion target chamber to avoid the error of laser beam diagnostics for the inertial confinement fusion (ICF) experiments. Compared with silicate glasses, the iron and Co doped 1ω and 2ω absorptive fluoride-containing phosphate-based glass exhibits much lower absorption and higher pulse laser-induced damage thresholds (LIDTs) at 3ω wavelength [8]. Unfortunately, several types defects will form in these phosphate glasses during the glass preparation process and post processing that are harmful for their transmittance and will significantly decrease their LIDTs particular at UV region. And, the nature of the defects in these specific glasses is very complex and still not explicit, especially for the evolutionary mechanism of the produced defects. Therefore, to explore the information about the defects is critical for understanding of their evolutionary mechanism of the produced defects.

In this chapter, we will address the nature of the defects in phosphate-based glasses induced by gamma radiation, by first discussing the properties of most common defects in phosphate-based glasses. Then, we will report details about the effects of gamma radiation on the defects in the phosphate-based glasses. Finally, we will discuss the self-repairing capability of defects induced by gamma radiation during heat treatment process. Furthermore, this chapter will also address the effect of defects in phosphate-based glasses.

2. Properties of various defects in phosphate-based glasses

There are two types of defects that are generated in phosphate-based glasses, intrinsic defects that arise from glass matrix and the raw materials, and extrinsic defects which are caused by impurities or dopants [9]. It is well established that the basic structural unit of phosphate glass is the P-tetrahedra that made up phosphate chains in phosphate-based glass [10]. Modifier cations, glass preparation process including thermal annealing conditions, glass melting, and energetic radiations may influence the above mentioned phosphate chains, which subsequently form several intrinsic defects, such as phosphate-related oxygen hole center (POHC) characterized by an unpaired electron shared between two orbitals of two non-bridging oxygens bound to a phosphorus atom, oxygen-related hole center (OHC), and phosphate-related electron centers (PEC) including PO_2-EC, PO_3-EC and PO_4-EC defects etc. [11, 12] which are common defects in various phosphate glass systems. On the other hand, some unavoidable trace impurities such as iron, cobalt, and other intentionally or unintentionally doped transition metals could produce numerous extrinsic defects [13], such as Fe^{2+}, Fe^{3+}, Co^{2+} which have large absorption in the UV-VIS range. In addition, it is well established that the absorption bands of holes defects lie in the low energy region, and several bands connected with electrons defects are positioned near the high energy region.

3. Defects induced by gamma radiation in phosphate-based glasses

High-power UV laser irradiation, with potential use of the series of fluoride containing phosphate-based glasses in megajoule class lasers as NIF and SG III will also suffer from the irradiation of the gamma rays and X-rays in the experimental chamber [14]. So, gamma radiation is a general tool to investigate the nature of the defects in phosphate-based glasses.

Various defects are formed during the gamma radiation process, which determines obvious absorption in the visible range, as shown by the gradually deepened maroon color as the total gamma radiation dose increases as shown in **Figure 1**. The details can also be found in the transmission spectra (**Figure 2**). Gamma radiation causes several defects in phosphate-based glass that have large absorption in the region of UV-VIS spectrum range, as shown by the decreased transmittance in **Figure 2**. By increasing the total radiation dose, the transmittance decreases further, especially for the absorption bands at around 385 and 530 nm which is related to the POHC defects and PO_3-EC defects [15], respectively. This suggests that more PO_3-EC and POHC defects are generated during the irradiation process with increasing total dose. Besides, it can be found that the UV absorption edges of these glass samples gradually red-shifts with the increase of irradiation dose, which is ascribed to the increased defects concentration of both Fe^{3+} and PO_3-EC [13]. To better illustrate the absorption characteristics of these defects, one of the absorption spectra was fitted and separated into multi Gaussian peaks, as shown in **Figure 3**. It can be found that the positive charged hole center defects lie in the low energy region i.e. POHC at 2.36 eV and OHC at 4.28 eV, while several negative charged electron center defects are positioned near the high energy region such as PO_3-EC at 5.94 eV and PO_4-EC at 5.17 eV [16]. Besides, the band of the two positive charged hole center defects at around 3.22 eV are also related to the PO_3-EC, which corresponds to the large absorption at 385 nm as shown in **Figure 2**.

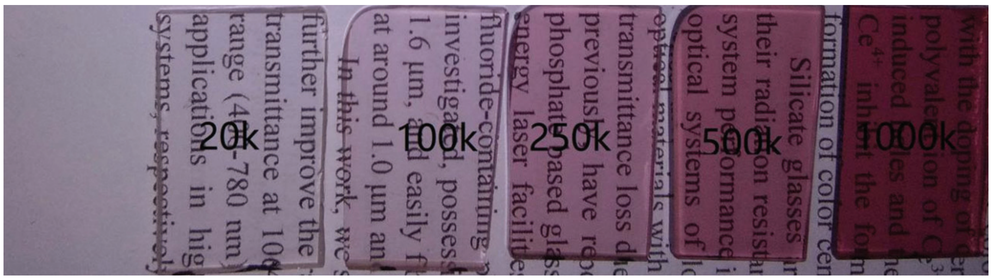

Figure 1. Photographs of a series of phosphate-based glasses with different radiation doses (20k, 100k, 250k, 500k and 1000k rad (Si)).

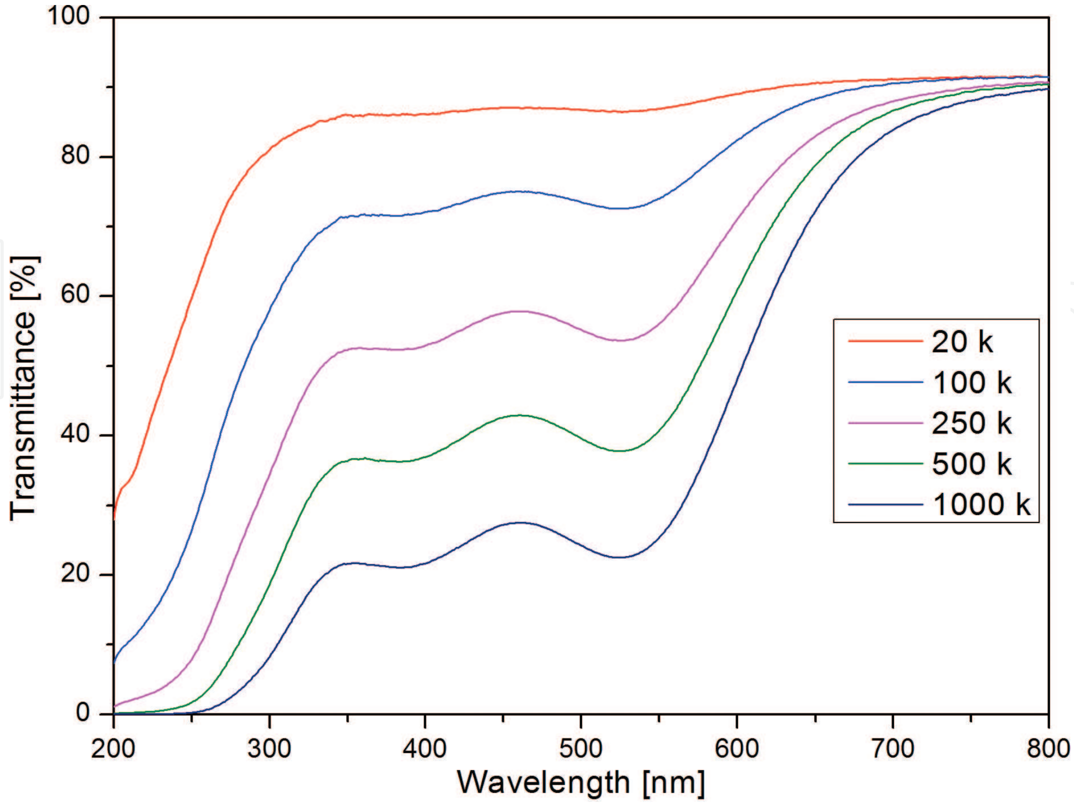

Figure 2. Transmission spectra of the series of phosphate-based glasses with different radiation doses (20k, 100k, 250k, 500k and 1000k rad (Si)).

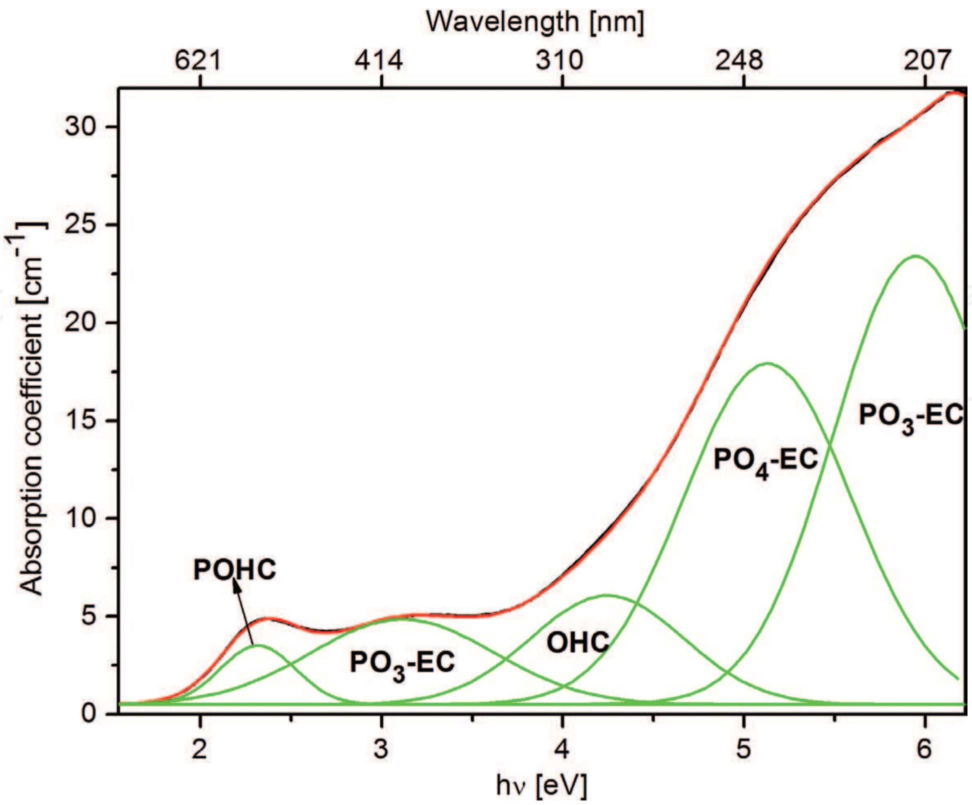

Figure 3. Separation of radiation induced absorption band for the phosphate-based glasses [14].

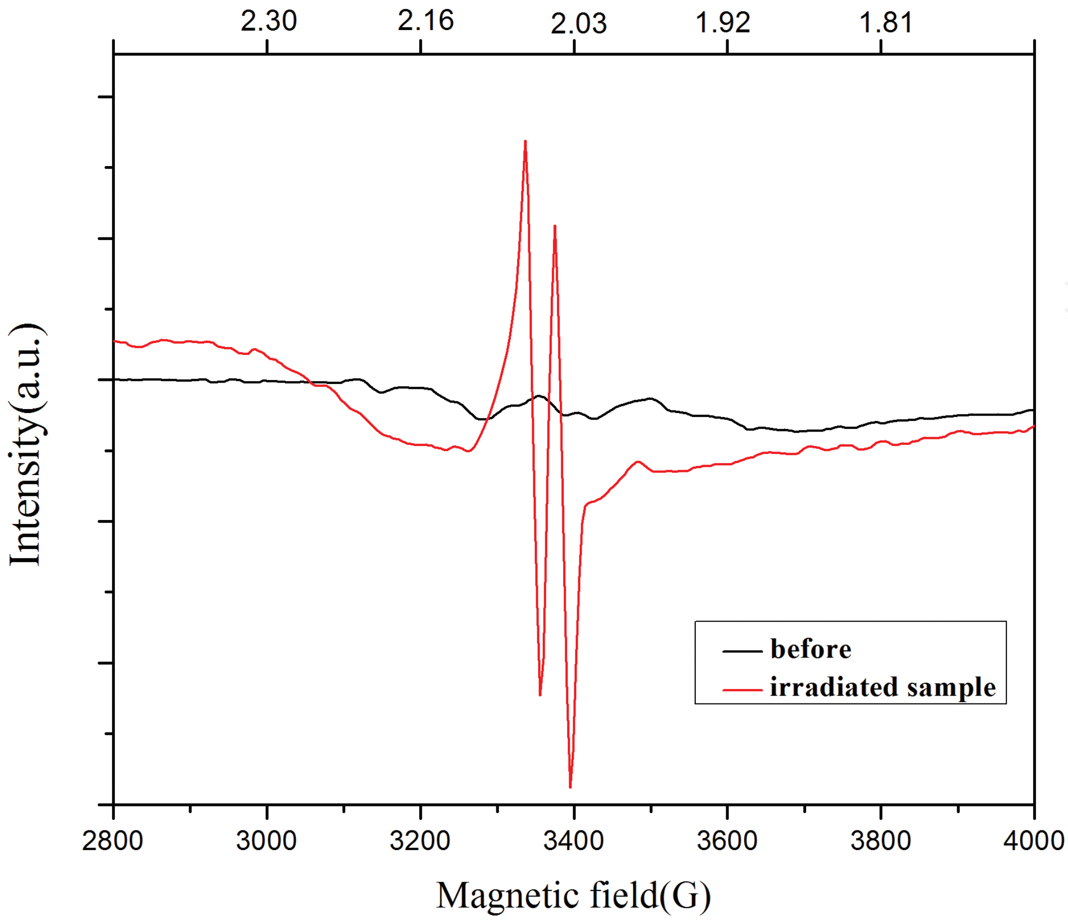

Figure 4. The EPR spectra of the samples before and after gamma radiation.

Typical EPR spectra of phosphate-based glass before and after gamma radiation are shown in **Figure 4**. All EPR spectra are dominated by the signals of intrinsic defects. The main signal is the POHC defects with the g-value around 2.06 [17]. After gamma irradiation, this signal becomes significant. Another signal located close to the POHC signal can also be found in the irradiated samples, which is associated with the OHC defects caused by gamma radiation. It can be noticed that the signals of PO_3-EC and PO_4-EC are enhanced if compared with that of the un-irradiated samples. These results suggest that gamma irradiation causes much more defects in glass.

Gamma irradiation causes the increase of various defects in the phosphate-based glasses, resulting in an obvious decline of the transmittance in the UV and visible range, indicating that more color centers are generated in these glasses.

4. The influence of heat treatment on the defects in the fluoride-containing phosphate-based glasses

Post heat treatment is an effective method to investigate the information of the defects and reveal their evolutionary mechanism [9]. Post heat treatment can remove the defects caused by gamma radiation in phosphate-based glasses. In order to illustrate the changes of the main defects concentration in these phosphate-based glasses upon the post heat treatment, **Figures 5** and **6** present the relations between the absorption-peak's area of the corresponding defects and the post heat treatment temperatures. As one can see, the POHC concentration is significantly higher in Co-doped than that in FP sample (made in air atmosphere). With the increase of radiation doses, POHC defects concentration increased, while their concentration decreases with the increase of post heat treatment temperature as shown in **Figure 5a**. In **Figure 5b**, it is obvious that the concentrations of OHC defects decrease with the increase of post heat treatment temperature. Besides, the corresponding decrease tendency is obvious although at low heat treatment temperature. It was also found that the OHC concentration level increases relatively slow in the FP and Co doped samples when increase the total gamma radiation doses. The variations in the phosphate-based glasses irradiated with different radiation dose and heat treated at different temperatures are shown in **Figure 5c**. In details, the FP:Fe sample maintains the highest FD defect concentration level, and the concentration levels could be described as an order of FP:Fe > FP (air) > FP > FP:Co.

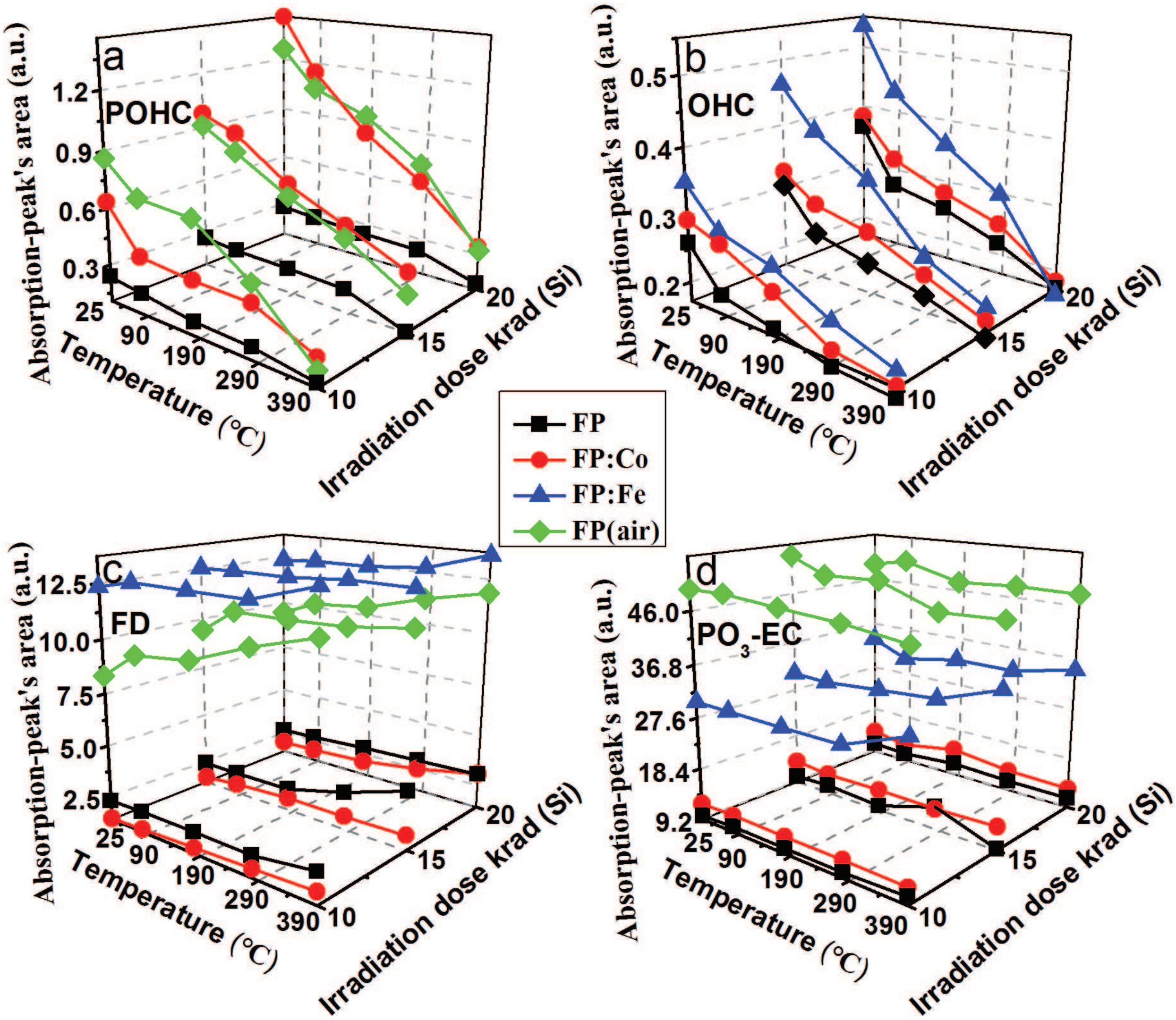

Figure 5. Line chart displaying the absorption-peak's area of corresponding intrinsic defects (a: POHC, b: OHC, c: FD, d: PO_3-EC) in the FP, FP: Co, FP: Fe and FP (air) samples irradiated with different radiation dose and heat treated at different temperatures [9].

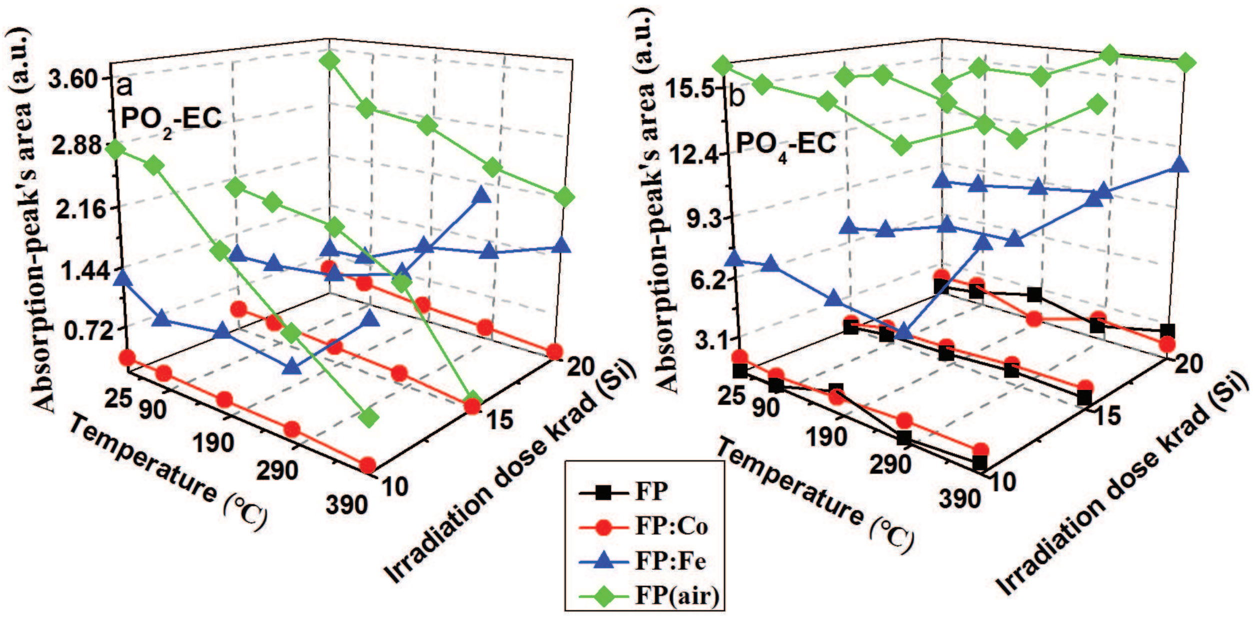

Figure 6. Line chart displaying the absorption-peak's area of PEC defects (a (PO_2-EC), b (PO_4-EC)) in the FP, FP: Co, FP: Fe and FP (air) samples irradiated with different radiation dose and heat treated at different temperatures [9].

In addition, the concentration levels of FD defects in Fe-doped sample is much higher than others, indicating that Fe is likely contributing to the generation the FD defects in these phosphate-based glass. Similarly, the FD defect is insensitive to the total gamma radiation doses, and its concentration increases slowly at low temperature i.e. ≤190°C, but with further increase their post heat treatment temperature, its concentration increases apparently. As seen in **Figure 5d**, the concentration level of PO_3-EC defect in these phosphate-based glasses is higher than other defects, and their concentration is insensitive to the total gamma radiation dose and the post heat treatment temperature, this is due to the PO_3-EC defects is the main defect in these glass, and their structure is like to the glass's network. The same phenomenon can also be observed in **Figure 6b**. This might be because PO_3-EC and PO_4-EC defects are mainly associated with the skeleton structure of these phosphate-based glasses. Meanwhile, phosphate contents dominate the glass composition and therefore, PO_3-EC will be the main defects in these phosphate-based glasses, thus its concentration level is much higher than others. And their concentration is relatively stable in the investigated phosphate-based glasses. Based on the above-mentioned results, we can infer that OHC and POHC defects are mainly ascribed to gamma radiation in our experiments, and these defects could be reduced in the considered phosphate-based glasses by post heat treatment near their glass transition temperatures.

Thermal energy at room temperature may induce the release of trapped electrons in the gamma radiated samples, and post heat treatment can accelerate this process. In details, part of the trapped electrons in PO_3-EC, PO_4-EC and PO_2-EC defects recombines with POHC defects through the conduction band to form Q^3 units under thermal energy. Meanwhile, some free electrons are captured by OHC defects to form Q^0 units under air atmosphere, which result in the decreased OHC defect. Heat treatment is effective way to remove the gamma radiation-caused defects by recombination of HC with EC defects in the considered phosphate-based glasses.

5. Factors that affect the defects in phosphate-based glasses

5.1. Influence of Ce and Sb doping on the defect-state in phosphate-based glass

As we all know, the induced transmittance decrease in optical glasses is mainly due to the absorption by color centers in glass matrix [18]. The radiation resistance [19], i.e. the suppression of the decreased transmittance in optical losses, of the optical components including optical glasses, color-separation gratings and protective filters can be improved by doping of cerium [20, 21]. Cerium ions have two valence states, Ce^{3+} and Ce^{4+} in these phosphate-based optical glasses. Trivalent ions can be converted into tetravalent ions by capturing the radiation-induced holes, thus inhibiting the generation of hole centers. And tetravalent ions inhibit the formation of electrons centers resulting from trapped electrons, which prevents to some extent the formation of color centers that have large absorption in the visible range [22].

Figure 7 shows the O1s XPS spectra of Ce doped samples. These bands located at the higher and lower binding energy are ascribed to bridging oxygen (BO) and non-bridging oxygen [23] (NBO), respectively. It can be found that NBO (the ratios of the peak's area of NBO to the sum peak's area) in Ce-doped sample decrease from 58.7 to 54.6%, while BO increase, compared with the Ce-free sample. This indicates that NBO bond can be destroyed by Ce-doping

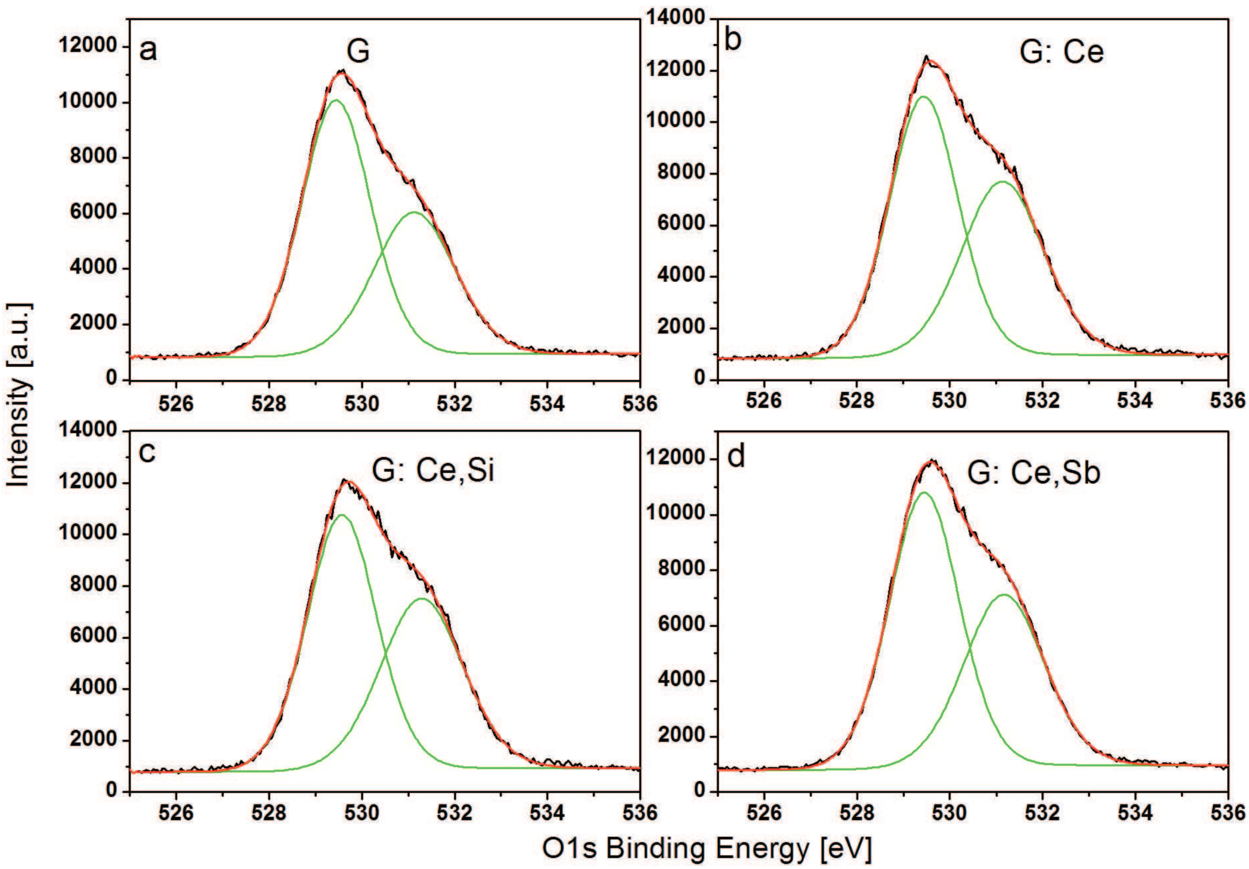

Figure 7. Measured O1s XPS spectra of G (a), G: Ce (b), G: Ce,Si (c) and G: Ce,Sb (d) glasses with Gaussian peak fittings [18].

in these types of phosphate-based glasses. Nevertheless, as for these co-doped samples, the ratio of NBO in the Ce and Sb co-doped sample increase from 55.1 to 57.6% and BO decrease compared with that of Ce and Si co-doped sample. This suggests that the trend of breaking NBO bond can be suppressed by doping of Si or Sb in these Ce-containing phosphate glasses.

Figure 8a shows that more color centers are generated in these phosphate-based glasses when exposed to the gamma radiation. These color centers have large absorption in the UV and visible region as shown by the transmittance decline. By increasing the total radiation doses, the transmittance further decreases, especially at around 385 and 525 nm, which is ascribed to POHC and PO_3-EC defects [15]. Under gamma radiation with the total dose of 250k rad(Si), the radiation resistance (transmittance ratio of the irradiated to that of the non-irradiated sample at certain wavelength) of cerium-doped glass is improved from 56.4 to 61.9% at 385 nm, and from 57.39 to 73.9% at 525 nm. This radiation resistance can be further enhanced in co-doped samples, especially for the Sb co-doped sample, i.e. their radiation resistance increases to 92.4% at 525 nm. This is in accordance with the changes of glass color in **Figure 8** (inset). These results indicate that the radiation resistance of gamma radiation can be significantly improved by doping Sb^{3+} in Ce-containing phosphate glasses. As we further increase the

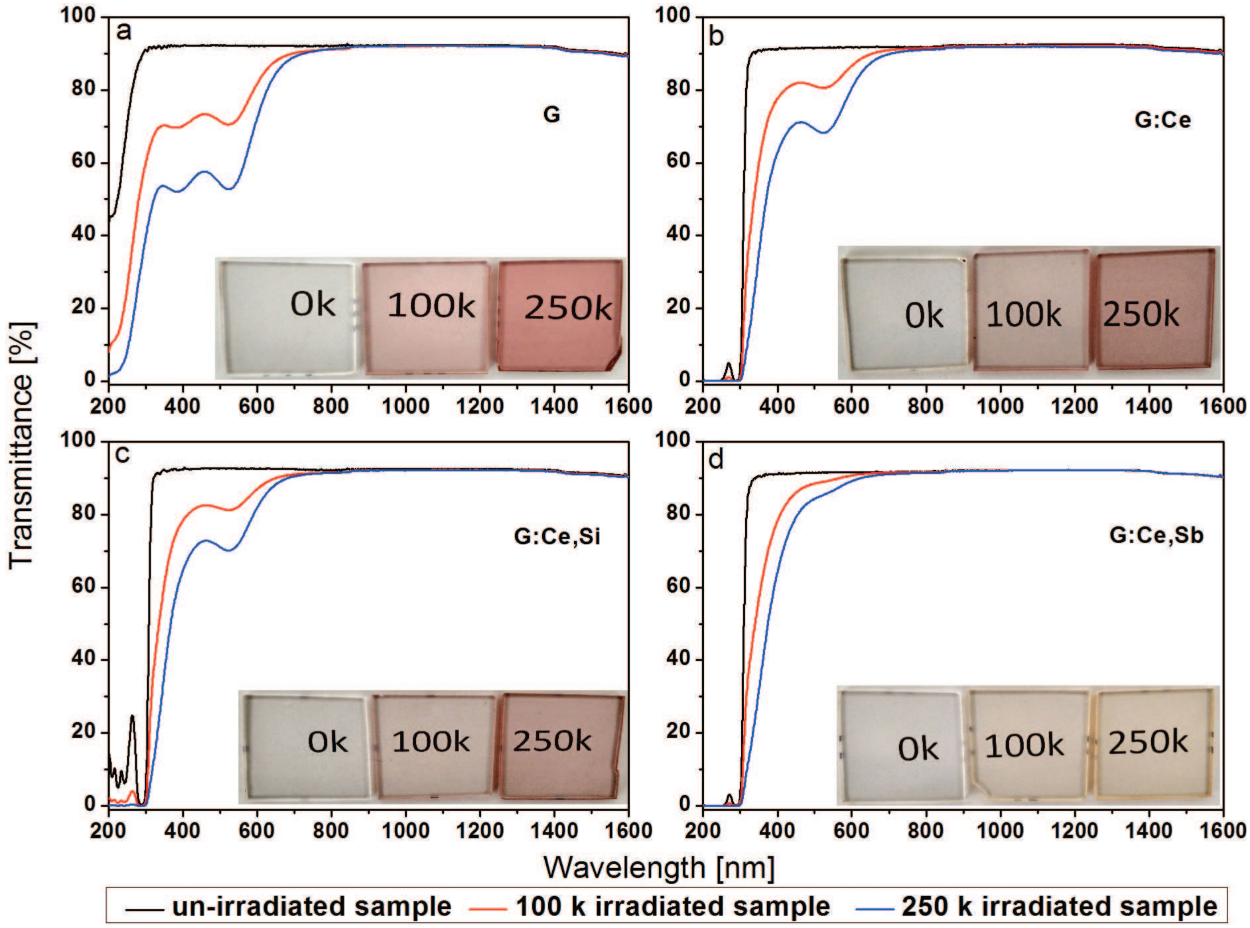

Figure 8. Measured transmission spectra and (inset) photograph of G (a), G: Ce (b), G: Ce,Si (c) and G: Ce,Sb (d) glasses before and after gamma radiation (100k and 250k rad (Si), respectively) [18].

content of cerium (to 0.66 wt% (0.75 mol%)) in the Ce, Sb co-doped sample, its radiation resistance further increases to 82.5% at 385 nm and 99.3% at 525 nm, the corresponding transmission spectra being shown in **Figure 9**. In details, the absorption at around 385 and 525 nm are 0.95 and 0.035 cm^{-1}, respectively. This result is better than that reported by Heng X, et al. [24].

Figure 10 compares the EPR spectra of these Ce-doped and Ce-free samples before and after gamma radiation with total dose of 250k rad(Si). The EPR spectra of these samples before irradiation are dominated by the signals with the magnetic field in the range of 3100–3500 G and around at 3355 G and are associated with PO_3-EC and POHC defects [17], respectively, especially for the Ce-free samples. It is obvious that PO_3-EC's signals decrease when CeO_2 was doped into these glasses; this is ascribed to the decreasing NBO associated with the precursors of PO_3-EC defects in the considered phosphate-based glass. Co-doped with Si in these samples, these signals become apparent. It can be found that these POHC defects signals are significantly enhanced when exposing to gamma radiation, as shown the red line in **Figure 10**. This is associated with the increase of POHC defects caused by gamma radiation. However, this signal becomes weaker in co-doped samples, i.e. Ce, Sb co-doped glasses (their defects signals significant decrease when compared with others). These results suggest that co-doping with Si and Sb can efficiently decrease the POHC defects in these Ce-containing phosphate glasses, especially for Sb ions.

It is well known that cerium ions in these phosphate-based glasses exists as Ce^{4+} that can be converted to Ce^{3+} by capturing the electrons caused by gamma radiation, thus decreasing the PO_3-EC defects. Therefore, Ce-doping causes the concentration decrease of NBO bonds,

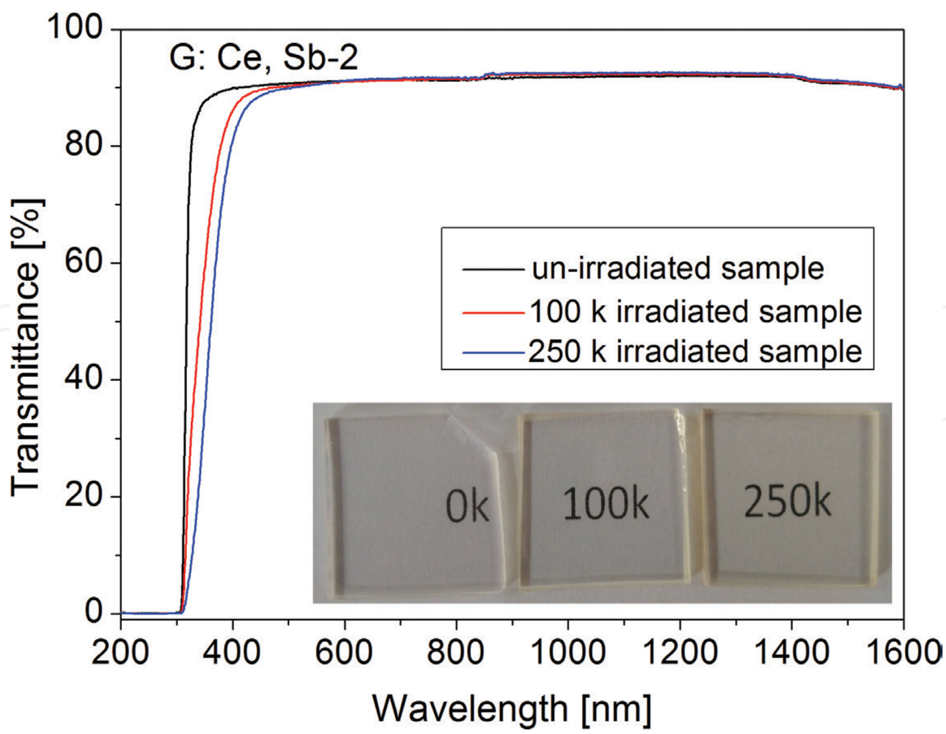

Figure 9. Measured transmission spectra and (inset) photographs of G: Ce, Sb-2 (higher Ce doping concentration) glasses before and after gamma radiation (100k, 250k rad (Si), respectively) [18].

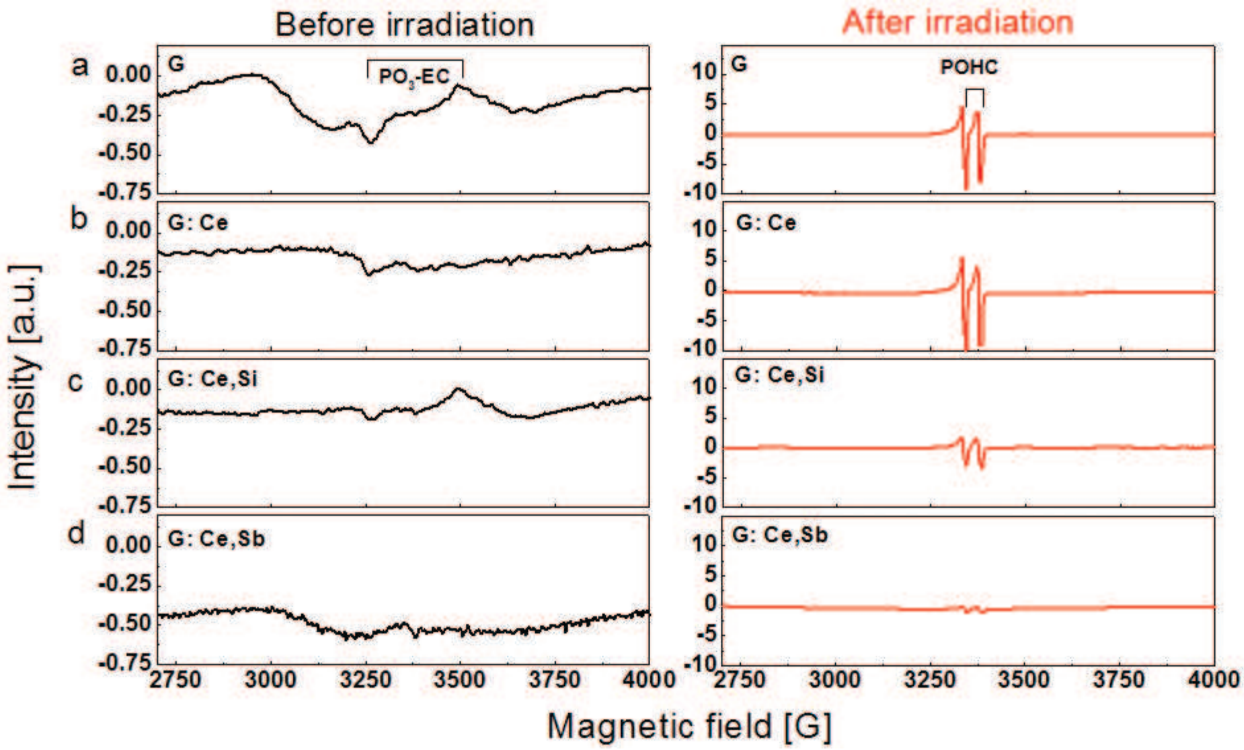

Figure 10. Measured EPR spectra of a (G), b (G: Ce), c (G: Ce,Si) and d (G: Ce,Sb) glasses before and after gamma radiation (250k rad (Si)) [18].

resulting in more limited POHC and PO_3-EC defects precursors. Besides, some Ce^{3+} ions are converted to Ce^{4+} by capturing the holes induced by gamma radiation and then suppress the generation of POHC defects. Although doping by Sb ions in Ce-containing phosphate glasses can increase the precursors concentration of POHC defects, Sb^{3+} can be easily photo-oxidized to Sb^{4+} by capturing the gamma radiation induced holes when exposed to the gamma radiation. Besides, to improve their stability, Sb^{4+} can be converted to Sb^{5+} by further capturing these induced holes. Therefore, the concentration of gamma radiation induced electrons and holes decreases in the considered phosphate-based glasses.

5.2. Influence of H_3BO_3 addition on the defect-state of phosphate-based glass

It is known that B_2O_3 addition can decrease the melting point and the crystallization temperature of the host glass, further depressing the volatilization of phosphorus and fluorine, but also improving their chemical durability and thermal stability [25, 26]. Therefore, the effects of B_2O_3 addition on the defects is critical for understanding the change of the property for the considered phosphate-based glasses.

Figure 11 presents the Raman spectra of phosphate glass samples [25]. It can be found that the peaks at around 1262 cm^{-1} decrease with the increase of B_2O_3 content, and the small peak almost disappears when the H_3BO_3:SiO_2 ratio reaches 7.5:2. Meanwhile, the intensity of the peaks located at about 666 cm^{-1} increase, which is related to the increase of B_5O_8 units [27]. The intensity of bands at around 590 cm^{-1} decrease as the H_3BO_3:SiO_2 ratio became larger, this

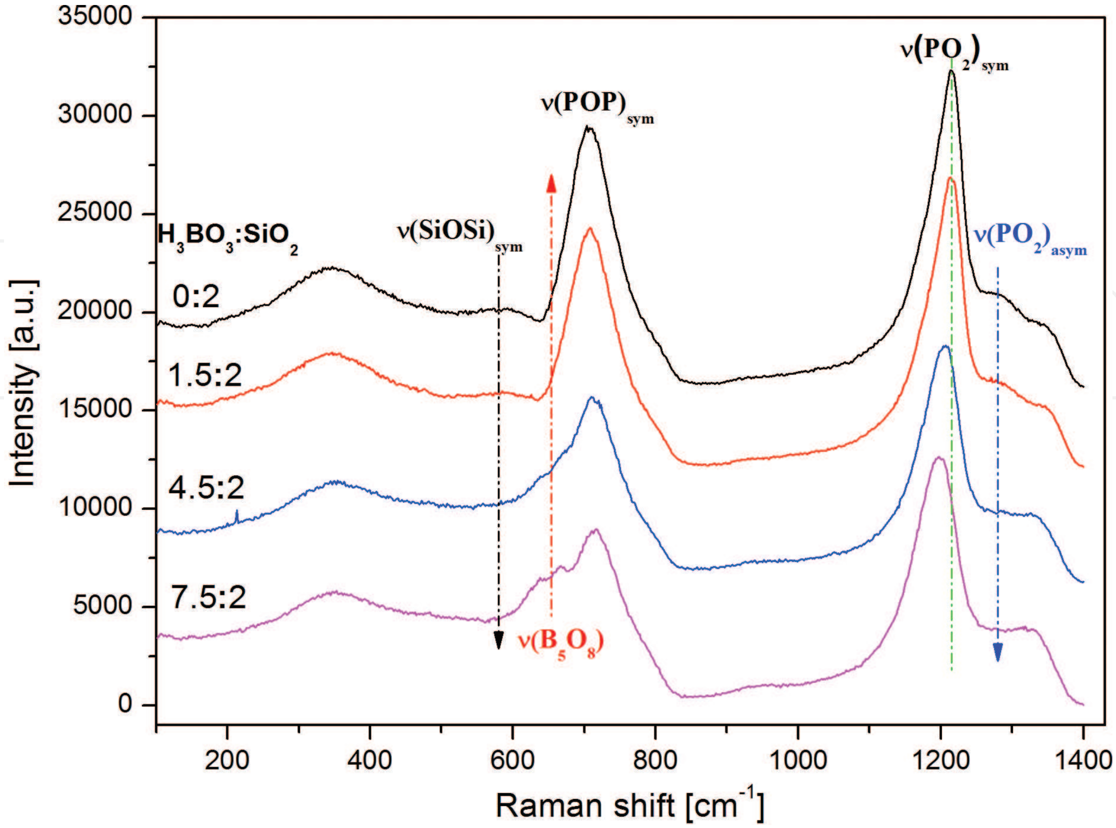

Figure 11. The Raman spectra of the series of phosphate-based glasses with different H_3BO_3: SiO_2 ratio (0:2, 1.5:2, 4.5:2 and 7.5:2, respectively) [25].

being associated with the increase of B_2O_3 and corresponding decrease of SiO_2 concentration in the final glasses. The existence of bands involving B_5O_8, together with the Rajbhandari's results [28] indicate that B_5O_8 units do not form mechanically isolated network units but rather they are bonded to each other to form a vitreous networks.

Figure 12 shows the O1s XPS spectra for different B_3O_3 content. The peaks near the lower (at around 529.5 eV) and higher (at around 531.5 eV) binding energy are assigned to NBO and BO, respectively [23]. With the introduction of B_2O_3, the non-bridging oxygens decrease, whereas the bridging oxygens increase. This is in agreement with the changes in Raman spectra in **Figure 11**.

It is interesting that the absorption of Fe^{3+} increase with B_2O_3 addition. And with further increase of B_2O_3 content, the absorption of Fe^{3+} is nearly invariant. As we all know, iron is one of the undesirable transition metal impurities that is very easily introduced through raw materials. Herein, the concentration of iron ions in the phosphate-based glasses is almost the same due to the same raw materials and preparation process. Besides, the introduction of B_2O_3 will cause the breakage of phosphate chains (**Figure 13d**) and contribute to form PO_3-EC defects. However, further increase the content of B_2O_3 in the considered phosphate-based glass, B_2O_3 could enter the glass network structure (**Figure 13e**) and form B_5O_8 units that will enhance the connectivity of these long phosphate chains, and decrease the concentration of PO_3-EC defects.

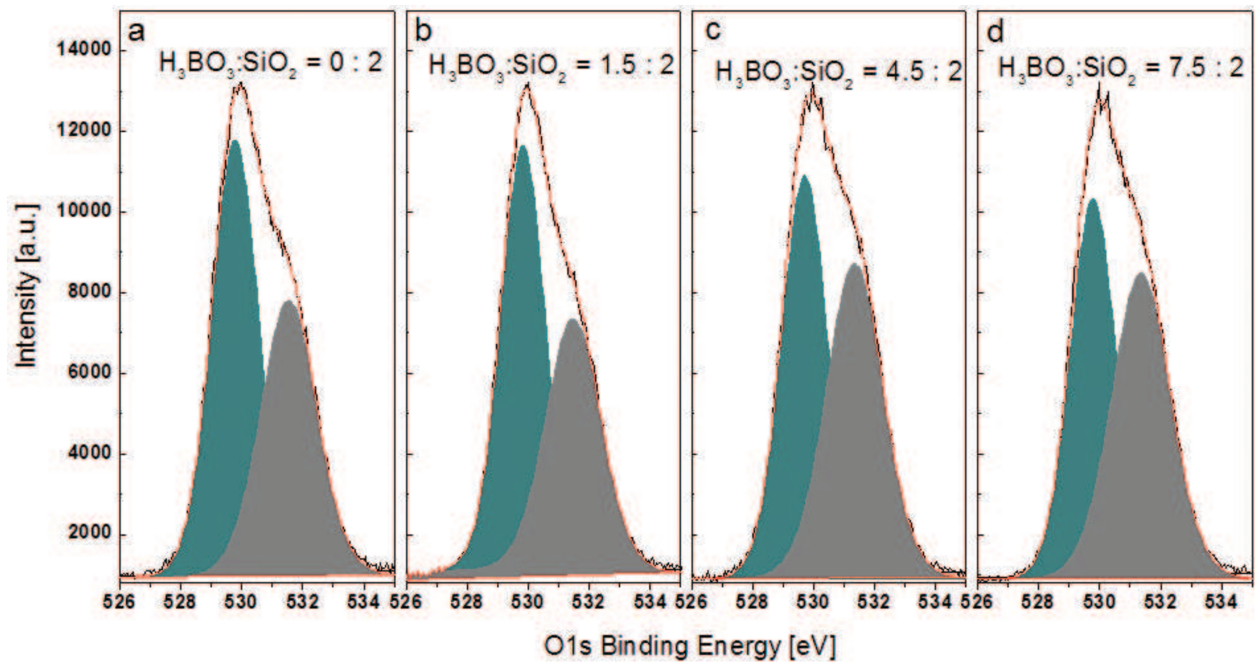

Figure 12. XPS spectra of the series of phosphate-based glasses with different H_3BO_3: SiO_2 ratio (a (0:2), b (1.5:2), c (4.5:2) and d (7.5:2)) [25].

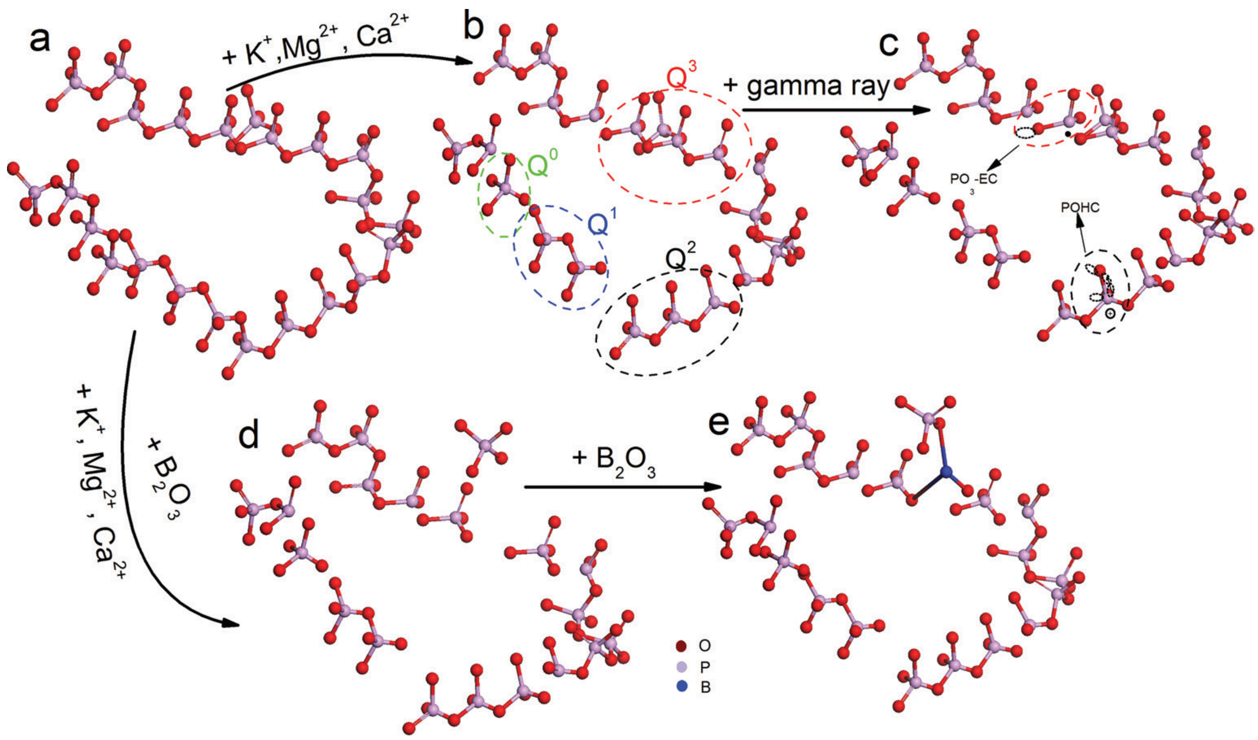

Figure 13. Schematic representations the changes of phosphate glasses network (a (the structure of basic glass), b (the structure with doped R^+ and R^{2+}), c (the structure after gamma radiation), d (the structure with doped SiO_2 and B_2O_3) and e (the structure with doped more B_2O_3)) caused by alkali (R^+), alkaline earth metal cations (R^{2+}) and B_2O_3 as well as gamma irradiation (oxygen atoms (red), phosphorus atoms (pink), boron atoms (blue)) [25].

By increasing B_2O_3, the tendency of the transmittance to decrease in the UV-VIS region is gradual until a critical H_3BO_3:SiO_2 ratio (4.5:2), when exposed to gamma radiation with high dose. By further increasing the content of B_2O_3, this trend becomes weak. These results suggest that the formed B_5O_8 can suppress the formation of PO_3-EC and POHC defects. The results provide evidence for enhanced gamma radiation resistances in the considered multicomponent phosphate glasses. Therefore, B_2O_3-doped phosphate glasses could be used as a new type of host materials for applications in space exploration and radioactive wastes treatments.

5.3. Influence of iron and cobalt on the defect-state of phosphate-based glass

Many types of doping ions together with unwanted impurities, as extrinsic defects, also influence the UV absorption and damage property of the considered glass optics [29]. Iron and cobalt-doped phosphate-based glasses show a various degree of red-shift (**Figure 14**) as compared with un-doped glass, which is dominated by the charge-transfer transition of Fe^{3+} and the absorption of cobalt, respectively [3, 13]. According to Ref. [30], the low transmittance at around 215 and 250 nm is dominated by the charge-transfer absorption of Fe^{2+} and Fe^{3+}, respectively. And the two bands between 1.9 and 2.4 eV are related to the cobalt ions [3].

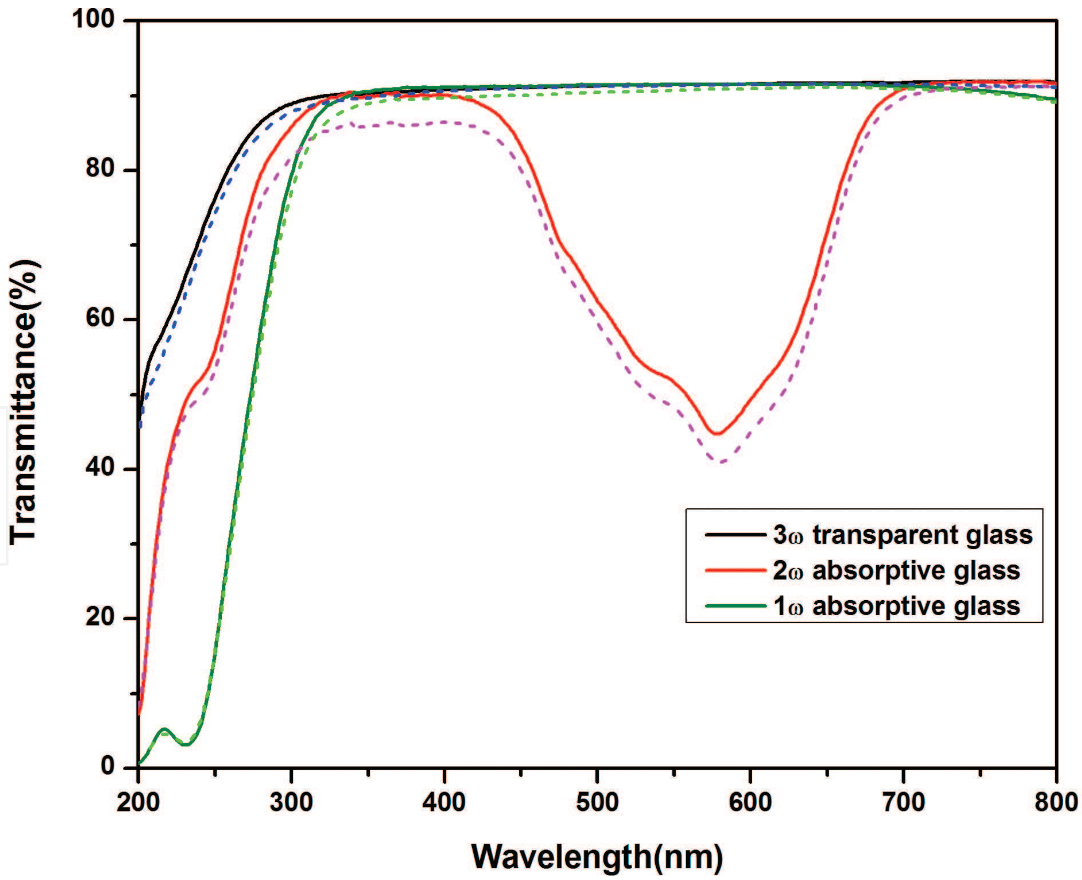

Figure 14. The UV/VIS transmission spectra of the series of fluoride-containing phosphate-based glass samples before (solid line) and after (short dash line) thermal treatment in H_2 atmosphere [29].

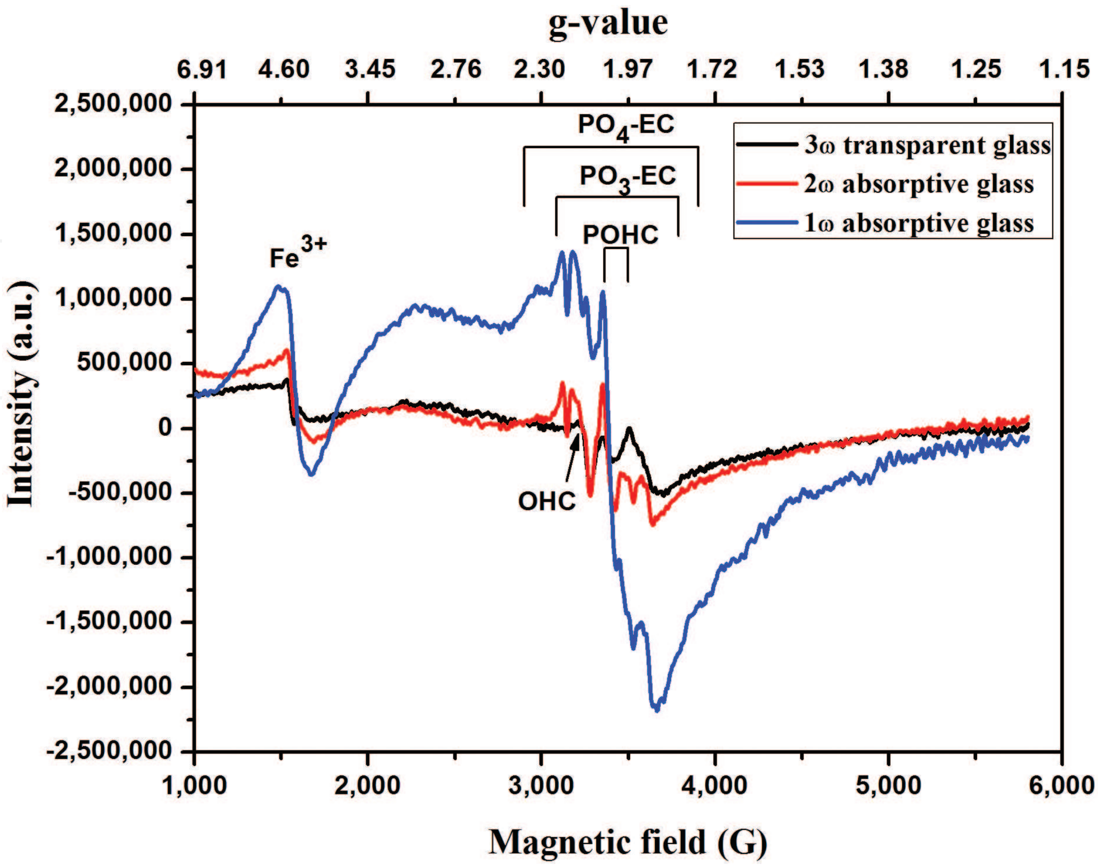

Figure 15. The ESR spectra of 1ω absorptive, 2ω absorptive and 3ω transparent glasses [29].

ESR measurements give direct evidence of the paramagnetic color centers in glasses. The ESR intensity of Fe^{3+} (g-value around at 4.3) [31] shows an order of 3ω, 2ω and 1ω glass, which is in agreement with the changes of the UV absorption edge as shown in **Figures 14** and **15**. The signals of PO_3-EC, PO_4-EC, POHC defects become apparent after doping with iron or cobalt ions, indicating that cobalt and iron contribute to form these defects. No obvious cobalt signal was found in 2ω absorptive glasses. The absence of Co^{2+} signal might be associated with the distortion of their complexes, which signal could only be detected at the practical laboratory temperature (77 K) [32].

To our best knowledge, the heat treatment in reducing atmosphere leads to the shift of the $Fe^{3+} \leftrightarrow Fe^{2+}$ equilibrium in the glasses toward the right side. Thus, it is reasonable to put forward that Fe^{3+} are favorable to form POHC defects. On the other hand, the presence of Fe^{2+} and Co^{2+} favors the formation of FD center defects, which have a large absorption cross section at ~5.50 eV. It is known that Co^{2+} is the main valence state [33, 34], in the weak basicity host glass, like phosphate-based glass; therefore, these results indicate that Co^{2+} suppresses the formation of POHC defects in this types phosphate-based glasses.

Doping with iron and cobalt shows significant impact on the transmittance of these two absorptive glasses, especially for the UV transmission edges, by influencing the concentration of other defects. The results indicate that Fe^{3+} suppress the formation of FD defects, while promotes the formation of POHC defects. Besides, Co^{2+} inhibits the formation of POHC and PO_4-EC defects, and Fe^{2+} promotes the formation of POHC defects.

6. Summary

In this chapter, we outlined some of the basic properties of the common defects in phosphate-based glasses. Gamma radiation was employed to investigate the influence of dopants on the nature of defects in phosphate-based glasses. And the evolutionary mechanism of defects associated with the post heat treatment was also discussed.

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