

Structural Investigation of Heavy Metal Oxide Glasses: A Review

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Abstract

Heavy metal oxides have gained significant attention due to their diverse structural and electronic properties, making them promising materials for applications in electronics, catalysis, and energy storage. In this review, we focus on the synthesis and characterization of heavy metal oxide of bismuth silicate glasses materials employing the innovative melt-quench technique. The melt-quench method offers a unique and controlled approach to fabricate glasses and glass-ceramics, providing precise tuning of composition and microstructure. Key parameters such as the melt-quench temperature, cooling rate, and quenching media play pivotal roles in determining the resulting properties of heavy metal oxides. To comprehensively understand these materials, a combination of advanced analytical techniques is employed, including X-ray diffraction (XRD), Fourier-transform infrared (FTIR) spectroscopy, and Raman spectroscopy. XRD analysis delivers valuable insights into the crystal structure and phase transitions, elucidating the impact of melt-quench parameters on the material's overall structure. Furthermore, FTIR and Raman spectroscopy provide crucial information about the vibrational modes and molecular structure, offering a detailed understanding of the chemical bonds and functional groups present. By systematically exploring the intricate relationships between melt-quench parameters and material properties, this review aims to advance the knowledge of heavy metal oxide materials and foster their tailored development for diverse technological applications.

INTRODUCTION

Heavy metal oxide (HMO) glasses represent a remarkable class of materials, enriched with substantial levels of bismuth and lead oxide, making them highly valuable for diverse technological applications [1]. Their unique properties and appealing characteristics have positioned them as promising candidates for advancements in electronics, optical devices, and photonics. HMO glasses have garnered significant attention due to their exceptional optical nonlinearity, outperforming traditional vitreous silica by an impressive 50 times [2]. While their nonlinearity may not reach the levels seen in semiconductors or organic materials, their potential for low-loss optical waveguide fabrication makes them attractive for optical switching applications. The amorphous structure of rapidly cooled HMO glasses sets them apart, offering enhanced properties compared to slowly cooled counterparts. This property grants them superior versatility and enables the formation of intricate shapes, rendering them ideal for various applications [3]. Notably, HMO glasses boast high chemical resistance and thermal shock resistance, particularly in the case of borosilicate glasses, which also exhibit excellent transparency and low dispersion with a high refractive index. These glasses have found practical use in immobilizing radioactive ions from nuclear reactor waste, showcasing their importance in the nuclear physics field and beyond [4]. Moreover, HMO glasses showcase a vast transmission window, spanning from the ultraviolet domain to the mid-infrared region, with some formulations achieving transmission cutoffs at around 8 μm . This outstanding transparency in a wide spectral range further accentuates their potential for photonic and optoelectronic device

applications [2]. Furthermore, when compared to fluoride glasses, HMO glasses offer a compelling advantage in terms of chemical durability and may present a promising alternative for specific applications [2-4]. The research on bismuth-based glasses indicates their close resemblance to lead-bearing formulations, making them an attractive substitute with similar glass-forming properties. In addition, bismuth silicate glass has demonstrated superior shielding properties, positioning it as a potential replacement for lead glasses in certain applications [5]. Overall, heavy metal oxide glasses hold immense promise for technological advancements, offering a rich array of properties such as high nonlinearity, wide transmission windows, and excellent resistance to chemical and thermal stresses. Embracing these glasses opens up new avenues for innovative developments in electronics, photonics, and other cutting-edge fields [5-6].

Silicate Glasses in HMO Applications:

Silicate glasses hold profound historical significance across various applications, including their vital role in health maintenance organizations (HMOs) and medical devices. The evolution of glass craftsmanship dates back to ancient civilizations, where skilled artisans crafted primitive glass objects, blending silica-rich materials, for both utilitarian and ornamental purposes. The ancient Egyptians, around 3000 BCE, ingeniously pioneered early glassmaking techniques, producing exquisite glass beads and vessels employing a soda-lime-silica composition. Across centuries, the art of glassmaking spread to civilizations like the Romans and Phoenicians, who honed the craft and expanded its practical applications [7]. In the modern era, the advancement of sophisticated glass compositions and manufacturing methodologies unlocked new horizons for medical applications. The intrinsic inertness and non-reactive nature of silica-based glasses proved ideal for containing and handling diverse pharmaceuticals and biological substances, becoming integral to medical instruments like test tubes, syringes, and vials. A pivotal milestone arrived with the advent of borosilicate glasses, exemplified by the renowned Pyrex, early in the 20th century [6-7]. These glasses offered exceptional thermal resistance, rendering them fit for laboratory equipment like beakers and flasks, elevating glass utility in medical settings. Notably, in HMO applications, silicate glasses have made significant strides in medical imaging devices. Scintillators, crafted from doped silicate glasses, utilize specific additives, such as rare-earth elements, to convert high-energy radiation into visible light, enabling superior medical imaging and revolutionizing the field of radiology and non-invasive diagnostics [8]. Furthermore, silicate glasses' integration into optical fibres, deployed in medical lasers and endoscopic procedures, has accompanied in a new era of minimally invasive surgeries and precision laser treatments. The remarkable flexibility and light-transmissive properties of glass fibres expedite patient recovery and advance medical outcomes [9-10].

Comparison of Silicate glasses with different doping Material

From literature review we can conclude the point that Doping in bismuth silicate glasses entails purposefully introducing minute quantities of specific elements, known as dopants, into the glass matrix. This deliberate process aims to enhance and customize the glass's properties for targeted applications. Through doping, a myriad of benefits can be achieved, including the introduction of novel functionalities, alteration of optical, electrical, or mechanical characteristics, and overall enhancement of performance in various technological fields. Several commonly employed dopants in bismuth silicate glasses encompass. Within bismuth silicate glasses, bismuth itself serves as a dopant, resulting in remarkable nonlinear optical properties [11]. These bismuth-doped glasses garner considerable interest for optical devices, such as lasers and amplifiers.

- **Rare-Earth Elements:** Dopants like yttrium (Y), holmium (Ho), or gadolinium (Gd) are harnessed to create rare-earth-doped bismuth silicate glasses. These glasses play a vital role in fiber lasers, amplifiers, and optical telecommunications, as they can emit and amplify light at specific wavelengths [12-15].
- **Transition Metals:** Elements such as vanadium (V), cadmium (Cd), or yttrium (Y) chromium, iron, nickel, cobalt can be incorporated as dopants in bismuth silicate glasses to bolster their magnetic and electrical properties. Applications of these glasses encompass magneto-optic devices and sensors [16,17].
- **Alkaline Earth Metals:** Dopants like calcium (Ca) or strontium (Sr) impart influence over the thermal and mechanical properties of bismuth silicate glasses, rendering them suitable for specific structural applications [18-19].
- **Rare Earth and Transition Metal Combinations:** Advanced bismuth silicate glasses are occasionally doped with combinations of rare-earth elements and transition metals, resulting in tailor-made and synergistic properties for specific applications [13-19].

The doping process assumes a critical role, as the concentration and distribution of dopants profoundly impact the final properties and performance of the glass.

2. Experimental work

2.1 Glass Preparation Methods

Oxide glasses are primarily synthesized using three main methods: Melt Quench Technique, Sol Gel Method and Chemical Vapour Deposition. The Melt Quench Technique, being one of the earliest discovered methods for glass preparation, involves precise steps to achieve the desired glass composition [20]. To begin, raw materials are precisely weighed and thoroughly mixed in acetone media using a pestle mortar or ball mill. The blended mixture is then dried before being positioned into a superior quality alumina Crucible. This Crucible is then subjected to controlled temperatures in a furnace, resulting in the melting of the homogeneous mixture. Once the melt is achieved, the glass is made up, where the molten material is quickly quenched in the Crucible. Following this step, the glasses undergo annealing at relatively lower temperatures close to the glass casting temperature. This annealing process helps to confiscate any residual internal stresses that may have been induced during the establishing and preservation stages. This technique offers various advantages, including the capability to produce materials of larger sizes associated to single crystals or polycrystalline porcelains. Additionally, it provides a greater flexibility of composition compared to the Sol Gel Method and Chemical Vapour Deposition [1,21].

However, there are some disadvantages to consider. For instance, impurities from Container or incinerator materials may inadvertently be introduced into the glass. Moreover, some refractory materials requiring extremely high temperatures, such as SiO_2 , TiO_2 , Al_2O_3 , and ZrO_2 , may pose challenges in this technique [6]. It is essential to ensure each component used in the glass formation maintains a purity level of 99% to guarantee high-quality results. Despite certain limitations, the Melt Quench Technique remains a pivotal method for synthesizing oxide glasses. Its ability to create homogeneous glass melts and accommodate various compositions makes it a versatile and valuable choice for a wide range of applications. By carefully addressing the purity and processing conditions, this technique enables the production of superior glasses with diverse properties and functionalities [6,21].

2.2 Glass Phase Characterization comparison by Using XRD

The obtained glass underwent characterization through the X-ray diffraction (XRD) technique, utilizing an X-ray powder diffractometer. This method is particularly valuable for discerning the internal structural of solid materials, exclusively when distinguishing between amorphous and crystalline substances. During the analysis, it was observed that the measured XRD intensity, represented by number of counts per second, is influenced by various instrumental and experimental factors. As a result, it proves more advantageous to use relative intensity rather than absolute intensity for accurate comparisons. To determine the relative intensity, the absolute intensity of each peak is divided by that of most intense peak. This calculation is then converted into a percentage, yielding the relative intensity. The peak with the highest intensity is set as the 100% reference point [22]. Using the X-ray diffraction technique in this manner enables researchers to gain valuable insights into the structure of the glass material. By examining the relative intensity of different peaks, they can identify key characteristics and distinguish between crystalline and amorphous phases. This information is crucial for understanding the material's properties and behaviour, facilitating advancements in various scientific and technological fields. If the crystal size is too small, sample composition, crystallinity and face purity can be determined by this method. It is a arrangement of electromagnetic radiation by wavelength among 0.01 to 10 nm. These x-rays can be used in diffraction technique to identify the atomic or molecular structure of the crystal. A diffraction pattern is produced by the diffraction from different plane of atom and contains information about the atomic arrangement within the crystal and analysed material is finely ground, homogenized and average bulk composition is determined [22,23].

If the crystal size is too small, sample composition, crystallinity and face purity can be determined by this method. It is a form of electromagnetic radiation with wavelength between 0.01 to 10 nm. These x-rays can be used in diffraction technique to identify the atomic or molecular structure of the crystal. A diffraction pattern is produced by the diffraction from different plane of atom and contains information about the atomic arrangement within the crystal and analysed material is finely ground, homogenized and average bulk composition is determined [20-23]. From literature survey Meenakshi et al. have been investigated composition by literature review like CdO-B₂O₃-SiO₂, SiO₂-ZnO-Bi₂O₃, V₂O₅-Bi₂O₃-B₂O₃, V₂O₅-CdO, and V₂O₅-ZnO, V₂O₅-Bi₂O₃-CdO, Bi₂O₃-Y₂O₃-B₂O₃ and other compositions a broad hump in the XRD pattern shows its amorphous nature or non-crystalline nature of a material [4].

XRD patterns for all doped glasses will display broad peaks, characteristic of amorphous materials, indicating that the doping process does not induce significant crystallinity. The presence of rare-earth or transition metal dopants may lead to minor shifts or shoulders in the XRD pattern, reflecting local structural changes or clustering. Doping with alkaline earth metals may cause slight modifications in the XRD pattern, primarily due to changes in the glass network's connectivity and packing [12,13,14,15].

Overall, the XRD patterns of bismuth silicate glasses doped with, alkaline earth metals, transition metals and rare-earth metals will generally be similar, showcasing the amorphous nature of the glass structure. However, careful analysis of the XRD data can provide valuable information on any subtle structural modifications induced by the dopants. Other complementary techniques, such as spectroscopy and microscopy, can be employed to gain further insights into the specific properties and behaviour of these doped glasses.

Table 1: XRD pattern for heavy metal oxide glasses with different dopant.

Analytical Technique	Dopant Type	Results	References
X-ray Diffraction (XRD)	Rare-Earth Metals	Broad peaks, amorphous structure, minor shifts and shoulders near dopant sites	[12-17]
		Additional peaks indicating possible formation of rare-earth-containing crystalline phases	
	Transition Metals	Broad peaks, amorphous structure, minor shifts and shoulders near dopant sites	
		Slight changes in peak width or intensity suggesting localized structural modifications	
Alkaline Earth Metals	Broad peaks, amorphous structure	18-19	

FTIR Spectroscopy

FTIR, an acronym for "Fourier Transform InfraRed," is a powerful tool renowned for its effectiveness in characterizing the structure of glasses. Each chemical bond and building block within the samples possesses a distinctive vibrational frequency akin to a unique fingerprint. To discern and identify these chemical bonds and blocks building in the illustrations or samples, Fourier Transform Infrared spectrometer was employed at room temperature, covering a wide range from 400 to 4000cm⁻¹. Powder samples were thoroughly mixed and by pressed to create pellets appropriate for precise IR dimensions [24]. Notably, every FTIR band exhibits multiple peaks, each representing a specific type of vibration, necessitating the separation of individual peaks for accurate analysis. This de-convolution process was carried out using a Gaussian Distribution Function based program. Glass structure exploration further entailed the combined use of FTIR and Raman spectroscopy [21]. In the context

of FTIR, infrared radiation passes through the sample, with certain and differentiation. The preference for FTIR lies in its non-destructive nature, enhanced speed compared to older techniques, heightened sensitivity, and precise results. The application of the Fourier transform mathematical function allows the interferogram to be converted into a spectroscopy spectrum graph, where wave number is depicted on the X axis and transmittance on the Y axis [24-25]. FTIR spectroscopy is a potent and invaluable technique for investigating the structural arrangements and functional groups present in materials. By literature review the vibrations observed in the FTIR spectra are categorized into three distinct IR regions, as supported by previous literature. Trigonal groups exhibit B-O bonds with vibrational modes of asymmetrical stretching, predominantly found in the primary region between 1200 to 1600 cm^{-1} . second region (800-1200 cm^{-1}), octahedral units involving Bi-O bonds are identified. Additionally, tertiary region (400-800 cm^{-1}) reveals octahedral units due to Bi-O bonds [15,16].

Bismuth Silicate Glasses doped with rare-earth metals having FTIR spectra display characteristic peaks with stretching vibrations to Si-O-Si bond around 1000-1100 cm^{-1} and Si-O bending vibrations around 450-600 cm^{-1} , consistent with the glass's amorphous nature [12,15]. In addition to these vibrations, the presence of rare-earth dopants introduces distinctive absorption bands at specific wavenumbers, signifying rare-earth-oxygen (RE-O) bonding or rare-earth clustering within the glass matrix. These unique bands provide valuable insights into the local coordination environment and bonding characteristics of the rare-earth dopants, contributing to the glass's optical and electronic properties [13-14].

Secondly Bismuth silicate glasses doped with Transition metal oxides also exhibit FTIR peaks corresponding to Si-O-Si bending and stretching vibrations, similar to pristine bismuth silicate glass [16]. Minor shifts or intensity variations in these peaks may indicate localized structural modifications near the dopant sites, suggesting alterations in the vibrational modes within the vicinity of the transition metal ions [24,16]. These changes in the FTIR spectrum provide crucial information about the interaction between transition metal dopants and the glass network, influencing the glass's magnetic and electrical properties [16,17].

In the case of alkaline earth metal-doped bismuth silicate glasses, their FTIR spectra feature absorption bands associated with stretching vibrations of Si-O-Si bond around 1000-1100 cm^{-1} and Si-O bending vibrations around 450-600 cm^{-1} , consistent with the glass's SiO₂ network [18]. The introduction of alkaline earth metal dopants may cause slight modifications in the FTIR spectrum, impacting the connectivity and packing of the glass network. These subtle changes provide insights into how alkaline earth metal dopants affect the glass's local structure and bonding, influencing its thermal and mechanical properties. In summary, FTIR spectroscopy is a powerful tool for analysing bismuth silicate glasses doped with alkaline earth metals, rare-earth metals and transition metals [24]. The distinctive peaks and absorption bands in the FTIR spectra offer valuable information about the dopant-glass interactions, structural modifications, and bonding characteristics. This knowledge is essential for tailoring the glass properties for specific applications in photonics, optics, sensors, and other technological fields [25,26].

Table 2: FTIR pattern for heavy metal oxide glasses with different dopant.

Doping Material	FTIR Spectra Observations	Impact on Glass Properties	References
Rare-Earth Metals	Si-O-Si stretching vibrations (1000-1100 cm^{-1})	Provides insights into local coordination environment and bonding characteristics of rare-earth dopants	[12, 13, 14, 15]

	Si-O bending vibrations (450-600 cm ⁻¹) Unique absorption bands at specific wavenumbers indicating RE-O bonding or rare-earth clustering within the glass 600-800 cm ⁻¹ usually.	- Contributes to the glass's optical and electronic properties	
Transition Metals	Si-O-Si stretching (900-1100 cm ⁻¹ bending vibrations (450-600 cm ⁻¹) similar to pristine bismuth silicate glass Changes in FTIR spectrum provide information about interaction between transition metal dopants and glass network	Minor shifts or intensity variations indicate localized structural modifications near dopant sites Influences the glass's magnetic and electrical properties	[16, 17]
Alkaline Earth Metals	Si-O-Si stretching vibrations (1000-1100 cm ⁻¹) Si-O bending vibrations (450-600 cm ⁻¹)	Provides insights into connectivity and packing of the glass network Affects the glass's local structure and bonding Slight modifications in FTIR spectrum Influences the glass's thermal and mechanical properties	[18-19]

Raman spectroscopy

Raman spectroscopy, a widely utilized technique for molecular structure analysis, serves as a valuable complement to infrared spectroscopy. This method relies on the inelastic scattering of photons, resulting in interactions with molecular vibrations, excitations, and phonons within the system. Laser light interacts with the sample, inducing shifts in the energy levels of the photons—both upwards and downwards—providing insightful information about the vibrational modes present. During the Raman spectroscopy process, a laser beam illuminates the sample, and electromagnetic radiation emanating from the illuminated spot is collected through a lens. The collected radiation then passes through a monochromator, which filters the wavelength corresponding to the laser line. The elastic scattered radiation is subsequently filtered out by employing a combination of notch filters, edge pass filters, and bandpass filters. The remaining light is then dispersed and detected for further analysis. In Raman spectra, the distinctive Raman bands of Bi₂O₃ can be categorized into four regions, encompassing Raman modes with low wave number (<100cm⁻¹), ion vibrations of heavy metal (70-160cm⁻¹), in

intermediate existence of bridged anion modes (300-600 cm^{-1}), and at larger wave numbers breathing anion modes is present [3,6,21].

A comparative study of bismuth silicate glasses doped with transition metals, and alkaline earth metals, rare-earth metals can be performed using Raman spectroscopy to analyse their vibrational characteristics and bonding environments. In Raman spectra of rare-earth-doped glasses, characteristic peaks associated with Si-O-Si stretching vibrations at approximately 450-1000 cm^{-1} and Si-O bending vibrations at around 400-600 cm^{-1} are observed, consistent with the amorphous nature of glasses [6]. The incorporation of rare-earth dopants may introduce additional Raman peaks or shifts in existing peaks, indicating interactions between the dopants and the glass matrix. This provides valuable insights into the local coordination environment and bonding of the rare-earth dopants, influencing the glass's optical and electronic properties [12-14,15]. Similarly, in Raman spectra of transition metal-doped glasses, peaks related to stretching vibrations of Si-O-Si bond approximately 450-1000 cm^{-1} and Si-O bending vibrations at around 400-600 cm^{-1} are observed, similar to pristine bismuth silicate glass. Minor shifts or intensity variations in the Raman peaks may indicate local structural modifications near the dopant sites, suggesting alterations in the glass's vibrational modes within the vicinity of the transition metal ions [6,27,16]. The Raman data reveal how transition metal dopants affect the glass network and provide insights into their influence on the glass's magnetic and electrical properties. In the case of alkaline earth metal-doped glasses, Raman spectra exhibit peaks corresponding to stretching vibrations of Si-O-Si approximately 450-1000 cm^{-1} and Si-O bending vibrations at approximately 400-600 cm^{-1} , consistent with the glass's SiO_2 network [6,16,17]. Doping with alkaline earth metals may cause slight shifts in the Raman peaks, indicating variations in the glass network's connectivity and packing. The Raman data offer insights into how alkaline earth metal dopants influence the glass's local structure and bonding, affecting its thermal and mechanical properties. In conclusion, Raman spectroscopy provides valuable vibrational information for all doped glasses, highlighting similarities in the Si-O-Si bending and stretching vibrations indicative of their amorphous nature [6,16,18,28]. The presence of additional peaks or shifts in Raman spectra reveals specific dopant-induced structural changes, making this analysis essential for tailoring the glass properties for various applications in photonics, optics, sensors, and other technological fields [19].

Table 3: RAMAN pattern for heavy metal oxide glasses with different dopant.

Doping Material	Raman Spectra Observations	Impact on Glass Properties	References
Rare-Earth Metals	(~450-1000 cm^{-1}) Si-O-Si stretching vibrations	Provides insights into local coordination environment and bonding characteristics of rare-earth dopants	[6,12-14,15]
	(~400-600 cm^{-1}) Si-O bending vibrations Additional peaks or shifts indicating interactions with dopants	Contributes to the glass's optical and electronic properties	

Transition Metals	Si-O-Si stretching (450-1000 cm^{-1}) and bending vibrations (400-600 cm^{-1}) similar to pristine bismuth silicate glass. Minor shifts or intensity variations in Raman peaks	Minor shifts or intensity variations indicate localized structural modifications near dopant sites. Influences the glass's magnetic and electrical properties	[6,27,16]
Alkaline Earth Metals	(~450-1000 cm^{-1}) Si-O-Si stretching vibrations	Provides insights into connectivity and packing of the glass network	[6,18,19]
	Si-O bending vibrations (~400-600 cm^{-1}) Slight shifts in Raman peaks	Affects the glass's local structure and bonding. Influences the glass's thermal and mechanical properties	

Conclusion

In conclusion, the comprehensive comparative study of bismuth silicate glasses doped with transition metals, rare-earth metals, and alkaline earth metals through numerous investigative techniques such as Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and Raman spectroscopy, provides valuable insights into the unique influence of different dopants on the glass properties. The XRD analysis reveals that all doped glasses maintain an amorphous structure with broad peaks, indicating that the doping process does not induce significant crystallinity. However, subtle shifts and minor changes in peak intensity may occur, suggesting localized structural modifications near the dopant sites. FTIR spectroscopy demonstrates that the fundamental vibrational characteristics, such as the Si-O-Si stretching and bending modes, remain preserved in all doped glasses, consistent with their amorphous nature. The introduction of dopants results in additional bands in the FTIR spectra, offering crucial information about dopant-glass interactions and alterations in the local bonding environment. Similarly, Raman spectroscopy confirms the amorphous nature of all doped glasses by showing characteristic peaks associated with Si-O-Si stretching and bending vibrations. Dopant-specific shifts and additional peaks provide insights into the local coordination and bonding of the dopants, influencing the glass's optical, electronic, magnetic, and thermal properties. The comparative analysis highlights that rare-earth dopants introduce unique vibrational modes associated with rare-earth-oxygen bonding or clustering, making them highly desirable for tailoring optical and electronic properties. Transition metal dopants induce localized structural changes near their sites, influencing the glass's magnetic and electrical behaviour. Alkaline earth metal dopants impact the glass network's connectivity, thereby influencing the glass's thermal and mechanical properties. This extensive comparative study sheds light on how each dopant modifies the structural and vibrational properties of bismuth silicate glasses. Such insights are crucial for designing tailored glasses with specific functionalities, rendering them highly promising materials for diverse applications in photonics, optics, sensors, biomedical devices, and other advanced technological fields. Continual research and exploration of these doped glasses are expected to unlock new avenues for innovative materials and enhanced technologies.

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