Ceramics-Silikáty 69 (2), xx-xx (2025)
www.ceramics-silikaty.cz doi: 10.13168/cs.2025.0004

DEFECT FORMATION AND RADIATION RESPONSE IN PHOSPHATE GLASSES: THE INFLUENCE OF LANTHANIDE AND OTHER EFFECTIVE DOPANTS

ANURAK PRASATKHETRAGARN, #ARRAK KLINBUMRUNG

School of Science, University of Phayao, Phayao, 56000, Thailand

#E-mail: Arrak.kl@up.ac.th

Submitted November 13, 2024, accepted February 2, 2025

Keywords: Defect formation, Radiation response, Phosphate glasses, Lanthanide dopants

Lanthanide-doped phosphate glasses show promising applications due to their improved mechanical, optical, and radiation shielding properties. This review examines the effects of lanthanide and other dopants on defect formation and radiation response, emphasising advancements in material performance. Lanthanide ions have unique electronic structures that affect the types and distributions of defects within the glass matrix. This significantly alters the properties, such as luminescence, mechanical stability, and radiation resistance. A comprehensive understanding of how the defects relate to the dopant concentration and glass structure is crucial for optimising these materials for applications in radiation shielding, photonic devices, and medicine. This study compiles essential insights on defective behaviour and its impact on glass performance under radiation, creating a framework for developing advanced phosphate glass materials with adjustable properties for high-stakes environments.

INTRODUCTION

In recent decades, extensive research has been conducted on the formation of defects in lanthanide phosphate glasses and their response to radiation [1]. These glasses exhibit distinctive optical, magnetic, and luminescent properties [2, 3]. The materials are crucial in laser technology and optical devices and have promising potential in radiation detection, biomaterials, and nuclear waste encapsulation. An improved understanding of how radiation affects glass defects leads to the enhanced reliability of these materials in various industries.

Phosphate glasses have their optical and mechanical properties modified by adding various metal oxides, altering their properties for specific applications due to their unique structure and atomic arrangements [3]. As the content of the metal oxide modifier increases, the structure of the glass changes from a network to chains, which allows for the adjustment of its properties [4]. To fulfil specific requirements, various metal oxides, including Na_2O, CaO, Ag_2O, TiO_2, MgO, and ZnO, were mixed to adjust the features of the glass [2]. These glasses possess exceptional mechanical, electrical, optical, and magnetic properties, making them suitable for applications [5]. Due to their limitations, phosphate glasses have issues with the density of low-energy excitations, which affects their vibrational properties.

Nevertheless, adding lanthanide ions, such as samarium (Sm), can decrease these excitations, improving the glass's behaviour [6]. Adding modifier cations reduces ionic bonds in phosphate glasses, impacting the durability and stability. However, adjusting the concentration of modifier ions can impact the coupling between structural units and potentially enhance the properties of the glass. Phosphate glasses might contain water or OH groups, which can significantly impact their high-temperature acoustic loss, suggesting that controlling the composition to minimise these defects could improve the performance [7].

Rare earth-doped phosphate glasses have excellent optical properties and high solubility of rare-earth ions, making them attractive for engineering photonic devices. Lanthanide elements possess remarkable optical and luminescent properties [8]. Their unique atomic electron layer arrangements significantly affect their physical and physicochemical properties. Depending on the specific lanthanide, they can emit light across various colours from UV to NIR [9]. These elements have proven valuable in various applications due to their narrow and identifiable 4f-4f transitions, making them generally safe for optical applications [9]. Their low human systemic toxicity also supports their application in fields such as photovoltaic devices, electronics, and sustainable energy research [10]. Lanthanide ions in phosphate glasses have unique emission peaks and extended luminescence lifetimes, making them useful for scintillation devices and optical amplifiers. However, radiation exposure can alter their optical and mechanical properties [11]. Thus, understanding this impact is crucial, especially in the detection field.

While the addition of lanthanide ions is known to improve the glasses' luminescent and radiation-shielding properties, the mechanisms underlying defect formation and its impact on material behaviour under radiation remain insufficiently explored. Most prior research has focused on individual effects, lacking comprehensive insights into the interplay between the lanthanide concentration, defect types, and resulting glass performance under various radiation types. This review aims to explore the mechanisms behind the defect formation in lanthanide-doped phosphate glasses and how these materials respond to various types of radiation. By examining recent advancements in defect-controlled glass technology, we establish a basis for developing materials optimised for durability and performance in high-radiation environments. This is particularly important for applications such as radiation shielding, optical amplifiers, and photonic devices.

REVIEW

Defect formation in lanthanide phosphate glasses

Defects in phosphate-based glasses may arise from the glass matrix, impurities, or dopants. These glasses comprise P-tetrahedra that form phosphate chains [12]. Various factors can influence the formation of these chains and the occurrence of defects within the glass. Lanthanide phosphate glasses can be affected by defects caused by ionising radiation, thermal treatment, and variations in composition, as presented in Table 1. These factors can significantly impact the properties of the glasses for specific applications. It is essential to understand the mechanisms behind these imperfections to optimise the properties of lanthanide phosphate glasses for different purposes.

Fabrication-induced defect mechanisms

Non-stoichiometry

Properly balancing the lanthanide dopant and phosphorus composition is crucial when creating lanthanide phosphate glasses. If the non-stoichiometry is not adequately maintained, it can form vacancies and interstitials in the glass structure. Defects in the glass composition can considerably impact its optical and luminescent properties. The presence of lanthanides, such as cerium (Ce), praseodymium (Pr), neodymium

Table 1. Defect formation mechanisms in lanthanide phosphate glasses.

Defect Mechanism	Description	Effects on Glass Properties	References
Non-stoichiometry	An imbalance in the ratios of lanthanide dopants and phosphorus leads to vacancies and interstitial defects in the glass	Alters the optical and luminescent properties by creating non-bridging oxygens (NBOs)	Sun et al., 1986 and Maciejewski et al., 2023
Interstitial Defects	Lanthanide ions or phosphorus atoms occupy spaces between the phosphate tetrahedra	Reduces the luminescence efficiency and structural integrity	He et al., 2018
Cooling Rates	The rate of cooling impacts the balance between the amorphous and crystalline phases	Slower cooling increases the structural strength, but may introduce softening defects	Nelissen et al., 2007
Thermal Treatment	High-temperature annealing to relieve stresses or adjust atomic arrangements	Can cause oxygen vacancies or rearrange lanthanide ions, impacting the durability	Pukhkaya et al., 2014
Radiation-Induced Defects	Exposure to gamma, X-ray, or neutron radiation displaces the atoms and creates point defects	Alters the optical transparency, increases the UV absorption, changes the mechanical strength	Wang et al., 2016 and Rautiyal, 2021

(Nd), and gadolinium (Gd), in the phosphate glass matrix disturbs the structure and properties of the glass, resulting in a deviation from its expected chemical composition. The component is referred to as the non-stoichiometry in lanthanide phosphate glasses. This chemical imbalance induces alterations in the glass network, like the creation of non-bridging oxygens (NBOs) and the conversion of phosphate chains, which critically impact determining the optical and structural characteristics of the glass.

Moreover, interstitial defects can be observed in lanthanide phosphate glasses, where lanthanide ions or phosphorus atoms occupy interstitial spaces between phosphate tetrahedra. The defects of the luminescence efficiency can significantly impact the material's optical properties. The phosphate glasses doped with lanthanide ions (Pr^{3+} and Eu^{3+}) have shown that these defects can lead to changes in the luminescence characteristics [13]. Phosphate glasses can be altered through its unique structure by adding lanthanum oxide [14]. The structural properties and preparation of lanthanum phosphate glasses lead to changes in the physical properties and the phosphate network's evolution from a cross-linked triphosphate to a chain-like metaphosphate structure with the increasing lanthanum oxide content. The arrangement of phosphate glasses depends on their composition and the bonding of phosphor-oxygen tetrahedrons [14]. The phosphate composition in lanthanum (La) glasses is more complex than in glasses made with lithium (Li). This complexity can be explained by the fact that lanthanum atoms (La^{3+} cations) strongly attract the phosphate components (anions) due to their coulombic interactions. Similarly, Pr-incorporated phosphate glasses have indicated the asymmetric stretching vibrations of terminal oxygens on tetrahedra with different bonding configurations [15]. Adding lanthanides to the phosphate glass matrix is managed to simulate the containment of radioactive waste, aiming to preserve the non-crystalline structure of the glass while refining its physical and optical attributes.

Cooling rates

The cooling rate plays a significant role in determining the structure and properties of lanthanide phosphate glasses. Low cooling rates, as observed in solidifying phosphate melts containing nuclear waste, lead to partial crystallisation and elemental partitioning between crystalline and glass phases. Glass composition changes can significantly impact the La elements' leachability [16]. Note that the quantity of Al_2O_3 in the glass impacts the leachability. However, glasses can be formed across various compositions even with relatively slow cooling. Therefore, the cooling rate plays a significant role in determining the mechanical behaviour. The cooling rate influences the balance between the amorphous and crystalline phases of the material. A slower cooling rate leads to increased strength and a tendency towards softening, while a faster cooling rate results in more empty spaces that affect the material's strength and ability to deform. The presence of lanthanum oxide in calcium phosphate glasses suggests that the cooling rate may also affect the distribution of lanthanide elements within the glass structure, potentially altering the optical and physical properties [17]. The observation shows that the cooling rate is critical in determining the structure, imperfections, and properties of lanthanide phosphate glasses.

Thermal treatment

Thermal treatment methods often improve lanthanide phosphate glasses by relieving stress. Incorrect conditions cause flaws in the glass structure. High temperatures during annealing may lead to atom migration and defect formation. This atomic disorder can generate oxygen vacancies or rearrange lanthanide ions. The treatment is essential in forming and repairing imperfections in glass materials. When exposed to radiation, glasses containing Yb develop paramagnetic point defects. The type and extent of these defects are profoundly affected by the structure of the glass network. To restore the defects, it is necessary to manipulate the glass thermally, and certain types of defects are more noticeable in specific glass configurations [1]. The solubility and integration of OH groups into the apatite framework in natural phosphates rely on temperature variations [18]. Similarly, thermal assessments on lanthanide polyphosphates indicate that crystallisation and weight loss occur in distinct phases. This finding suggests that applying thermal treatment parameters can influence the transition between phases and the formation of defects in these materials. Besides lanthanide dopants, the thermal treatment effectively reduces the defect levels in binary zinc phosphate glasses subjected to X-ray radiation. The swift melt-quench method used to produce phosphate-based glasses with diverse compositions highlights the impact of composition and thermal processing alterations on the thermal endurance and defect configurations, including crystalline entities [19]. The effects of gamma and X-ray radiation on glasses infused with phosphate and fluoride have revealed that heat treatment can reduce the damage caused by radiation. This result suggests that heat treatment could be a way to improve the defects caused by radiation. The optimisation of the thermal treatment parameters is crucial to minimise the defects and achieve the desired glass properties.

Radiation-induced defect mechanisms

Lanthanide phosphate glasses may develop additional defects upon exposure to ionising radiation, which can be induced in various ways.

Atom displacement

High-energy radiation, such as gamma rays or energetic particles, can displace atoms within the glass matrix. Atomic displacement occurs when the radiation interacts with the atoms, transferring enough energy to eject them from their original lattice positions. The displaced atoms can then create vacancies, interstitials, and other structural defects that can affect the optical and mechanical properties of the glass. The type and density of these radiation-induced defects depend on the energy, type, and glass composition.

Radiation, including gamma rays, X-rays, and α-particles, can cause imperfections in the phosphate-based glass that affect its optical characteristics and increase its absorption of ultraviolet light. These imperfections typically take the form of point defects, and their development and repair can be influenced by the glass network structure and additives [20, 21]. For instance, the type of glass network impacts the creation of paramagnetic point defects related to phosphorus [20]. The generation and repair of radiation-induced imperfections can be affected by the oxidation state and interaction of additives, such as cobalt, nickel, and certain lanthanides, with the glass matrix [22]. Molecular dynamic simulations suggest a universal principle governing the formation of defects in lanthanide phosphate glasses induced by atomic displacement due to radiation, as changes in the lattice parameters and the concentrations of defects are connected [23]. Various factors, including the radiation type, glass composition, network structure, and additives, influence the defects in glass materials due to radiation.

Electronic excitations

The defects in lanthanide phosphate glasses are influenced by electronic excitations caused by high-energy radiation. The generated energy level induces the creation of colour centres. Colour centres are formed when confined charges alter the optical absorption and luminescence features of the glass. The abundance of colour centres is influenced by the amount of radiation exposure and the glass composition.

The interaction between the mechanisms of radiation-induced defects and the formation of defects in lanthanide phosphate glasses is complex. This interaction creates, alters, and possibly repairs defects within the glass structure. The defects caused by electronic excitations in radiation correlate with those formed in lanthanide phosphate glasses. Various types of high-energy radiation, such as gamma rays, X-rays, and electron irradiation, can induce defects in glass that can negatively impact the optical characteristics of the material. The defects are primarily associated with the formation of electron centres (ECs) and hole centres (HCs) and are crucial in understanding the behaviour of lanthanide phosphate glasses [18]. Exposure to gamma and X-rays can cause defects that absorb the UV spectrum, degrading the glass's UV functionality. Heat treatments can restore some defects by releasing and capturing electrons in the conduction band [21]. Adding specific additives, CeO_2 and Sb_2O_3, can enhance the resistance of phosphate glasses to gamma radiation [24]. The type of glass network and the presence of trace impurities significantly impact the characteristics and restoration of defects induced by radiation. Electron irradiation with energies of 5 and 50 keV causes the redistribution and concentration increase of silver molecular clusters in lanthanum-phosphate glasses, significantly impacting their luminescent properties beyond the irradiation region [25]. This phenomenon stresses the involvement of electronic excitations in changing the landscape of defects within the glass. As is well-known, the generation, alteration, and restoration of defects are influenced by the interplay of radiation with the glass structure, the composition of the glass, and the presence of specific additives and impurities. Mitigating r-POHC defects is linked to the glass structure, and the glass composition and thermal treatment can affect their repair [26].

Furthermore, the proportion of H_3BO_3/SiO_2 in the glass may impact the healing response of defects induced by gamma radiation, with specific compositions exhibiting a more significant recovery of defects at ambient temperature [27]. The computational analyses have highlighted the feasibility of integrating additives of cerium (Ce^{3+}) and europium (Eu^{3+}) into the glass structures to reduce the occurrence of radiation-induced colour centres, presenting a strategy to enhance the radiation endurance of lanthanide phosphate glasses [26]. These factors influence the optical properties and functionality of the glasses, and understanding their relationship is essential for developing radiation-resistant glass materials.

Implications of the defects on the lanthanide phosphate glass

Implications of the defects on structural and mechanical properties of the glasses

Vacancies and interstitials in lanthanide phosphate glasses cause atomic deficiencies, affecting their structural and mechanical properties. These defects disrupt the glass structure, leading to density and atomic organisation changes. Structural irregularities may weaken the glass's strength and resistance to fracture. Although dislocations are exceptional in amorphous glasses, they can still affect mechanical properties by creating crack propagation sites. These defects influence the glass's response to external stresses and its ability to withstand mechanical loads and thermal fluctuations.

Phosphate glasses possess unique mechanical, electrical, optical, and magnetic characteristics, intricately linked to their atomic arrangements and structure [3]. However, imperfections can significantly impact their structural soundness and mechanical performance. For example, the addition of dopants and the resulting defect chemistry can notably influence the structural and mechanical attributes of lanthanum phosphate materials. Computational methods have demonstrated that understanding the structural aspects of deformation imperfections is crucial to comprehend the mechanical responses of bulk metallic glasses, which are illuminated through the shear transformation zones (STZs) [1]. Additionally, imperfections induced by gamma radiation could modify the optical characteristics of multi-component phosphate glasses, potentially affecting their mechanical properties. The chemical compositions of phosphate glasses, including the types of modifier ions and glass formers, play a critical role in determining their structural robustness and elastic modulus [28]. The introduction of lanthanum oxide in calcium phosphate glasses alters their structure, which could imply changes in their mechanical properties due to modifications in the glass network [29]. Imperfections in materials like phosphorene have been shown to create local stress concentrations and premature bond ruptures, leading to a significant failure in the mechanical properties [30]. This fracture emphasises the significant role of imperfections in influencing the fracture strength and overall mechanical integrity of lanthanide phosphate glasses. The mechanical and structural characteristics of iron-aluminium-phosphate bulk glass and fibres suggest that the glass composition and imperfections affect the tensile strength and Young's modulus [31]. Finally, the transformation of the phosphate network in glasses with varying lanthanum oxide content indicates that imperfections impacting the La-coordination environment could have repercussions for the mechanical properties of these glasses [32]. The structural and mechanical properties of lanthanide phosphate glasses are significantly affected by their imperfections, whether intrinsic or induced by dopants and radiation. These properties are essential for their application in fields that require precise mechanical behaviour and structural reliability.

Electrical conductivity

The defects significantly influence the electrical conductivity of lanthanide phosphate glasses. These imperfections can either help or hinder the movement of electrical charges within the glass structure. Introducing transition metal oxides, like iron oxide, into phosphate glasses causes structural defects due to ion and polaron migration. The atomic disorder can interfere with the crystalline framework and reduce conductivity by creating gaps in the pathways for conduction [33]. The electrical conductivity of phosphate and germanate glasses can be changed by introducing lanthanide ions. The ions have nearly empty or incompletely filled 4f electron shells. The change in conductivity occurs because of carrier hopping between metal ion sites with different valency states. The electronic configuration of lanthanides affects the electrical properties of the corresponding glasses [34]. When strontium is added to the lanthanum ultraphosphate and neodymium oxyphosphate glasses, the protonic defects impact the electrical conductivity. This impact varies depending on the temperature and surrounding atmosphere. The incorporation of lanthanum oxide into vanadophosphate glasses enhances the overall conductivity. This indicates that the mechanism of mixed ion–polaron conduction is influenced by the lanthanum content, which affects the activation energy of polarons [35]. Moreover, the transformation of cerium and lanthanum phosphate glasses through recrystallisation substantially enhances the glass's conductivity. The improvement underscores the influence of alterations in microstructure on the electrical characteristics [36]. Deviations in the conductivity observed in vanadate-phosphate glasses containing alkali ions are attributed to variations in the environment surrounding the vanadium ions. The alteration suggests that the conductivity of these glasses is responsive to specific structural arrangements induced by doping [37]. A comprehensive examination of phosphate glasses highlights the significance of reducing the charge density and maximising the proximity of sites. This optimisation is necessary to improve the conductivity, emphasising the crucial role played by the structural organisation of cations [38]. In conclusion, the conductivity of lithium-doped vanadophosphate glasses demonstrates an involved interplay between the composition and temperature. The effect of dopant emphasises the impact of structural modifications on the electrical properties of these materials [39]. Doping, recrystallisation, or changes in the composition affect the electronic structure and movement of charge carriers, influencing the electrical properties of the glass.

Optical and luminescent properties

Lanthanide phosphate glasses are commonly utilised in lasers, optical amplifiers, and phosphors, yet their optical and luminescent qualities may be compromised by imperfections that absorb and scatter light. Gamma ray-induced imperfections in multi-component phosphate glasses can change the optical properties, including UV absorption, but certain flaws can be mitigated through heat treatment, enhancing the resistance to gamma radiation when co-doped with oxide substances. Lanthanide-doped phosphate glasses display unique emission lines across spectra from ultraviolet to infrared due to intra-4f electron transitions. The intensity of these emissions is enhanced through heat treatment, the utilisation of defect states, and the manipulation of band structures, which can boost the lanthanide luminescence by creating more efficient excitation pathways [40].

Additionally, the formation of imperfections, such as oxygen hole centre defects and colour centres related to fluorine, is closely linked to the luminescent properties of fluoride-containing phosphate-based glasses, indicating that micro-imperfections play a pivotal role in determining the photoluminescence characteristics. The effects of ionising radiation on the luminescent properties in phosphate glasses reveal that the clustering of Yb or Er restricts defect formation at high doses, influencing the luminescence duration and suggesting a mechanism involving specific defect types [41]. Additionally, defects induced by lasers in (fluoride-) phosphate glasses doped with polyvalent ions such as Zr, Nb, and Ta demonstrate that reduced dopant species serve as external hole centres, impacting the defect restoration and stability, which is crucial for applications in optics and photonics. The creation of luminescent Eu(III) coordination glasses also showcases the influence of coordination structures on glass formability and luminescence, producing intense emission due to the specific regiochemistry of substitution [42]. The association between defect formation induced by X-ray radiation in zinc phosphate glasses and luminescent properties emphasises the significance of defect generation and restoration in determining the optical performance of these materials [25]. The imperfections in lanthanide-doped phosphate glasses significantly impact their optical and luminescent properties, with implications for their use in high-energy laser systems, lighting, and photonics.

Radiation Response

The response of lanthanide phosphate glass to ionising radiation is affected by imperfections, leading to changes in the optical properties. Radiation exposure forms defects acting as colour centres, impacting the absorption and luminescence. Radiation-induced voids and extra atoms create charge carrier recombination sites that influence the electrical conductivity. The type and number of imperfections depend on the radiation factors and glass composition, which is crucial for using these glasses in radiation-related applications.

The optical absorption and luminescence characteristics of lanthanide phosphate glasses can be altered by imperfections induced by exposure to gamma, X-ray, and laser radiation, affecting their functionality in specific applications. Studies have shown that introducing certain ions into these glasses can impact their response to radiation [43]. For instance, co-doping with CeO_2 and Sb_2O_3 can enhance the resistance of phosphate glasses to gamma radiation, suggesting a technique to enhance their durability and performance in demanding radiation environments [44]. Similarly, incorporating Nb and Sb can reduce radiation-induced attenuation, indicating a protective function of these additives against radiation damage [26].

During irradiation, imperfections, such as hole centres (HCs) and electron centres (ECs), are generated. The charge centres can either remain stable or undergo recovery processes depending on the glass composition and the presence of specific dopants. For example, the glass composition has influenced the recovery of defects caused by gamma radiation, indicating that certain compositions facilitate self-healing [24]. The interaction between inherent and introduced defects and the impact of impurities, such as iron, has been emphasised, demonstrating that even small amounts of contaminants can significantly affect the formation and endurance of radiation-induced defects [45]. Adjusting the glass composition and doping elements presents a way to manage and improve these defects, ultimately improving the optical performance and durability of these materials in the presence of radiation.

Impact of the glass composition on the radiation response

Impact of the lanthanide content on the radiation response

The behaviour of lanthanide phosphate glasses under radiation depends on their composition, which affects factors such as the defect production, luminescence, and overall performance, as exhibited in Table 2. The quantity, type, network modifiers, and glass-forming substances of the lanthanide ions present interact to determine the glass's response to ionising radiation. The presence and density of lanthanide ions impact the behaviour of lanthanide phosphate glasses towards radiation. Different ion sizes can disorder the glass structure, affecting its radiation response.

The influence of the glass composition on the radiation response of lanthanide-doped phosphate glasses is markedly affected by the lanthanide content, as demonstrated in diverse research studies. Adding Nd_2O_3 to phosphate glasses has improved their ability to sense radiation, resulting in a higher density and a lower molar volume. The emerging increases photon attenuation parameters, such as the mass attenuation coefficient and adequate atomic number. This finding indicates a clear correlation between the effectiveness of radiation shielding and the presence of Nd_2O_3 [46]. Sm_2O_3-incorporated glasses exhibit changes in gamma-ray shielding characteristics. Although the mass attenuation coefficient remains unchanged after adding Sm_2O_3, the exposure and energy absorption build-up factors show significant changes in the intermediate energy range. This energy level suggests Sm_2O_3 impacts the gamma-ray shielding properties [47]. Besides the lanthanide addition, tungsten oxide (WO_3) in glasses made of lithium oxide (Li_2O), zinc oxide (ZnO), and phosphorus pentoxide (P_2O_5) results in an increase in the

Table 2. Influence of the Glass Composition on the Radiation Response.

Glass Composition Factor	Description	Effects on Radiation Response	References
Lanthanide Content	Different lanthanide ions (e.g., Nd, Sm, Yb) affect the glass density and response to radiation	Increased density improves the photon attenuation and UV blocking with Nd doping	Deol et al., 2023 and Kolavekar et al., 2023
Lanthanide Ionic Radii	Larger ions (e.g., Ce, Nd) cause network distortions, affecting the defect types and concentrations	Smaller ions (e.g., La) create fewer defects, leading to greater stability	Liang et al., 2011 and Saudi et al., 2020
Oxide Modifiers (e.g., WO_3)	Adding modifiers such as tungsten oxide can improve the radiation shielding capabilities	Higher linear attenuation, making the glass more effective for protective shielding	Saleh et al., 2022
Co-Doping with Multiple Ions	Combining dopants of CeO_2 - Sb_2O_3 increases the resistance to gamma rays	Reduces the formation of colour centres and improves the optical clarity under radiation	Heng et al., 2015
Hydration and OH Groups	Presence of OH groups impact high-temperature performance and acoustic properties	Minimising the OH content can enhance the radiation endurance and structural stability	Masai et al., 2019

linear attenuation coefficient. The improved value is due to the presence of tungsten, which enhances the glass's ability to attenuate radiation. This increase in radiation attenuation is a desirable property for protective masks used in diagnostic radiation therapy.

Additionally, lanthanide doping is used to attain specific properties in glasses. Phosphate glasses containing Ce^{3+} have been observed to exhibit strong luminescence and scintillation properties when exposed to radiation, indicating that cerium plays a critical role in modifying the glass's radiation response. These properties are essential for radiation detection applications. Ytterbium-doped oxide glasses exhibit modifications in optical and emission properties after irradiation. These alterations depend on the source and dose of irradiation, demonstrating ytterbium's impact on the glass's photo-response to radiation. Praseodymium-doped glasses maintain their emission spectra and decay times following γ-ray irradiation, suggesting that praseodymium does not negatively impact the scintillation mechanisms of the glass [48].

Furthermore, glasses containing different levels of CdO exhibit enhanced shielding properties against gamma rays and fast and slow neutrons. An optimal percentage of CdO enhances neutron filtering abilities, highlighting the significance of glass composition in determining its radiation response [49]. Rare earth-doped SiO_2-Al_2O_3-La_2O_3 (SAL) glasses used for radiation dosimetry demonstrate that rare earth ions do not directly induce the optically stimulated luminescence (OSL) response. It is suggested that the lanthanide content interacts with intrinsic defect centres induced by radiation-induced defects, which affect the dosimetric behaviour. Adding lithium fluoride in high LiF-content phosphate glasses enhances their thermoluminescence intensity and stability in response to radiation [50]. Finally, the interaction between the radiation and optics in phosphate glasses activated by Nd^{3+} ions have revealed that the scattering of phonons on point defects is an essential factor in modifying the radio- and thermoluminescence spectra. This features the significance of the glass composition and the specific lanthanide content in determining the radiation response of phosphate glasses [45].

Lanthanide ionic radii and glass network structure

The ionic radii of lanthanide ions affect their arrangement in glass. Larger ions, such as Ce and Nd, prefer high-coordination sites, causing distortions. The lanthanide ions in glass lead to more defect sites and impact radiation behaviour. Smaller ions of La integrate smoothly with fewer disturbances. Lanthanide dopants with different radii influence defect formation in lanthanide phosphate glasses.

The effect of the glass composition on the radiation response of lanthanide-doped phosphate glasses is complex. It depends on factors such as the amount of lanthanide present, ionic radii, and the structure of the glass network. Adding lanthanide oxides, including Nd_2O_3 and Sm_2O_3, to phosphate glasses causes significant alterations in their physical and radiation detection properties. Increasing the Nd_2O_3 content in phosphate glasses improves the photon attenuation capabilities, leading to higher mass attenuation coefficient values and reduced mean free path values [47]. Sm_2O_3 is introduced in phospho-tellurite glasses, impacting their elastic and radiation shielding properties, but the presence of Sm_2O_3 does not affect the mass attenuation coefficient [46]. The ionic radii of lanthanide ions are crucial in shaping the glass network structure and, consequently, influencing the response of the material to radiation. Glasses that contain larger lanthanide ions of Dy_2O_3 have higher density and adequate atomic number, which is beneficial for radiation shielding purposes [51]. In lithium borate glasses, gamma irradiation can cause changes in the structure. These changes can create non-bridging oxygens (NBOs) and affect the glass's radiation shielding capability [52]. The arrangement of the glass network, determined by the type and concentration of lanthanide ions, which significantly impacts the radiation response. The presence of Yb^{3+} ions in different glass compositions affects the optical and spectroscopic properties after radiation exposure, indicating the emergence of defects within the glasses [53]. The structural integrity and luminescence characteristics of Ce^{3+}- doped phosphate glasses demonstrate the vital role of glass composition in influencing the response to radiation. The doped phosphate glasses emphasise the energy transfer mechanism from Gd^{3+} to Ce^{3+} ions [50].

Influence on the Luminescent Properties

The behaviour of lanthanide phosphate glasses is influenced by lanthanide ions, impacting the light emission. Glass luminescence is affected by the lanthanide dopant's type and concentration. Developing glass for detector and dosimeter applications requires careful consideration of the interaction between the lanthanide ion concentration, defect generation, and luminescent properties.

The amount of lanthanide present in a glass composition significantly impacts the radiation response of lanthanide-doped phosphate glasses. This affects both their luminescent properties and their ability to sense radiation. Adding neodymium oxide (Nd_2O_3) to phosphate glass compositions has increased the glass density and decreased the molar volume. It also enhances its characteristics for radiation sensing, such as the mass attenuation coefficient and adequate atomic number. The modified glass indicates a strong correlation between photon-sensing properties and the amount of Nd_2O_3 in the glass composition [46]. Incorporating erbium oxide (Er_2O_3) in metaphosphate glass systems has affected their thermoluminescence (TL) dosimetric properties, resulting in a noticeable linear thermoluminescence dose-response signal. The finding suggests that the lanthanide content plays a crucial role in determining the radiation response of these glasses. In addition, the addition of gadolinium (Gd) and cerium (Ce) to phosphate glasses is known to enhance their luminescence and scintillation properties, making them suitable for radiation detection applications. The energy transfer from Gd^{3+} to Ce^{3+} ions affects the luminescence intensity in glass. The detected signal indicates that the type and amount of lanthanide ions in the glass directly impact its radiation response [52]. When europium (Eu) is added to gallate glasses, distinct luminescence peaks are observed upon irradiation. The intensity of the luminescence and scintillation peaks at specific Eu_2O_3 doping levels further emphasises the importance of the lanthanide content in the radiation response. The composition of lanthanide phosphate glasses plays a crucial role in their luminescent properties and radiation response.

Radiation-induced changes in lanthanide phosphate glasses

The exposure to radiation causes complex changes in lanthanide phosphate glasses, resulting in localised effects, the formation of colour centres, and alterations in the chemical bonding. The addition of different lanthanide ions, such as Cerium (Ce), Samarium (Sm), Ytterbium (Yb), and Praseodymium (Pr), to phosphate glass matrices leads to significant modifications in their physical, optical, and luminescent properties. These changes have been observed before and after exposure to various forms of radiation, such as gamma rays, helium ions, electrons, and protons [48, 53, 54]. This impacts the connectivity of the glass network through effects on the non-bridging oxygen (NBO) production and changes in the Ce^{3+}/Ce^{4+} ratio due to the incorporation of CeF_3. The introduction of lanthanide ions affects the glass structure, leading to the development of colour centres after gamma irradiation [55]. Sm and Yb doping levels influence microscale structural changes and UV/NIR absorption spectra. Glasses doped with Pr^{3+} show resilience to radiation, maintaining emission spectra and decay times after irradiation, indicating localised structural alterations [56]. Radiation exposure creates colour centres such as phosphorus-oxygen hole centres (POHCs) and electron centres (POECs) in lanthanide-doped glasses, enhancing absorption without affecting scintillation mechanisms, and revealing defects induced by radiation.

Applications and implications

Lanthanide-doped phosphate glasses have unique properties and diverse applications due to their atomic arrangements. Incorporating lanthanides enhances their functionality in technologies, for instance, biomedicine, optics, and electrochemistry and as hosts for nuclear waste [3]. An essential application could be in biomedicine for bone regeneration and infection management. Lanthanide-doped phosphate glasses have a wide range of applications in biomedicine, photonic devices, environmental remediation, and solid-state lighting [57]. These glasses have multiple applications, including creating nanoparticles for bone regeneration and drug release, light-emitting devices, energy technologies, and bioimaging [58]. They exhibit strong up-conversion, converting lower-energy photons to higher-energy ones. Besides their biomedical and photonic applications, lanthanide-doped glasses have environmental implications, particularly in water treatment. These glasses are particularly effective in eradicating pollutants due to their superb adsorption and photocatalytic activity. Additionally, the glasses are utilised in solid-state lighting to enhance the energy efficiency and promote sustainability. Lanthanum phosphate activated with terbium is used in optopharmacology and photodynamic therapy for bone diseases. Their distinctive characteristics, such as hydrophobicity, are advantageous for creating non-wetting surfaces [59]. Furthermore, exploring their acoustic vibrational properties assists in designing solid-state devices [60]. The studies confirm that lanthanide-doped phosphate glasses have potential in healthcare, sustainability, and energy efficiency.

Challenges and Future Directions

Lanthanide-doped phosphate glasses possess unique properties that make them attractive for solid-state lighting and optical data transmission. However, several challenges are associated with their development, including material degradation, inhomogeneous spectral distribution, and insignificant colour rendering [61, 62]. One of the primary challenges is the reaction between the phosphor material and the glass host. Additionally, the acoustic vibrational properties of these glasses have been studied less than their electrical and optical properties. Although incorporating lanthanide oxides into the transparent phosphate host network has been explored, the structural implications are not clearly understood. Future research should focus on improving white light emission and understanding the effects of temperature and pressure on the ultrasonic wave velocities. Molecular dynamics simulations can reveal structural features of glasses containing lanthanum oxide. Addressing the challenges related to the durability and spectral distribution and understanding the structural and elastic properties are crucial for advancing lanthanide phosphate glasses.

CONCLUSION

This review has emphasised the essential role of lanthanide and effective substances, defect formation, the impact of glass composition, and the changes induced by radiation in lanthanide phosphate glasses. These factors significantly affect the glass's properties, from the mechanical strength to the radiation attenuation. Understanding these phenomena is crucial for developing advanced radiation-shielding materials. The properties of glass are influenced by various defects, which include vacancies, interstitials, and colour centres. The effects of these defects are further influenced by lanthanide ions. Radiation exposure induces changes in the glass structure, adding complexity to the behaviour. The correlation between the defect formation, glass composition, and radiation-induced changes in lanthanide phosphate glasses is essential in materials science. This understanding advances glass materials and offers solutions for advanced radiation shielding. Continued research in defect-controlled glass materials holds immense potential for addressing challenges in radiation protection and unlocking new applications. Lanthanide phosphate glasses can be remarked on as having the potential to be applied in various technologies.

Acknowledgments

The authors gratefully acknowledge the Unit of Excellence on Advanced Materials for the Sensors, the Advanced Glass and Ceramics Research Unit, and the School of Science, University of Phayao, Thailand, for their meaningful support of this work. This research project was supported by the Thailand Science Research and Innovation Fund and the University of Phayao.

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