A REVIEW: STRUCTURAL STUDY OF ALKALI METAL OXIDEGLASSES

Abstract

Glasses predominantly composed of alkali metal oxides like lithium oxide $(Li₂O)$, sodium oxide $(Na₂O)$, and potassium oxide (K_2O) find extensive use in diverse fields owing to their distinctive characteristics. The innovative melt quench technique is used for creating the glass material. This review chapter likely delves into details of how the synthesis method is carried out. The classical melt quench method is used to analyse the glass containing alkali metal oxides. Indeed key parameters like melt quench temperature, cooling rate quenching media and other factors determine the resulting properties of alkali metal oxide throughout the stages of synthesis and processing. Alkali metal oxide such as lithium sodium potassium etc. properties varies on how they are prepared and processed. Modern analytical techniques are used to gain a complete understanding of these materials, including XRD (X-ray diffraction), FTIR (Fouriertransform infrared spectroscopy), and Raman spectroscopy. The XRD analysis offers valuable information of crystal structure and phase transitions. Additionally, the use of FTIR and Raman spectroscopy offers a thorough knowledge of the chemical bonds and functional groups present by providing vital information about the vibrational modes and molecular structure. This study seeks to increase understanding of alkali metal oxide materials and encourage their technological applications by examining the different parameters and material characteristics.

Keywords: XRD, FTIR, RAMAN, OPD, UV Spectroscopy.

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I. INTRODUCTION

Glass is a solid inorganic material characterised by its transparency or translucency as well as its hardness, brittleness, and amorphous, non-crystalline structure. Electrical devices, optical switches, optical filters, mirrored windows, light-absorbing materials, mechanical sensors, and formulas for sealants are a few examples of its numerous technical uses[4- 5].These glasses exhibitcharacteristics such as high ionic conductivity, good thermal stability, and tuneable optical properties.Alkali metal oxides are generally white or colourless crystalline solids with high melting points. Alkali metal oxides have various applications in different industries and fields due to their unique properties and reactivity.Alkali and alkaline earth oxides can modify the network, resulting in the emergence of non-linear optical characteristics. Glasses that incorporate alkali metal oxide often demonstrate an elevated coefficient of thermal expansion, which can have a detrimental impact on hydrolytic stability when the concentration of these oxides surpasses a specific threshold.The inclusion of two alkali metal oxides, even insmall proportions, showcases a beneficial influence on preventing undesired crystallization and enhancing the properties of glasses. Other oxides, such as $A₁O₃$, TiO₂, and ZrO₂, can be added to the glasses to give them particular properties. Low levels of boron trioxide in the composition (less than 13% of its weight) reduce the melting and operating temperatures and increase hydrolytic stability. $Fe₂O₃$, $Cr₂O₃$, and CaO are often used as colouring agents in glass matrix. The other transition metals (nickel, manganese, vanadium, copper, titanium) and rare earth metals (likely praseodymium and neodymium) are incorporated to produce various coloured glassesand to broaden the spectrum of colours. Calcium oxide (CaO) is the primary alkali earth metal oxide employed for modifying glass properties. Notably, calcium oxide accelerates the phase separation process in borosilicate glasses. In specific cases, minor quantities of zinc oxide (ZnO), magnesium oxide (MgO), barium oxide (BaO), and strontium oxide (SRO) are also carefully incorporated to meet specific requirements. Alkali-metal oxides of sodium and potassium are employed to alter the silica-based glasses used in the manufacture of commercial glass production.Upon introduction to the furnace alongside silica sand and cullet (recycled glass), sodium carbonate (Na_2CO_3) and calcium carbonate $(CaCO_3)$ break down to produce the modifying oxides and release carbon dioxide. Sodium oxide $(Na₂O)$ finds extensive use as a flux in glass production, particularly in borosilicate glass compositions. It is often accompanied by additional alkali metal oxides like lithium dioxide (Li₂O), potassium dioxide (K₂O), and lead oxide (PbO). These alkali metal oxides havean impact on glass and can be categorized according to their chemical composition.

- 1. In alkali glass fibre the content of alkali metal oxide is higher than 12%.
- 2. Medium-alkali glass fibres: alkali metal oxide is in the ranges from 6% to 12%.
- 3. Low alkali glass fibre: Alkali metal oxide falls within the range of 2% to 6%, often used in civil construction.
- 4. Micro alkali glass fibre (non-alkali glass fibre) content of alkali metal oxide is below 2%, primarily utilized in electrical or military-industrial applications.

Alkali metal oxide glasses show significant potential for driving technological advancements by providing a diverse range of properties, including substantial nonlinearity, expansive transmission capabilities, and remarkable resistance to both chemical and thermal stress. Embracing the utilization of these glasses paves the way for pioneering developments in fields such as electronics, photonics, and various other cutting-edge disciplines.

II. ALKALI METAL OXIDE WITH DIFFERENT DOPANTS

- **1. Alkali Borate Glass:** A wide range of technological applications, such as solar energy converters, lasers, phosphors, and more, utilise alkali borate glasses.Alkali borate glasses can be established as solid electrolytes, which are essential components in batteries and fuel cells. Advantages over the liquid electrolytes, alkali borate glass electrolytes exhibit isotropic (uniform in all directions) conductivity. Alkali borate glasses can have their characteristics customized to fit any application because of their wide compositional range. Thermal stability and largely available composition rangemake them a potential candidate for technological applications [13-14].
- **2. Borate Glass with Alkali Ion:** Borate glasses containing alkali ions like Li, Na, and K represent a crucial material category within the realms of optics, microelectronics, and optical fibres, owing to their profound technological scientific significance. Currently, research is being done on borate glasses that have been combined with other transition metal oxides, such as CoO and NiO, and which might be used in a variety of industrial sectors [4]. However, because of their lower charge and smaller sizes, alkali metal cations such as lithium, sodium etc. also considerably contributes to the electrical conductivity of glasses and enhances the dielectric properties. ZnO is beneficial for adjusting the glasses' optical absorption, refractive index opticalband gap, etc. [3].The significant impact of zinc oxide on the glass's semiconductor characteristics is attributed to its costeffectiveness, higher polarizability, lower melting point, non-toxic nature, and environmentally friendly and as emphasized in studies [6-11]. ZnO can serve a dual role within the structure, acting both as a modifier and a former. When functioning as a modifier, it disrupts B-O-B bonds, leading to the creation of non-bridging oxygen (NBO) atoms along with the formation of defects termed dangling bonds. Zinc oxide (ZnO) holds significance as an additive that effectively lowers the melting temperatures during the formation of oxide glass. These exceptional properties make ZnO a valuable inclusion for enhancing glass characteristics, rendering it well-suited for an array of applications like photovoltaic cells, optoelectronics, and gas sensors [3]. Research findings have revealed contrasting behaviours, potassium borates tend to vaporize more readily than sodium borates when exposed to temperatures exceeding 1000 °C. In contrast, lithium borates exhibit greater stability against evaporation when subjected to heat in glass formation processes. Significantly Li+ ions establish strong and durable bonds within the glass structure, thereby increasing the glass's resistance to acidic environments [6-11].
- **3. Heavy Metal Oxide with Alkali Oxides:** The heavy metal oxides with alkaline earth borate glasses exhibit high solubility of rare-earth ions. PbO-containing glasses have a high refractive index and a low glass transition temperature (T_g) [Dimitrov et al., 1996]. Intriguing non-linear optical features, strong chemical resistance, and low melting points are all characteristics of glasses containing $TeO₂$ [Yousef et al., 2007; Singh et al., 2008; Agarwal et al., 2003]. Alkaline earth oxides increase the capacity to create glass, but heavy metal oxides produce excellent optical qualities like second harmonic generation. Alkaline earth and heavy metal oxides may both function as glass network formers (GNF) or glass network modifiers (GNM), depending on their composition in the glass.

[Abdul Hameed et al.]HMO glasses show great potential for driving technological progress, presenting a diverse range of characteristics including substantial nonlinearity, broad transparency ranges, and remarkable resilience against chemical and thermal pressures. Embracing these glass materials paves the way for novel opportunities in the realms of electronics, photonics, and other forefront disciplines, encouraging innovative advancements.

- **4. Bismuth Borate Glass:** Heavy metal oxide, such as bismuth borate, offers outstanding physical characteristics, including a high density, high efficiency, and optical absorption [5]. These glasses have found use in the fields of superconducting materials, reflecting windows, thermomechanical sensors, and glass ceramics[1][9].Bi₂O₃, owing to the distinctive combination of high polarizability and relatively low field strength of the Bi^{3+} ion, doesn't typically act as a conventional glass former. However, when combined with other oxides like B_2O_3 , PbO, Si₂O, and V₂O₅, it participates in the formation of a glass network consisting of $[BiO_3]$ and $[BiO_6]$ pyramids [1]. These materials find applications in various processing devices, particularly low-loss optical fibres, contributing to advancements in optical telecommunications [5]. $Bi₂O₃$ -based glass with transition metal oxides like V_2O_5 has intriguing spectroscopic features that renderitappropriate for application as non-linear optical (NLO) materials, phase conjugation and optical switching [2].
- **5. Alkali Oxide with Transition Metal:** Borate glasses combined with different transition metal oxides, such as CoO, NiO, V_2O_5 , and Cr_2O_3 , are the subject of research investigations and may have a wide variety of uses in today's industrial sectors [4]. Bismuth borate glasses have gained extensive application in various advanced technologies, encompassing Magneto-Optical Current Transducers (MOCTs) utilized inhigh-voltage current systems, as well as optical rotators and isolators featuring large apertures.Additionally, they find roles in switches, circulators, and Polari meters [4]. Exploring the incorporation of alkali and transition metal (TM) ions into borate glass compositions has emerged as a promising direction in the domain of nonlinear optics research. The introduction of TM ions into glass networks has proven instrumental in the development of highly efficient luminescent devices. It is valuable to gain insights into the glass's local structure and subsequently establishcorrelations with various properties, all stemming from their variable oxidation states [3].Modifier transition metal ions induce localized alterations within the glass network, affecting bond energies, structural groups, and chemical stability. This enhances the semiconducting and conduction properties of the material [5-6].Glasses containing multiple transition metal ions exhibit altered behaviour in terms of their physical, electrical, and spectroscopic properties. This phenomenon often referred to asthe "Mixed transition effect" leads to notable variations in the overall characteristics of the material. The structural and optical characteristics of bismuth borate glass incorporating TMIs have garnered significant attention from researchers [3-10].Vanadium glasses find extensive utility in diverse domains including radiation shielding, battery cathode materials, solar cells, and optical and electrical switching devices [6]. Consequently, the introduction of vanadium into glass compositions leads to the incorporation of vanadyl ions $(VO²⁺)$, inducing alterations in the local glass structure. The presence of vanadium (V) in various oxidation states significantly impacts the electrical conductivity of glasses containing vanadium. Researchers have delved into investigating andestablishing correlations between the

optical, structural, and dielectric properties of these glasses and the varying oxidation states of vanadium [3].Elements like vanadium (V), cadmium (Cd), yttrium (Y), chromium, iron, nickel, and cobalt can be introduced as dopants into bismuth silicate glasses to enhance their magnetic and electrical attributes. These modified glasses find application in various areas, including magneto-optic devices and sensors.

III.METHODOLOGY FOR EXPERIMENTAL WORK

1. Glass Preparation Methods: Glasses are mainly prepared by several methods each tailored to specific requirements and application. Melt Quenching (rapid cooling), Sol– gel process, Float glass process, Fused deposition modelling (FDM), Vapour deposition etc. Sol –The gel method involves a sol that undergoes a controlled chemical reaction in the form of a gel. And again heating creates a glass material. FDM is a 3D printing technique that involves melting glass filament and depositing it layer by layer to create an intricate glass structure.Melt quench is widely used in bulk glass production. As mentioned earlier this method involves melting the raw materials at high temperatures and then rapidly cooling them to prevent crystallization, resulting in amorphous glass.These methods can produce a wide variety of glass types with tailored properties, making them suitable for diverse applications across industries like optics, electronics, construction, and art. The "melt-quench method" is a technique used in materials science and solid-state physics to create amorphous or glassy materials. It involves the process of melting a material and then rapidly cooling it down to prevent the formation of a crystalline structure. This rapid cooling inhibits the atoms from arranging themselves in a regular, ordered lattice, resulting in the formation of an amorphous or glassy state.The starting material, kept in a crucible which can be a compound or mixture, is heated to a temperature range in a muffle furnace where it becomes completely molten. Resulting in a homogenous mixture.After reaching the molten state, the material is quickly cooled down at a rate that prevents the atoms from having enough time to arrange themselves into a crystalline structure. This rapid cooling lock the atoms into a disordered, amorphous arrangement.The melt-quench method is widely used to produce amorphous materials for various applications, such as glasses, thin films, and amorphous alloys. The resulting amorphous materials often have distinct properties compared to their crystalline counterparts, making them valuable for specific technological and scientific purposes.Nonetheless; there are some drawbacks to take into account. For instance, inadvertent introduction of impurities from container or incinerator materials can occur during the glass formation process. Additionally, certain refractory materials, such as K_2O , SiO_2 , Al_2O_3 , and ZrO_2 , which require extremely high temperatures, may present challenges when using this method [6]. It is imperative to ensure that eachcomponent utilized in the glass-making process maintains a purity level of at least 99% to ensure high-quality outcomes.Despite these specific limitations, the Melt Quench Technique remains a crucial approach for synthesizing oxide glasses. Its capacity to generate uniform glass melts and accommodate diverse compositions renders it a versatile and valuable option for a wide spectrum of applications. By meticulously addressing issues related to purity and processing conditions, this technique enables the production of superior glasses endowed with a variety of properties and functionalities.The synthesized glasses undergo a characterization process that involves X-raydiffraction (to confirm the presence of amorphous phase), DSC (to assess characteristic temperatures), UV-IR spectroscopy (to understand absorption phenomenon and ligand field coordination around

transition metal ions), and FTIR spectroscopy (for structural insights). Physical parameters,includingmolar volume, density, oxide ion polarizability, theoretical optical basicityand others,were calculated for all synthesized compositionsof glass [4].Theoptical, structural, and thermal characteristics of these glasses have been studied through XRD (X-ray diffraction), DSC (Differential Scanning Calorimetry), UV-IR spectroscopies and FTIR (Fourier transform infrared)[2].

IV.XRD CHARACTERIZATION

XRD (X-ray diffraction) is anexceptionally potent methodforuncovering the inherent structural properties of solid materials, particularly in discerning the difference between amorphous and crystalline substances. In XRD analysis, the measured intensity can be influenced by various factors. Therefore, for accurate comparisons, using relative intensity is often moreadvantageous than absolute intensity. Relative intensity is calculated by dividing the absolute intensity of each peak by that of the most intense peak, and the result is expressed as a percentage. This approach in X-ray diffraction helps researchers understand the glass structure better. By examining relative peak intensities, they can identify important characteristics and differentiate between crystalline and amorphous phases.XRDfunctions as a swift analytical technique primarily focused on identifying the phase present in a crystalline material, whilealso providing insights into unit cell dimensions. The examined material undergoes precise grinding, leading to the determination of its average bulk composition. XRD (X-ray diffraction), a stream ofmonochromatic X-rays, carefully collimated and focused onto the sample, leads to the phenomenon of constructive interference.

XRD offers valuable insights into various parameters like the material structure, crystal orientations, phases, and additional factorslike crystallinity, grain size, strain, and crystal defect. XRD helps determine the crystal structure of alkali oxides. Common crystal structures include cubic (e.g., NaCl-type), hexagonal (e.g., wurtzite), and others. Lattice parameters offer researchers insights into the arrangement of alkali and oxygen atoms within the crystal lattice.XRD can supply valuable insights into the preferred orientation (texture) of crystallites in polycrystalline samples, aiding in the comprehension of their alignment within the material. In XRD analysis the presence of a broad hump in the graph indicates thatthe material lacks a well-defined crystalline structure, suggesting an amorphous nature. Conversely, the absence of this hump signifies that the material possesses a crystalline structure. According to a review by Meenakshi et al., various compositions such as CdO- $B_2O_3-SiO_2$, SiO_2 -ZnO-Bi₂O₃, $V_2O_5-Si_2O_3$ -B₂O₃, V_2O_5 -CdO, V_2O_5 -ZnO, $V_2O_5-Si_2O_3$ -CdO, $Bi₂O₃-Y₂O₃$ and others were investigated. In the XRD patterns of these compositions, the presence of a broad hump indicates that the material is amorphous or non-crystalline [16- 17].For all doped glasses studied, the XRD patterns will exhibit broad peaks, which are characteristic of amorphous materials. This suggests that the process of doping does not significantly induce crystallinity. The introduction of rare-earth or transition metal dopants might result in slight shifts or shoulders in the XRD pattern, indicating localized structural changes or clustering. Additionally, doping with alkaline earth metals could lead to subtle modifications in the XRD pattern, primarily attributed to alterations in the connectivity and packing of the glass network. Yet, a meticulous examination of the XRD data holds the potential to yield insightful details concerning even subtle structural alterations brought about by the dopants.

V. FTIR SPECTROSCOPY

FTIR, which stands for "Fourier Transform InfraRed," represents the prevailing technique in infrared spectroscopy for capturing the infrared spectrum of absorption or emission from solids, liquids, or gases.Distinct structures give rise to diverse spectra due to the unique molecules they encompass. These spectra serve as identifiers, allowing for differentiation among molecules.FTIR proves invaluable in characterizing glass structures as it exploits the distinct vibrational frequencies, akin to fingerprints, associated with every chemical bond and building block. Consequently, FTIR spectra are instrumental in identifyingboth the chemical bonds and building blocks present inside the samples, particularly under ambient conditions [3-5]. To gain insight into the structural alteration of local arrangements in glass and glass ceramics, a combination of FT Raman and FTIR spectroscopy techniques is applied. Borate glasses, serve as an excellent case study to highlight the effectiveness of IR spectroscopy when compared to other glass systems [6]. When we analyse the spectra, we observe that all vibrational bands in borate glasses appear above 500 cm^{-1} . This phenomenon can be attributed to the relatively small mass of boron in comparison to other elements that form glasses.For the measurements, FTIR spectroscopy is employed within the range of 400 to 4000 cm^{-1} . This range allows us to capture and study the unique vibrational characteristics and structural features of borate glasses effectively. The FTIR spectrum of glass consists of peaks and valleys that correspond to specific vibrational modes of bonds present in the glass structure.The positions of these peaks provide insights into the types of bonds, chemical groups and molecular arrangements within the glass.Each peak can be associated with particular stretching or bending vibrations of bonds like B-O, C-O, etc. By comparing the position of these peaks with known reference spectra we can identify the molecular components of glass. FTIR can reveal information about the types and proportions of bonds present in the glass.Additionally, shifts in peak position can indicate changes in bond strength or interactions, which might be related to variations in glass composition.According to the literature, there are three leading IR bands in which the vibrations seen in FTIR spectra may be classified. Trigonal groups have B-O bonds with asymmetrical stretching vibrational modes, which are primarily seen in the range between 1200 and 1600 cm⁻¹. In the second region (800–1200 cm⁻¹), octahedral units with Bi–O bonds are also discovered. Additionally, B-O-B bonding in the third group of bands $(400-800 \text{ cm}^{-1})$ exhibits octahedral units. The glass structure comprises ortho-borate and pyro-borate units, alongside a contribution from metaborate triangles [13-14].Incorporating rare-earth dopants not only introduces characteristic vibrations but also creates unique absorption bands at specific wavenumbers. These bands indicate rare-earth-oxygen (RE-O) bonding or clustering within the glass structure. These distinctive bands offer insights into the local coordination and bonding of rare-earth dopants, influencing the glass's optical and electronic attributes.Similar to bismuth borate glass,bismuth borate glasses that are doped with transition metal oxides also show FTIR peaks corresponding to Bi-O-Bi bending and stretching vibrations [16]. Minor shifts or fluctuations in peak intensity might point to localized structural changes close to the dopant sites, indicating changes to the vibrational modes close to the transition metal ions.The introduction of transition metals results in a gradual replacement of boroxol rings by $[BO_3]$ and $[BO_4]$ groups. De-convolution of the spectrum was carried out using a Gaussian Distribution Function based program. Like Origin 8 pro software. In conclusion, FTIR spectroscopy proves to be a potent tool for the analysis of bismuth borate glasses containing dopants of rare-earth metals, heavy metal oxides and transition metals.

VI.RAMAN SPECTROSCOPY

Raman spectroscopy involves capturing and examining the spectrum resulting from scattered photons. The Raman spectra of borate glasses containing multiple types of borate groups can be intricate, primarily serving to identify specific structural units within these glasses.During a Raman spectroscopy procedure, a sample is illuminated with monochromatic light, usually from a laser. The laser serves as a robust source of singlewavelength light. As the laser photons engage with the sample's molecules, they undergo elastic scattering. The ensuing scattered photons compose a spectrum that is collected and examined in Raman spectroscopy. Raman spectra obtained from borate glasses containing diverse borate groups are intricate. Their main purpose is to unveil and reveal the presence of distinct structural units within these glasses. Thedeconvolution of data shows the peak position, amplitude and full width of maxima. Distinct peaks have appearedto show different behaviour. The bands attributed in the range of $65-400$ cm⁻¹ to the vibrational modes of bismuth ions. Heavy metal vibrational bonds are present in trigonal and octahedral units. Within the frequency range spanning from 400 cm^{-1} to 700 cm^{-1} , typically found vibrational modes associated with the in-plane vibrations of aromatic and heteroaromatic compounds, along with skeletal vibrations ofdiverse molecules. Peaks within this interval can offer insights into the presence of ring structures and vibrations related to the Bi-O-Bi, Ni-O-Ni bonds of [BiO₆] octahedral units. In the spectral range spanning from 700 cm⁻¹ to 1200 cm⁻¹, valuable information abounds concerning functional groups including C-O, C-C, and C-N, B-O-B, B-O bonds. The bonds are present in the borate groups of triangular units. Peaks within this range frequently serve to discern particular molecular groups and their interconnections. In the interval extending from 1200 cm^{-1} to 1500 cm^{-1} , you encounter vibrational modes linked to C-C, C-O, and N-O bonds, along with vibrations indicative of aromatic rings. Moreover, this range can unveil insights into the presence of double and triple bonds within molecules [2],[13-14].To sum up, Raman spectroscopy proves to be a valuable tool for analysing doped glasses, offering significantvibrational insights. Particularly, bending and stretching vibrations in Bi-O-Bi, signifying the amorphous nature of these materials.

VII. CONCLUSION

In conclusion, the comparative study of alkali oxide glasses and bismuth borate glassesdoped with rare earth metals and alkaline earth metals investigated through differenttechniques like FTIR, XRD, and RAMAN spectroscopy. They give insightful information on the distinctive effects of several dopants on the characteristics of glass. All doped glasses showed an amorphous nature with wide peaks, in accordance withthe XRD study. The peak intensity may, however, move somewhat and alter slightly, indicating localized structural modifications close to the dopant sites. The basic vibrational properties, such as the B-O-B stretching and bending modes in all doped glasses are predicted by FTIR spectroscopy. Additional bands in the FTIR spectra caused by the addition of dopants provide vital details regarding interactions between the dopant and the glass as well as changes to the local bonding environment. Similar to this, by displaying distinctive peaks, Raman spectroscopy validates the amorphous nature of all doped glasses which is associated with B-O-B bonds. The optical, electronic, magnetic, and thermal characteristics of the glass are influenced by the local coordination and bonding of the dopants, which are revealed by dopant-specific shifts and extra peaks. According to the comparative study, rare-earth dopants contribute distinctive vibrational modes linked to rare-earth-oxygen bonding or clustering, making them very attractive for modifying optical and electrical characteristics. The magnetic and electrical properties of the glasses are affected by the localised structural changes caused by the transition metal dopants. This thorough comparison research clarifies how each dopant alters the structural and vibrational characteristics of glasses made of bismuth. Such knowledge is essential for creating custom glasses with particular features, making them very promising materials for a variety of applications in optical and technological.

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