Radiation effects on phosphate glasses: a mini review

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Abstract

Glass and its properties are subject to a variety of changes under the influence of high energy radiation. Therefore, radiation induced defects in glasses requires high attention due to the wide application of glasses in optics on board space craft, in image guides for reactor inspection in optical fiber wave guide and in mobilization of high level radioactive waste. In this paper, we present a mini-review on radiation effects on phosphate glasses. We review the influence of various irradiation sources on the response of phosphate glasses, focusing on the advances over the past decades.

1. Introduction

High-energy radiations (X-rays, γ-rays, ultraviolet to NIR light and neutrons) on glasses have attracted attention as they can be used to modify the chemical, electrical, magnetic, mechanical as well as optical properties of the glasses due to the formation of defects in the structure of the glasses. Therefore, understanding the response of a glass to ionizing radiation is of interest, for example, in relation to specific space missions, as 87% of protons, 12% of alpha particles and 1% of heavy elements constitute the ionizing radiation originating outside of Earth's atmosphere. Electron beam irradiation of the glasses has been intensively investigated to simulate nuclear explosion and X-ray radiograph [1]. Another example of effort focused on radiation effect on glass is the electron beam radiation, which has been used to modify locally the glass, in particular in the submicron region offering the possibility to fabricate holograms in the volume of the glass, waveguide, etc. Finally, laser irradiation has been recognized as a useful tool to structure glasses. For the past 20 years, pulsed laser direct-write technique has been under investigation for the fabrication of waveguides [2], power splitters [3], couplers [4] and gratings [5], just to cite few examples. Excimer UV laser has been used to investigate the solarization in glasses which is of interest for photosensitive or photoresistant applications [6]. These radiations can produce ionization and displacement in the elements of the glasses forming electron centers and hole centers. Studies on defects in glasses induced by these different sources of radiation are then important to determine their nature, the possible mechanisms during and after the radiation and the changes in the glass properties. Therefore, many studies have been focused on investigating these radiation induced defects formed in glasses and especially in phosphate and phosphorous containing glasses, the first studies on the radiation response of phosphate glasses being reported more than 50 years ago [7]. Phosphate glasses have been intensively investigated because of the interest in developing new glasses suited to the demands of industry and low glass transition temperatures.

Presented here is a short review on some radiation effects in phosphate glasses. First, we present a general introduction of phosphate glasses before discussing the strength of the photo-response of various phosphate glasses, the response of which depends on the radiation sources, the glass composition and structure. We present first the main defects generated in the irradiated glasses and the most common techniques used to characterize them. Then, we review the response of phosphate glasses, which contain transition metal, other metals from groups IV and V as well as rare-earth ions. Finally, we discuss how the radiation can be used to crystallize and structure the glass.

2. Description of phosphate glasses

Phosphate glasses have been studied for more than 100 years ago as such glasses can find applications in a variety of industrial applications, such as high power laser [8], medical application [9], nuclear waste hosts [10], hermetic seals [11] and solid state electrolytes [12], just to cite a few applications. The applications of phosphate glasses are clear, so a better understanding of the response properties of phosphate glasses to irradiation could lead to further applications or improved glass compositions.

Phosphate glasses can be engineered with low melting temperature and high thermal expansion coefficient. Their composition can be tailored so phosphate glasses can also possess high transparency in the UV-Visible-Near Infrared (UV-Vis-NIR) region, low dispersion and relatively high refractive indices. Most of the phosphate glasses can also incorporate a large amount of rare-earth as opposed to silicate glasses. However, some of the phosphate glasses exhibit poor chemical durability limiting their applications and some of the phosphate glass melts can be corrosive leading to the corrosion of the crucible and so to impurities in the melted glass. Therefore, effort has been focused, for the past 70 years, on developing new phosphate glasses with low amount of impurities, tailored chemical durability and improved optical properties.

Phosphate glasses are usually prepared using the traditional melt-quenching method. Recently, the sol–gel process has been reported to be an alternative synthesis route [13]. Indeed, glasses prepared using the sol–gel and melt-quenched methods were found to possess similar structure [14]. Phosphate glasses with controlled morphology and composition were successfully prepared using the advantage of the low temperature of the sol-gel process and the homogeneous mixing of the reactants in the sol–gel synthesis.

The structure of phosphate glasses is formed by tetrahedral units, which are linked through covalent bridging oxygens to form various phosphate anions. The tetrahedra are classified using the Q^n terminology, where n represents the number of bridging oxygens per tetrahedron

[15]. The network can consist of a cross-linked network of Q^3 tetrahedra to polymer-like metaphosphate chains of Q^2 tetrahedra to “invert” glasses based on small pyro- (Q^1) and orthophosphate (Q^0) anions, depending on the [O]/[P] ratio as set by the glass composition. Reviews on the structure of phosphate glasses can be found in [16-17].

3. Types of radiation

The main types of radiation are

- **Ionizing radiation,** which takes a few forms: Alpha, beta, gamma and X-rays. Alpha radiation is high energy, typically in the MeV range, very short-range particle and is actually an ejected helium nucleus. Alpha radiation travels only a short distance in air, but is not an external hazard (Figure 1). Beta radiation has energies in the range of a few hundred keV to several MeV, short-range particle and is actually an ejected electron. Since electrons are lighter than helium atoms, the beta radiation are able to penetrate further than the Alpha radiation. As opposed to Alpha and beta radiation, gamma and X-ray radiations do not consist of any particles. Gamma radiation consists of a photon of energy being emitted from an unstable nucleus while X-rays originate from the electron cloud. Gamma radiation and X-rays are photons with high energy, typically from several keV to several MeV and are able to travel longer distance than beta radiation. Gamma radiation and X-rays are sometimes called "penetrating" radiation.

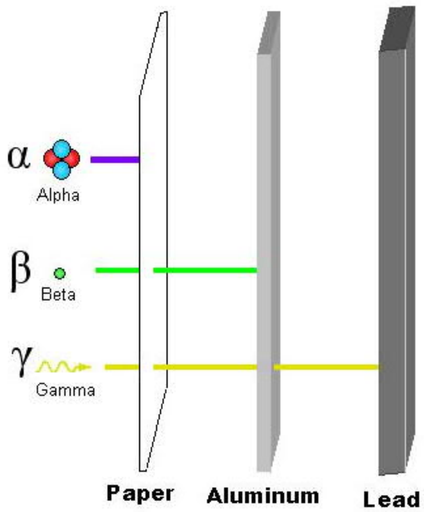

Figure 1: Radiation penetration

- **Non-ionizing radiation** or electromagnetic radiation, which refers to the photons of the electromagnetic field. It includes radio waves, microwaves, infrared, (visible) light and ultraviolet (see Figure 2).

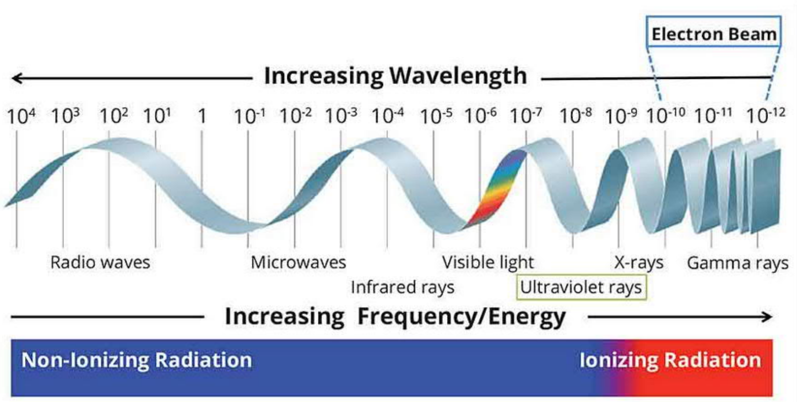

Figure 2: Schematic representation of the electromagnetic spectrum

4. Defects formation in phosphate glasses

The understanding of the response of a glass to radiation is a highly complex task as the response differs with the material under investigation and with the irradiation regime. It is well known that the irradiation of phosphate glasses can lead to the formation of defects and so to changes in the optical properties of glasses.

4.1 Types of defects

The defects have been classified according to their charge: negatively charged electron centers and positively charged hole centers. These defects are generated as a result of the creation and capture of electron and hole pairs during the irradiation process. The defects can be also classified according to their stability into transient or stable defects. The intrinsic defects result from the glass while the extrinsic defects arise from the ionization of dopants. The dopants can be either reduced or oxidized during the irradiation.

These defects include the P-related paramagnetic point defects referred as PO_2^{2-} (phosphinyl), PO_3^{2-} (phosphoryl) and PO_4^{4-} (phosphoranyl) complexes, which are characterized by an unpaired electron localized on the central P atom generally called phosphorus-oxygen electron centers (POECs) [18-19]. The other defects are the phosphorus oxygen hole center (POHC) which has an unpaired electron shared by two nonbridging oxygen atoms bonded to the same phosphorus and the oxygen hole centers (OHC). The defects are represented in Figure 3.

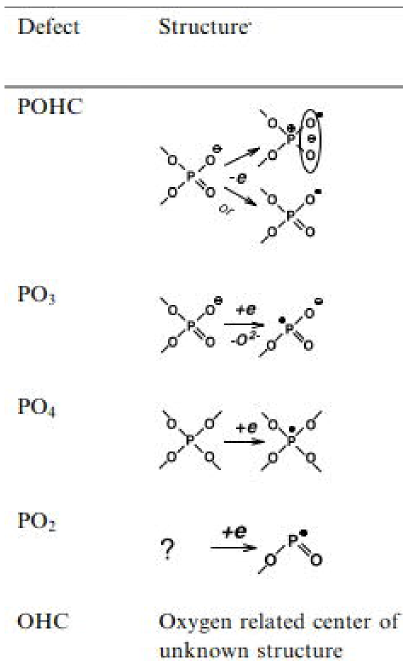

Figure 3: Representation of the various defects in phosphate glass.

Symbols: (O) oxygen ion; (P) phosphorus ion; (+) positive charge; (-) negative charge; (•) paramagnetic electron. Modified figure from [20].

As discussed in the next sections, changes in the glass composition might have an impact on the generation of defects. Indeed, the dopants added in the phosphate network can form extrinsic defects in addition to intrinsic defects in addition to intrinsic defects. They can also substitute the intrinsic defects as reported in [21].

4.2 Defects formation and stability

The type of defects and their formation rate depend on the glass (its composition and the concentration of impurities) and also on the irradiation (source and parameters). The concentration of these defects is typically in ppm.

The formation of these defects is a dynamic process. As observed in many studies [22-23], the number of the color centers first increases rapidly and then increases linearly with dose after a certain dose limit. It should be mentioned that the structure of the as-prepared glasses contains a large number of intrinsic defects, which may trap electrons or holes resulting in the formation of color centers during the irradiation. At the same time, the irradiation creates new defects, the number of which increases with an increase in the dose. The number of intrinsic defects that have not trapped electrons or holes then decreases with increasing irradiation. According to [24], the predominant effect should be related to the intrinsic defects and to the rate of formation and annihilation of the color centers associated with these defects. Equilibrium is expected when the rates of formation and annihilation become nearly equal after prolonged irradiation. It is also possible that the different growth behaviors might be due to the presence of several color centers with different rates or that there are multiple rate-determining processes operating concurrently during irradiation. When using a high energy radiation, a large number of electron hole pairs can be formed, which can be captured at pre-existing traps (precursors) associated with a hole capturing reaction in the vicinity of an electron capturing reaction.

A model of POHC formation in fluoride glasses describing the different defect generation mechanisms was reported when using ns and fs pulses [25]: Natura et al clearly showed that fs- and ns pulses had a different impact on the defects generation. The defect generation due to ns-pulses is thought to be a two-step absorption process introducing an energy transfer process. Later, Natura et al investigated the generation mechanism of the phosphorus-oxygen related hole center POHC in detail in Pb^{2+} containing glasses of various compositions (various phosphate and impurity contents) when using KrF and ArF excimer lasers [26]. They demonstrated that the generation of POHC is a two-step process including an energy transfer and a one-photon bleaching term. The generation of POHC was found to depend not only on the concentration of P_2O_5 but also on the presence of trace impurities of Pb^{2+}.

In the case of gamma as radiation source, a primary electron is ejected from an inner shell, which ionizes the medium generating electrons and holes, which can be captured at pre-existing traps. As a consequence, a hole capturing reaction takes place in the vicinity of the electron capturing reaction [27]. The two reactions are

$$PO + h^+ \rightarrow POHC \quad (1)$$

$$PO + e^- \rightarrow POEC \quad (2)$$

where h^+ and e^- are the holes and electrons, respectively, PO is a phosphorus-oxygen based defect precursor for the creation of POHC or of POEC.

Gamma radiation is suspected to also convert pre-existing defects to color centers whereas pulsed laser radiation generates free-electrons through multiphoton ionization or single-photon photoionization of the glass elements and defects when using femtosecond (fs) IR or nanosecond UV laser pulses, respectively [28]. The other reported processes could be that the radiation breaks some bonds leading to the formation of radiation induced defects and/or increases the temperature of the glass. The photo-response of the glasses is influenced by the laser processing parameters: laser fluence, translation speed, focused beam shape, beam polarization, pulse energy, pulse repetition rate, wavelength and pulse duration [29]. The radiation parameters such as the wavelength of the excimer laser was found to also impact the formation of the defects [21, 25].

The defect recovery was followed many years after the irradiation experiments [21, 30]. The intrinsic hole centers (HC) were found to either recombine with electron centers or converte into extrinsic hole centers whereras most of the extrinsic hole centers were very stable [30]. Some defects were found to increase overtime such as the amount of $(Fe^{2+})^{+}$ HC and $(Ni^{2+})^{-}$ EC although the samples were kept in the dark at room temperature [21]. Conversion of POHC into $(Co^{3+})^{+}$-HC was also reported over time in [21]. It is possible to heat the defect generation after the irradiation using thermal treatment and bleaching experiments. As reported in [26], a heat treatment and irradiation with a UVP lamp of phosphate glasses can lead to the recovery of POHC connection with the P-related paramagnetic point defects. The healing of strong defects at room temperature was postulated to be a diffusion-controlled process.

4.3 Defects characterization

The defects absorb strongly in the UV to visible spectral range and so they are often referred to as “color-centers” resulting in the coloration of the glasses as shown in Figure 4 by the gradually deepened maroon color as the total gamma radiation dose increases [31].

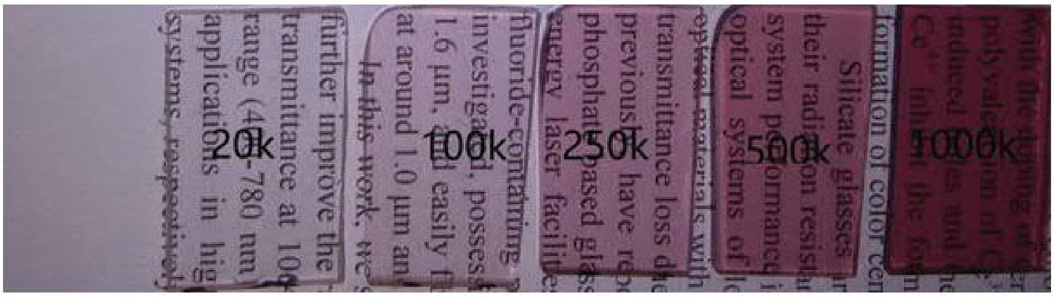

Figure 4: Picture of phosphate-based glasses with different gamma radiation doses (20k, 100k, 250k, 500k and 1000k rad [31] An increase in the total radiation dose usually increases the intensity of the absorption bands at around 385 and 530 nm suggesting that more POEC and POHC defects are generated during the irradiation process with increasing total dose.

Therefore, these defects are commonly identified using UV-Vis-NIR absorption spectroscopy from the difference between the absorption spectra after and prior to irradiation. The POHC defect has three large absorption bands in the visible (from 325 to 540nm) while the P-related paramagnetic point defects absorb in the UV from 210 to 265nm. The OHC exhibits a band at around 290 nm.

Electron paramagnetic resonance (EPR) spectroscopy has been used as a complimentary technique to analyze the defects. Complete EPR studies related to defects in phosphate glasses can be found in [19, 28, 32-33]. The phosphate bonded oxygen hole center and the phosphate related electron centers have signals in the EPR spectra, which are dominated by the POHC doublet (g~2.008, A_{iso}~4 mT). The phosphate related electron centers exhibit weaker signals (doublets between g~2.006–2.142 and with higher A_{iso} values between 27 and 126 mT) whereas the oxygen hole center has a broad singlet EPR signal, usually hidden by the POHC signal. A summary of the EPR parameters and optical absorption of the defects can be found in Table 1.

Defects	EPR parameters			Wavelength of the band maximum (± 5nm) (position of the band given in eV)
	W (mT)	A_{iso} (mT)	g_m	
POHC	1	4.0 ± 0.3	2.008±0.003	540, 430, 325 (2.30 eV, 2.88 eV, 3.81 eV)
PO_3	10	86 ±2	2.064±0.005	210 (5.9 eV)
PO_4	9	126 ± 2	2.142±0.008	240 (5.17 eV)
PO_2	7	27 ± 2	2.006±0.003	265 (4.68 eV)
OHC	7		2.014±0.001	290 (4.27 eV)

Table 1: EPR parameters and the optical absorption of radiation-induced defects in phosphate glasses. W is the half amplitude width of the line (mT), Aiso the hyperfine splitting due to ^{31}P, the distance (in mT) between two lines and g_m the middle value between g-values of both lines of a doublet. Modified table from [28]

Raman spectroscopy has been also reported to be a useful tool to analyze the structural changes induced by the irradiation. Fletcher et al. explained that the shift of the Raman band at 1209 cm^{-1}, associated with the stretching modes of Q^2 phosphate tetrahedra units, to higher and lower wavenumbers can be related to an overall expansion and/or contraction of the phosphate network after irradiation [34].

5. Impact of the glass composition on its response to radiation

The composition of the glass has an impact on the number of defects generated during radiation. Therefore, efforts have been focused on understanding the response of phosphate glasses with various compositions to different radiation sources.

5.1 Transition metal ions

Glasses prepared with transition metal ions have been of great interest as the transition metal elements can easily change their oxidation states under the action of radiation as reported in

[21,35]. Vanadium is one of the most investigated element among the transition metals as it can be incorporated in phosphate glasses with a large percent with three possible oxidation forms (trivalent, tetravalent, and the pentavalent states). The addition of Vanadium leads to the formation of glasses with interesting semi-conducting and magnetic properties [36].

The addition of transition metals leads to the appearance of new absorption bands after irradiation, which are characteristics for each transition metals [37]. The response of the glass to radiation depends primarily on the type and concentration of these dopants (or impurities). One should also mention that some ions could be photoionized during the irradiation whereas others could change their oxidation states more indirectly. According to [21], a decrease in the electro-negativity of the ions leads to an increased tendency toward photo-oxidation. For example, Möncke reported that V^{4+} in fluoride phosphate glasses could be photo-oxidized to the empty valence shell d^0 ion while Co^{2+}, Mn^{2+}, and Fe^{2+} were all photo-oxidized to the trivalent state when irradiating the glasses with an excimer laser in the UV range [21]. Mn^{2+} was reported in [21] to be more easily photo-oxidized than Fe^{2+}, and all three, including Co^{2+}, were found to be more easily photo-oxidized than Ni^{2+}. Ni^{2+} and Ti^{4+} were reported to be photo-reduced. Similar results were reported in [38] that a larger amount of defects can be formed in phosphate and fluorophosphate glasses when adding Co^{2+} or Ni^{2+}, the Co^{2+} having a stronger impact on the defects formation. The radiation photo-oxidizes Co^{2+} to $(Co^{2+})^+$ and photo-reduces Ni^{2+} to $(Ni^{2+})^-$ in phosphate glasses. These defects replace partially the intrinsic hole center defects.

Similar increase in the number of defects, besides the intrinsic phosphate-related positively charged hole centers and negatively charged electron centers, generated after X-ray irradiation was observed in phosphate glasses when adding S, Zn or Ag [39]. Those defects are for example sulfate-related electron centers (SEC), zinc centers (Zn*- positively charged hole centers) and $(Ag^+)^-$ and $(Ag^+)^{2-}$ negatively charged electron centers, as well as $(Ag^+)^+$-positively charged hole centers, respectively as explained in [39].

A retardation effect or shielding has been reported when adding high TiO_2 content (>5%) [40] or Nb_2O_5 or Sb_2O_3 [41]. When adding Nb_2O_5 in phosphate glasses, some of the electrons are captured by Nb^{5+} ions, which then become Nb^{4+}. These Nb^{4+} could then form Nb^{4+} - O - Nb^{4+} binuclear or Nb^{4+} - O - complex, and then Nb^{3+} - O - Nb^{5+} suggesting that the Nb^{5+} ions and some of the PO precursors compete for electrons. The addition of Nb_2O_5 is believed to suppress the formation of POECs and to partially inhibit the formation of POHC. In the case of Sb_2O_3, Sb^{3+} ions act as hole-trapping centers. The radiation leads to the formation of Sb^{4+} ions, which will convert to Sb^{5+}. The Sb^{5+} ions absorb electrons inhibiting the POEC formation. Similar shielding effect toward gamma irradiation was observed by adding transition metal oxide (for example MoO_3) or rare-earth such as CeO_2 [42-44]. Recently, Fayad et al. demonstrated that PbO could be also added in phosphate glass to retard or prohibit the free passage of free electrons or positive holes generated during the irradiation process [45].

Irradiation of silver containing glasses was also investigated [46,47]. Silver (and also other elements such as copper) can be in the form of ions, neutral atoms, charged or neutral sub-nanometer molecular clusters in the glass. After gamma radiation, the glasses were reported to exhibit emission bands at 500 and 620 nm probably due to the aggregation of Ag^0 and Ag^+, which probably generate additional chemically stable clusters Ag_m^{x+} such as Ag_3^{2+} [48]. An increase in the dose of the gamma radiation was found to modify the relative intensity of the 500 and 620 nm emission bands indicating the formation of Ag_m^{x+} with different m/x ratio. The electron traps Ag^0 which forms Ag^{2+} species and Ag_3^{2+} emitting centers as expressed below:

$$Ag^+ + e^- \rightarrow Ag^0 \quad (5)$$

$$Ag^+ + Ag^0 \rightarrow Ag_2^+ \quad (6)$$

$$Ag_2^+ + Ag^+ \rightarrow Ag_3^{2+} \quad (7)$$

Electron beam radiation has been of great interest as it can also be used to form metal nanoparticles as reported in [49]. Silver-containing lanthanum-phosphate glasses were irradiated using electron radiation and the spatial re-distribution of silver caused by field migration of silver ions was observed after irradiation [50]. Similar change in the state of silver and copper in glass was observed using a fs laser [51]. The use of fs laser allows one to modify the nanoparticles features allowing the control and optimization of the linear and non-linear optical properties of the particles containing glass. One of the main advantages of such irradiation is that these optical properties of the glass can be modified locally, in a submicron region leading to the possibility of fabricating hologram in glass for example as it is demonstrated in photochromic borosilicate glasses doped with microcrystals of silver and copper halides [52]. These irradiations have the advantage to be easy to use and low cost compared to other techniques such as lithography. A fs laser with high repetition rate can be used to reduce the silver ions in phosphate glasses and to diffuse the silver species resulting in the local precipitation of fluorescent silver clusters of less than 20 atoms as reported in [53].

These silver clusters can act as nucleation centers for larger entities such as nanoparticles after subsequent aggregation. A heat treatment can be further implemented to reduce the silver and grow them into metallic nanoparticles. Using this technology, three-dimensional patterning of metal–dielectric composites was successfully achieved at the sub-micrometer scale in zinc phosphate glass due to accurate control of the spatial shaping and/or orientation of the silver nanoparticles [54]. An example of laser-induced 3D structuring in silver-containing zinc phosphate glass is shown in Figure 5. A review on the recent advances in femtosecond laser-induced photochemistry in silver containing glasses can be found in [55].

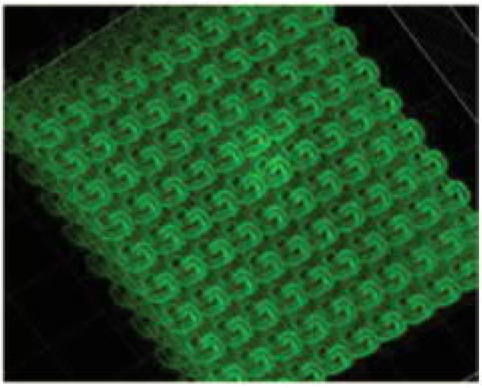

Figure 5: Bottom multi-scale blue/green-emitting fluorescent pattern in glass [55]

The response of phosphate glasses prepared with other metal and non metal ions from groups IV and V such as As, Sb, Sn and Pb upon irradiation with an excimer laser at 248nm can be found in [6]. It was reported that while Pb and Sb are predominantly in the lower oxidation states. The irradiation leads to the photoreduction of lead to $(Pb^{2+})^{-}$ and to photo-oxidation of antimony to $(Sb^{3+})^{+}$. As Sn and As are expected to be in 2 oxidation states in the as-prepared glass, both ions are suspected to be involved with different species and to form more than one defect center.

5.2 Rare-earth ions

It is now known that rare-earth ions can interfere in the releasing and trapping of electrons and their redox behavior can be related to the formation of the defect [56]. Therefore, understanding the photo-response of a lasing glass to high intensity light irradiation is a crucial importance. Additionally, degradation in the lasing property can occur during the operation of a fiber laser, especially in Yb^{3+} doped silica fiber, at high output power. This degradation phenomenon is commonly referred to as photodarkening (PD) which results to a continuous decrease in the fiber output over time [57]. Reduced PD loss was reported in phosphate fibers doped with Yb^{3+} compared to silica fiber when pumped at 980 nm [58]. Similar photodarkening was observed when using an irradiation at 193nm [59]. Luminescence quenching in the visible range was also reported after irradiating using nanosecond UV laser of Ag and Cu containing phosphate glasses, which contain molecular clusters of copper, Cu^{+} ions and/or Ag_nCu_m neutral hybrid molecular clusters [60]. It is interesting to point out that electron beam radiation was also reported to enhance the spectroscopic properties of rare-earth ions as reported for Eu^{3+} doped phosphate glass in the P_2O_5 - CaF_2 - Eu_2O_3 system [61]. The electron beam increases the inversion asymmetry site around Eu^{3+} ions improving then the electric dipole transition intensity.

Changes in oxidation states have been reported for rare-earth ions under X-ray, fs-laser, γ and β-irradiation which result in different emission properties of the glasses [62]. These changes can be usually reversible using an optical-illumination or a heat treatment of the glass at high temperature [18]. Below are the three possible reactions, which consume the generated electrons and holes, taken Sm^{3+} doping as an example. Also included is the inverse "secondary" reaction of Sm^{2+} to Sm^{3+} reconversion due to the capture of holes [63]

$$Sm^{3+} + e^{-} \rightarrow Sm^{2+} \quad (8)$$

$$PO + e^{-} \rightarrow POEC \quad (9)$$

$$PO + h^{+} \rightarrow POHC \quad (10)$$

$$Sm^{2+} + h^{+} \rightarrow Sm^{3+} \quad (11)$$

where Sm^{2+} ions have a metastable ionic environment.

It is expected that an increase in the Sm^{3+} content would decrease the POEC formation in the glass as the Sm^{3+} ions prevent the PO precursors of POEC from capturing electrons. A heat treatment of the glass above its glass transition temperature was found to return the irradiated sample back to its original un-irradiated state for reuse.

Similar changes in the oxidation states of Nd induced by gamma irradiation were also reported in [64]. An increase in the absorption below 600 nm was observed and was found to depend on the dose of irradiation. The irradiation also generated two additional absorption bands below

600 nm, which became one very broad band with high intensity when using an irradiation dose of 500 kGy. These changes in the absorption spectra confirmed that the irradiation produced different kinds of defects in the glass material but also led to the conversion of oxidation state of Nd^{3+} to Nd^{2+}. This change in the oxidation state was evidenced by the changes in the photoluminescence of Nd doped phosphate glass. A decrease in intensity of the two strong emission bands at 805 and 870 nm of Nd^{3+} which also red shifted was observed after gamma irradiation. This change was found irreversible at room temperature.

Studies of X-ray irradiation of rare-earth doped phosphate can be found in [65]. X-ray irradiation led to the formation of both $(Eu^{3+})^-$ and $(Eu^{2+})^+$ ions, $(Tb^{3+})^+$ ions and so to the suppression of the formation of the intrinsic POHC defects due to the formation of $(Eu^{2+})^+$ or $(Tb^{3+})^+$ - HC. $(Eu^{3+})^-$ -EC are expected to form at the expense of intrinsic non-paramagnetic EC of unknown structure absorbing in the far UV region.

6. Radiation to structure phosphate glasses

6.1 Phase transformation and crystallization during irradiation

Radiation can also be used to cause phase transformation and crystallization, acting like a heat treatment. Laser-induced crystallization is a novel technique to design spatially the nucleation site and to control the crystal growth direction. Indeed, a steep temperature gradient is created in the laser-irradiated local region, which is moved along laser scanning direction resulting in the patterning of crystals. Lines of $KSm(PO_3)_4$ crystals were locally precipitated in phosphate glass in the $K_2O \cdot Sm_2O_3 \cdot P_2O_5$ system using Nd:YAG laser with a power of 0.8 W and a moving speed of 0.5 $\mu m.s^{-1}$ [66]. Similar approach was used by Dubov et al. to fabricate high contrast waveguide in lithium-niobo-phosphate glass using femtosecond laser at high repetition rate [67]. The laser at high repetition rate leads to ultrafast heating and localized melting and so to local atoms/ions diffusion, non-local material transformations, and/or chemical changes in material. It is this diffusion of the chemical elements, which is thought to be the main mechanism for the refractive index contrast. The structural reorganization in glasses is typically lower if a low-repetition fs laser irradiation is used [68]. It should be pointed out that the length and rate of the ions diffusion can be controlled and tailored by optimizing the laser power and the translation speed. Finally, CO_2 laser has been also of great interest for irradiating phosphate glasses as this laser has a wavelength at 10.6 µm, which is easily absorbed by phosphate and hydroxyl groups. This laser can be used to melt or crystallize phosphate glasses while using a low energy density. As reported in [69], phosphate glasses in the $CaO-P_2O_5-TiO_2-Al_2O_3$ system can be deposited into a crystalized thin film on a substrate through melting and sintering by the laser irradiation.

6.2 Structuring of glasses

Radiation has been used to structure the surface of a glass. Especially, the use of pulsed laser for writing optical waveguides was introduced more than 20 years ago [70]. Pulsed laser irradiation is used to locally change the refractive index. According to [29], this refractive index change induced by such radiation can be related color center formation, densification (structural change) and thermal treatment (melting) of the glass.

In order to optimize the performance of the waveguide, it is crucial to determine the mode index and refractive index profiles along transverse and depth direction. Various techniques have been used to determine the refractive index profile of channel waveguides, the most common ones being based on the characterization of the near refracted field [71], different reconstruction approaches based either on the near field distribution of guided light [72], quantitative phase microscopy [73] and more recently imaging ellipsometry [74]. The change in the index induced by the fs-laser irradiation was found to be produced by ions migration [75]. The combined action of ultrafast non-linear absorption and slower heat accumulation and diffusion processes was found to significantly reduce the losses in the waveguides [76]. Recently, Fernandez et al demonstrated that the laser irradiation induces a transient plasma distribution which can be used to predict the distribution of the refractive index in the waveguide induced by the ion migration [77]. From the measurement in situ of the plasma emission during the writing process, they showed that the axis of the ion migration in a La-phosphate glass is determined by the long axis of the plasma distribution. The local increase in the refractive index was related to the ion migration. Due to the migration of heavy elements, waveguides were successfully written in commercial phosphate glasses [78-79].

One should point out that most of the phosphate glasses exhibit complex refractive index profile depending on the combinations of different laser processing parameters making the fabrication of index changed based glasses with high quality quite challenging [29]. Fletcher et al explained that the changes of the refractive index induced by the fs laser depends on the initial structure of the glass [80]. By tailoring the structure and the composition of phosphate glasses, positive changes in the refractive index induced by a femtosecond laser can be successfully obtained as in Zn-containing phosphate glasses as shown in Figure 6 [80].

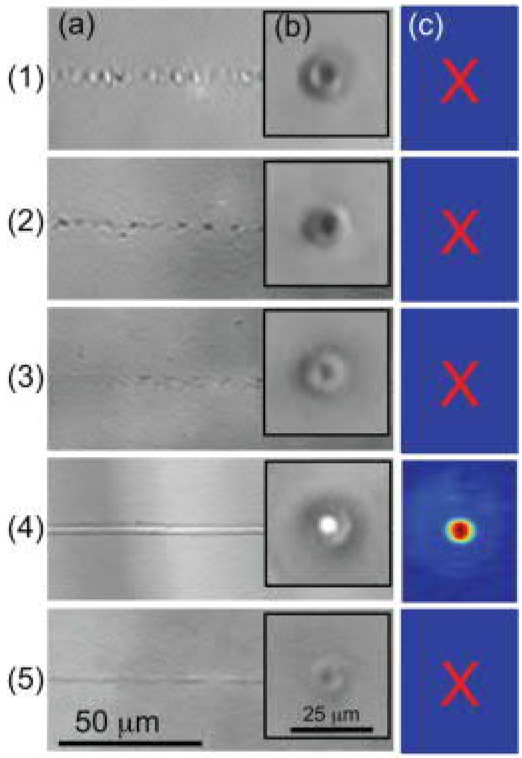

Figure 6: White light images of the modification along the waveguide direction (a), Transmission white light images of the modification cross-section (b) and 660 nm transmission near field images (c) of fs-modified zinc phosphate glasses with the composition: (1) 30.0ZnO-10.0Al_2O_3-60.0P_2O_5; (2) 50.0ZnO-50.0P_2O_5; (3) 55.0ZnO-45.0P_2O_5; 4) 60.0ZnO-40.0P_2O_5; (5) 0.7Er_2O_3-1.3Yb_2O_3-56.0ZnO-42.0P_2O_5 [80]

Laser with high intensity can also be used for the fabrication of micropores or cavities within the bulk of the glass due to local micro-explosions. These micro- or even nano-fabrications are based on laser induced changes of the refractive index which often results from the depolymerization of the phosphate network by the fs laser as explained in [81].

Radiation can also be used to increase the surface roughness of the glass surface. Electron beam irradiation was found to create micro-flaws resulting in changes in the wetting angle and also in a decrease in the microhardness as reported in [82]. Similar increase in the surface roughness was reported after alpha particles irradiation of the glasses within the P_2O_5-SrO-Na_2O-ZnO system which was found to increase also the intensity of the Er^{3+} emission at 1.5µm [83]. One should point out that although a complete study on the effect of alpha particle irradiation on four mid-IR materials was reported in [84], only very few studies on alpha particles irradiation of phosphate glass can be found.

Future Opportunities

The recent advances in the field of radiation effects on phosphate glasses were reviewed in this paper. Over the past decades, considerable progress has been achieved in understanding the response of phosphate glasses with different compositions to various radiation sources. Due to the growing interest in this research topic, studies are still in progress around the world to develop new phosphate glasses, which can better survive harsh environments needed in most applications or which are more sensitive to laser irradiation needed for the fabrication of high quality of waveguiding systems.

The ongoing research studies provide evidence for enhanced radiation resistances or enhanced sensitivity to radiation in multicomponent phosphate glasses. However, deeper knowledge of radiation effects on phosphate-based matrix still remains necessary for the development of phosphate glasses with better performances in radiative environments paving the way for a potential method for improvement of photonics devices for example.

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Figure caption

Figure 1: Radiation penetration

Figure 2: Schematic representation of the electromagnetic spectrum

Figure 3: Representation of the various defects in phosphate glass.

Symbols: (O) oxygen ion; (P) phosphorus ion; (+) positive charge; (-) negative charge; (•) paramagnetic electron. Modified figure from [20].

Figure 4: Picture of phosphate-based glasses with different radiation doses (20k, 100k, 250k, 500k and 1000k rad [31]

Figure 5: Bottom multi-scale blue/green-emitting fluorescent pattern in glass [55]

Figure 6: White light images of the modification along the waveguide direction (a), Transmission white light images of the modification cross-section (b) and 660 nm transmission near field images (c) of fs-modified zinc phosphate glasses with the composition: (1) 30.0ZnO-10.0Al_2O_3-60.0P_2O_5; (2) 50.0ZnO-50.0P_2O_5; (3) 55.0ZnO-45.0P_2O_5; 4) 60.0ZnO-40.0P_2O_5; (5) 0.7Er_2O_3-1.3Yb_2O_3-56.0ZnO-42.0P_2O_5; (6) 0.7Er_2O_3-1.3Yb_2O_3-58.8ZnO-39.2P_2O_5 and (7) 65.0ZnO-35.0P_2O_5 glass [80]

Table caption

Table 1: EPR parameters and the optical absorption of radiation-induced defects in phosphate glasses. W is the half amplitude width of the line (mT), Aiso the hyperfine splitting due to ^{31}P, the distance (in mT) between two lines and g_m the middle value between g-values of both lines of a doublet [28]