

Chapter 1

Introduction and Literature Review

Glass is one of the most fascinating materials, and it was invented 5000 years ago in human civilization when the ornaments and small containers of glass materials were first produced and used in the Middle East later this glass-making technology shifted in Roman society [1]. During the Middle Ages, making glass had a renaissance, as seen by the stained-glass windows in many of the churches and cathedrals constructed across Europe. Sand and flux were used to make glass, but the flux was no longer made mostly of sodium salts from Mediterranean coastal plants but rather of potassium salts produced by burning land plants and later with a few modifications, such as the ashes' purification, this mixture was in use when industrial soda ash was developed at the start of the 1800s [1]. Although coal was widely used throughout the 18th century, little changed in terms of furnace design when the Siemens brothers developed the regenerative gas furnace, which generated gas using a gas generator. By the late 1800s, the procedures of forming had been refined and industrialized and the automation trend gained momentum in the 20th century, and melting tanks were employed for all kinds of glass. However, until this point in time, the glasses' composition, consisting of generally 73 SiO₂, 1Al₂O₃, 11 CaO (+MgO), 14Na₂O, and 1K₂O (a percentage per weight), did not significantly alter from the Egyptian glass. During this period, several innovative glass compositions were initiated, the most well-known of which was likely the heat- and chemical-resistant glasses comprising vitreous silica and B₂O₃. Many more chemicals in glass were made possible by the creation and improvement of optical glasses. Recently, there has been a surge of theoretical interest which has resulted in the development of metallic glasses, which are also already in use in the industry, and non-oxide glasses containing substances like fluoride or sulfide (ZrF₄ or As₂O₃) [2].

Glass is defined as an inorganic product of fusion that has been chilled to a hard form without crystallization, in accordance with the German standard.

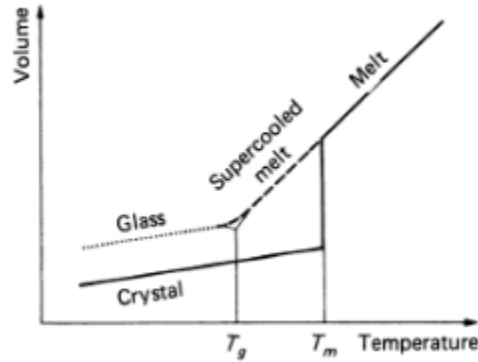


Fig. 1.1. Graphical illustration showing how volume depends on temperature [2].

The volume temperature correlations of glassy materials are shown schematically in **Fig. 1.1**, and the volume investigation should commence at elevated temperatures where a glass melt, or liquid, is present. A liquid or melt's volume usually reduces as it cools. Crystallization usually happens at the melting point T_m , which results in a volume reduction. The volume drops farther when the temperature drops, but it does so at a lower temperature coefficient—that is, the crystal's expansion coefficient is smaller than the liquid's. The entire, solid curve in **Fig. 1.1** is consistent with thermodynamic equilibrium circumstances. Following the dashed equilibrium curve, the volume continually decreases if no crystallization happens at T_m . Thus, even though it is metastable, this region of supercooled melt or liquid remains in thermodynamic equilibrium. The metastable equilibrium curve does not always decrease with temperature; instead, it exhibits a deviation at a particular temperature, and then it roughly follows a more or less parallel path to that of the crystal's equilibrium curve. From this point on, equilibrium conditions are no longer obvious. The reason for the divergence is that liquids get more viscous as they cool. In this manner, the liquid structure's equilibrium at each temperature is reached more slowly until, at some point, the viscosity rises to

the point where equilibrium can no longer be reached through continuous cooling. The liquid has solidified at this point. This analysis leads to the conclusion that this happens at a consistent viscosity, or roughly 10¹³ poise, regardless of composition. The transition temperature T_g is now widely used to refer to the temperature that corresponds to this viscosity. This transition phenomenon is known as the freezing-in process and thus, we can characterize glass as a frozen-in undercooled liquid in terms of physiochemistry.

The renowned scientist Zachariasen discovered that there are very few energy differences between glasses and crystals with the same composition. As a result, the same bonding states or structural units must exist in glasses like in crystals, such as the $[\text{SiO}_4]$ -tetrahedron seen in silicates. These tetrahedrons constitute an irregular network in the glass, contrasting the usual arrangement that exists in the crystal. On the premise of his views concerning what kinds of bonds are thus viable to build a network, Zachariasen proposed the following four requirements for the construction of oxide glasses.

- The cation's coordination number needs to be low.
- There can be no more than two cations associated with an oxygen ion.
- Only their corners-not their edges or faces-may be shared by the oxygen polyhedrons.
- Every oxygen polyhedron must share at least three of its corners with other polyhedrons.

The oxides of types R_2O_3 , RO_2 , and R_2O_5 satisfy these requirements; this is demonstrated by the presence of these oxides in the vitreous form in substances like B_2O_3 , As_2O_3 , SiO_2 , GeO_2 , and P_2O_5 . **Fig. 1.2** schematically depicts the layout of an arranged SiO_2 network, as opposed to **Fig. 1.3**'s depiction of the unorganized glassy silica network configuration. Anyway, only glasses composed of one oxide are used in the aforementioned cases. Nevertheless, systems with many components can also create glass; one such example is the binary system $\text{R}_2\text{O}-\text{SiO}_2$ (where R is an

alkali). The network, created by the $[\text{SiO}_4]$ tetrahedrons in the previously mentioned example, is the foundation for developing glass. Thus, the cations that create this type of polyhedron that builds networks are known as network formers, and the cations that disassemble or alter the network are known as network modifiers. Si, Ge, B, As, and P are examples of network formers; alkalis and alkaline earth (Na, K, Mg, Ca) are examples of network modifiers. Zachariasen and Warren postulate a stochastic distribution of network modifiers in glass structures as an addition to the unorganized network. While some intermediate oxides, including TiO_2 , ZnO , PbO , and Zr_2O_3 , cannot create glass on their own but can make glass in combination with former oxides, some conditional glass former oxides, like Al_2O_3 , Bi_2O_3 , WO_3 , and MoO_3 , may produce glass under specific conditions [3].

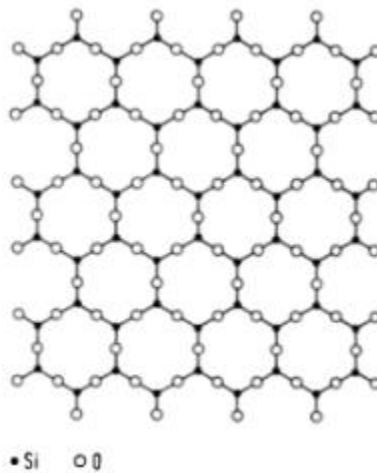


Fig. 1.2. Schematic of an arranged SiO_2 matrix in two dimensions [2]. (The Si's fourth bonds protrude either upward or below from the illustration's plane.)

Glass applications and production advancements accelerated to nearly miraculous dimensions following 1890. Significant new specialty glasses emerged in the late 1900s. Among the new specialty glasses were chalcogenide glass, an infrared-transmitting glass that may be used to create night-vision lenses, and transparent glass ceramics, which are utilized for manufacturing cookware. Optical fibers were created in the 1970s to serve as "light pipes" in laser communication

systems. These pipes keep the light being transferred throughout vast distances brilliant and intense. During the 1970s, glass that securely safeguarded radioactive wastes for thousands of years was also manufactured. Most glasses sold in stores are made of silica and other oxides. The kind of glass is determined by the kind, amount, and existence of one or more oxides; which also significantly impact the qualities and applications of glass. By way of example, introducing a transition metal oxide (cobalt oxide for blue glass, iron oxide for green glass) results in colored glass. Titanium oxide is added to heated glass to create crystalline glass ceramics.



Fig. 1.3. An arbitrary SiO_2 matrix is represented in two dimensions[2]. (From the illustrated plane, the fourth bonds of the Si might protrude either upward or below and dashed lines on the lower right represent the oxygens' relative surface area needs.)

Although the composition of glasses primarily determines their mechanical and physical properties, a further generalization can be made: Compared to metals, glasses are harder, the tensile strength of glasses ranges from 24 to 69 MPa, glasses possess little ductility & hence are brittle, the coefficient of thermal expansion and coefficient of thermal conductivity of glasses are low, electricity is well-insulated by glasses, glasses can withstand a wide range of substances, including water, salt water, chemicals, solvents, and alkaline solutions, certain glasses may withstand high temperatures (soda lime for windows at 700 °C; fused quartz-silica at 1580 °C). Glasses also have better optical qualities, which makes them a better material for windows and lenses. The glass

family is enormous and constantly expanding. Annually, new glass varieties with unique qualities expand their range of applications. Glass is utilized in a wide range of applications, from anti-nuclear irradiation vessels to basic panes or flasks; from photosensitive optical gadgets employed in control systems to sculptural and building glassware; from preparing food tanks to the latest fiber optics. However, the current focus of our research topic is on tint silicate and phosphate-based glasses that have been doped with appropriate amounts of transition, heavy metal, and rare earth oxides. These glasses can be used in commercial settings as external heat-absorbing window glasses, along with optoelectronic and photonic devices, and they may also find use in laser technology. Structural glass and glass ceramics have become frequently employed as the main exterior material in buildings with multiple stories globally during the previous several years. Without a doubt, the importance is growing daily, and contemporary glass research in particular regions-such as Saudi Arabia, the United Arab Emirates, India, and others- focuses on perfecting optical qualities including transmittance, absorbance, and reflectance. Where extremely clear pure silica glasses are employed as envelopes, the buildings will be subjected to extreme cooling loads and unpleasant circumstances. Pure silicate glass is beneficial for enhancing daylighting, but this restriction has been solved using clear tint glasses, that partially mitigate the sunlight that heats buildings. These tint glasses are created, usually, by incorporating metal oxides, including iron, tin, copper, manganese, chromium, vanadium, etc., within the melted glass. Furthermore, metallic coatings, such as gold, silver, copper, and aluminum, are coated on the glass's surface to enhance heat and light reflections. Some noteworthy studies and methods on reflective layers have been carried out to create single and multi-layer metal coatings, such as zinc sulfide anti-reflection layers, followed by layers of metal that have excellent infrared reflection abilities, such as gold, silver, or copper, to create heat-reflective glass employing the vacuum deposition technique [4]. A

thin heat-reflecting layer was made up of one or more metal oxides, including the oxides of heavy metals like Co, Cr, Ni, Fe, Sn, Mn, and Ti, that were produced by the thermal decomposition of appropriate complexes of the corresponding elements on the glass surface [5]. Simultaneously, additional investigation has been done to create low-emissivity building envelopes by creating various low-E glass kinds and hollow low-E glass for office building frames to increase yearly reductions in energy consumption [6]. In addition to emissivity and reflection, many academic studies have been conducted to regulate the amount of sunlight entering office buildings. These studies employed double-glazed windows with highly reflective blinds and variable blind tilt angles to allow daylight to pass through according to requirements. Thus, a numerical methodology for simulation has also been invented[7]. Utilizing XRD, FTIR, and UV-Visible spectroscopy, several earlier investigators have examined the composition of various glasses. From these characterizations, they have inferred physical and significant optical parameters, including molar refraction, optical band gap, Urbach energy, dielectric constant, and metallization parameter [8,9]. In addition, since tint glasses serve as envelope material, it is crucial to investigate their mechanical properties, such as their compressive strength. In associated research, bulk metallic glasses made of magnesium, copper, zinc, and yttrium ions with a high compressive strength were examined due to their low cost, growing popularity, and lightweight[10]. Additional research demonstrates that a series of quaternary Fe-B-Si-Zr bulk metallic glasses injected with a high concentration of Fe produced tinted glass with exceptionally high compressive strength and good soft magnetic characteristics[11].

Regarding transition metals, copper's valence state in glasses influences not only its chemical and physical characteristics but also its capacity to produce glasses[12]. According to ligand field theory, the presence of Cu^{2+} ions is what forms the excellent bright and noticeable bluish-green

color glass[13]. A copper atom has the electronic configuration $[\text{Ar}] 3d^{10}4s^1$, and it exists in the stable ionic states Cu^+ and Cu^{2+} . Cuprous ion (Cu^+) does not produce coloration since its five d-orbitals are fully occupied; instead, Cu^{2+} ion develops a color center featuring bands of absorption in the visible wavelength area and gives the material an appealing blue and occasionally green color and further investigation has shown that the Cu^{2+} content, its specific coordination, and the basicity of the glasses all affect how intense the color of the glass is [14,15]. Due to their optical biostability, Cu^{2+} ion-doped glasses are now the most researched material [13].

Along with doped by transition metals or rare earth ions, the glasses can be made more functional by incorporating certain concentrations of heavy metal oxides. This has been noticed that introducing heavy metal oxides (BaO , Bi_2O_3 , PbO , etc.) to the glasses enhanced a few of their special characteristics, including their density, chemical durability, refractive index, and resistance to devitrification, and they also reduced the processing temperature [16]. Furthermore, heavy metal oxide silicate glasses offer superior shielding capabilities against nuclear radiation and high mass attenuation coefficient values [17]. It has been noted by numerous earlier studies that silicate glasses with appropriate concentrations of heavy metal oxides exhibited superior infrared transmission, less crystallization propensity, and improved linear and nonlinear optical properties[18-20]. Because of their low processing temperatures, high resistance to devitrification, high chemical durability, high optical density, and refractive index, these multicomponent glasses including PbO are extensively utilized in enamels, optics, like optical lenses, ultrasonic delay cables, electro-optic modulators, electro-optic switches, solid-state laser materials, electron multipliers, TV picture tubes, and for additional crucial optical electronic uses and glass-to-metal sealing[21-23]. However, Pb^{2+} 's structural involvement in silicate glasses has previously been extensively researched, revealing its fascinating behavior in the glass production of numerous

systems, including silicates[24]. Prior research has demonstrated that Pb functions as a network modulator at low lead levels and as a glass former at high lead content in binary lead silicate glasses [18]. PbO alone cannot make a glass matrix; but, when combined in the right proportions with other oxides that can form glass, such as SiO₂, B₂O₃, TeO₂, and P₂O₅, it can form glass and provide an ionic or covalent link between oxygen atoms[25].

Furthermore, in addition to transition metal ions and heavy metal oxides, it has been discovered that adding the right quantity of SnO₂ to the structure of silicate glass enhanced the tinted glass's density, greatly boosting the glass's ability to withstand high photon energy[26]. Previous studies also demonstrated that adding the right amount of SnO₂ to glass composition improved the material's photosensitivity, microhardness, and thermal stability. Ziemath et al. used UV-visible optical absorption and diffused reflectance investigation in the infrared range to assert that Sn⁴⁺ cations in their glass composition functioned as a network former, leading to stronger glass formation[27]. However, the drawback of SnO₂ is that, because of its restricted solubility in silicate glass, rising concentrations of SnO₂ in the glass enhance its opacity, which is undesirable when the glasses are utilized as building materials[28].

While the natural world declines & resources become scarcer today, innovative scientific assets and affordable technologies grow increasingly important. The use of rare earth-doped multicomponent phosphate glass, which has possibilities in energy-efficient technologies and is environmentally good, may solve this problem. Considering the potential and wide range of applications in the field of luminous items including solid-state lasers, optical filters, cathode ray tubes, fluorescent lamps, plasma displays, field emission displays, white light-emitting diodes, traffic signals, automotive displays, cellular phone illumination, night-vision goggles, medical diagnostic devices, optical detectors, and sensors, several rare earth energized glass systems have

drawn a lot of research interest [29–32]. Phosphate (1084 cm^{-1}) and fluoride (580 cm^{-1}) groups in the matrix of glass exhibit less phonon energy than traditional silicate (1100 cm^{-1}) and borate (1387 cm^{-1}) groups. As a result, fluorophosphate groups are particularly appropriate to be the host material for numerous RE species in the case of the photoluminescence application field. This is caused by the fact that glasses with lower phonon energy possess longer excited state lifetimes and improved photoluminescence quantum efficiency[33]. When transition metal ions like ZnO are added to glass frameworks, many dopant sites form and the optical and spectral characteristics are greatly enhanced. ZnO also improves chemical endurance and functions as a network inhibitor[34]. When an appropriate quantity of optically active f-f electronic transitions of lanthanide ions is added to different glassy substrates, strong lines of emission emerge. Pr($[\text{Xe}]4f^36s^2$) and Sm($[\text{Xe}]4f^66s^2$) included glasses are among the RE species that have garnered the most attention because of their potential uses in optical communication and display technology. Furthermore, Sm^{3+} is suitable for improving characteristics and developing novel optical functions for glasses because of its large emission cross-section, high energy, notable fluorescence magnitude, and exceptional quantum efficiency[35]. Pr^{3+} ions in the glass matrix have also attracted considerable research interest in luminosity studies because of their strong emission lines that originate from three different energy levels (3P_0 , 1D_2 , and 1G_4)[36].

Inspired by the previous literature reviews, the currently mentioned three thesis contributing works deal with the following matter:

- The previously cited research studies prove the important roles that Fe, Cu, B, Zr, and Mg serve in enhancing the mechanical properties of glasses. Influenced by these studies, the first thesis contributing work focuses on synthesizing a novel structure composed of Fe along with Cu, which produces a blue color-pigmented stannic soda phosphate silicate glass system. This

work also assesses the optical, physical, and mechanical properties, all of which will help develop an economical solar passive building envelope.

- However, the study mentioned above indicates that introducing extremely low and limited levels of Sn^{4+} , Cu^{2+} , Cu^+ , and Pb^{2+} ions to a soda silicate glass enhances the glass's characteristics, making it potentially appropriate for widely utilized in a variety of sectors. Our 2nd contributing research activity is principally concerned with the creation of PbO-based tint glasses with improved optical and mechanical properties for broad uses, based on the literature analysis mentioned above. Another evident goal is to optimize the PbO concentrations in the tint glass compositions to get the best possible mechanical, optical, and physical qualities for building materials. The glass network topologies were investigated using a variety of characterization approaches, and these can be directly linked to the enhanced mechanical, optical, optoelectronic, and physical characteristics of the tint glasses under consideration.
- Motivated by the previously studied literature, the current third thesis contributing research concentrates primarily on producing new PbO-based colored fluorophosphate glass compositions infused with rare earth (RE) species, including Pr^{3+} and Sm^{3+} . For a variety of uses, improving their optical and fluorescent qualities is the goal of this research study. Several characterization techniques and Judd-Ofelt (JO) theory are used in the research, which also involves studies of the optical, radiative characteristics, and glass network topologies. Understanding and improving the optical, fluorescent, and physical properties of the RE-doped pigmented fluorophosphate glasses undergoing investigation is directly aided by these efforts.

- **OBJECTIVES**

Glass matrix composites are designed materials with substantially improved mechanical, optical, luminescent, and physical qualities composed of two or more constituent materials. One of the most significant developments in the history of materials is the creation of glass composite

materials and manufacturing techniques. Over the past few decades, glass ceramics and structural glass have been widely used as the main envelope material in buildings with multiple stories worldwide. Unquestionably, the importance is growing daily, and contemporary glass research is concentrating on optimizing optical characteristics like reflectance, transmittance, and absorbance in specific geographic regions like Saudi Arabia, the United Arab Emirates, India, etc. If very transparent pure silica glasses are utilized as envelopes, the buildings will experience uncomfortable conditions and a heavy cooling load. To overcome this limitation, clear tint glasses are being used, which partially block the solar radiation that causes heat to enter buildings. These glasses are made by adding metal oxides, such as iron, tin, copper, manganese, chromium, vanadium, etc., to molten glass in most cases. In addition, metal coatings, such as gold, silver, copper, and aluminum, are applied to the glass's surface to increase heat and light reflections. The inclusion of certain concentrations of heavy metal oxides enhances the glasses' utility in addition to doping them with transition metals or rare earth ions. Heavy metal oxides (BaO , Bi_2O_3 , PbO , etc.) have been shown to enhance some special qualities of glasses, including density, refractive index, chemical durability, increased resistance to devitrification, and lowered processing temperature. Additionally, the heavy metal oxide silicate glasses offer superior shielding capabilities against nuclear radiation and high mass attenuation coefficient values. Numerous earlier studies noted that silicate glasses with appropriate concentrations of heavy metal oxides exhibited low crystallization propensity, superior infrared transmission, and improved linear and nonlinear optical characteristics. Because of their low processing temperatures, high resistance to devitrification, high chemical durability, high optical density, and refractive index, these multicomponent glasses containing PbO are widely used in enamels, optics (such as optical lenses, ultrasonic delay cables, electro-optic modulators, electro-optic switches, solid-state laser

materials, electron multipliers, TV picture tubes), and glass-to-metal sealing. Due to environmental degradation and electricity constraints, new scientific resources and affordable devices are becoming increasingly important in the present era. Due to its potential use in energy-efficient technology and its environmentally friendly character, rare earth-doped multicomponent phosphate glass systems solve this current problem. The potential and wide range of applications in the field of luminous items, including solid-state lasers, optical filters, cathode ray tubes, fluorescent lamps, plasma displays, field emission displays, and white light-emitting diodes, as well as traffic signals, automobile displays, cell phone illumination, night vision goggles, medical diagnostic devices, optical detectors, and sensors, have drawn a lot of attention to various rare earth-energized glass systems.

However, the preparation and characterization of transition metal ions (Cu^+ , Cu^{2+} , Fe^{3+} , Zn^{2+}), heavy metal oxide (Pb^{2+}), and rare earth ions (Sm^{3+} , Pr^{3+}) incorporated in multicomponent phospho-silicate, silicate, and phosphate glasses, respectively, are the focus of this research investigation series. These glasses are designed for building construction envelopes, lasers, and optoelectronic applications. Several tests were conducted on these manufactured glasses to evaluate their optical, mechanical, and physical characteristics. Additionally, to assess the dependability of rare earth ion (Sm^{3+} , Pr^{3+})-doped multi-component phosphate glasses for laser technology applications, a fluorescence investigation was also conducted.

Therefore, the incorporation of the above-mentioned metal ions into our multicomponent phospho-silicate, silicate, and phosphate glasses was for augmentation of properties of synthesized glasses as follows.

- According to this study, deficient concentrations of iron oxide, tin oxide, copper, cupric oxide, and ammonium dihydrogen orthophosphate not only create a high-quality metallic tint glass

system that significantly lowers the amount of solar heat energy that passes through it but also greatly increase its compressive strength and young modulus.

- Because very little metallic concentration is needed to create this tint amount, the newly synthesized transition metals (Cu^+ , Cu^{2+} , and Fe^{3+}) incorporated phospho-silicate tint glass systems that exhibit good chemical durability and help lower air conditioning loads and the cost of artificial daylighting in buildings. They may also be produced at a very low price.
- Additionally, it can be observed that the refractive index (n), extinction coefficient (k), and complex dielectric constants (ϵ_r , ϵ_i) of the synthesized specimen glasses are improved by the addition of PbO ($0 \leq x \leq 10$, x in mol%) and metallic oxides ($\text{Cu}_2\text{O} + \text{CuO} + \text{SnO}_2$) (< 0.22 mol%) in sodium silicate glass networks.
- Density and absorbance are enhanced in phosphate and silicate glass systems by increasing metallic concentrations (Pb^{2+} , Sm^{3+} , and Pr^{3+}).
- The high refractive index and good metallization criteria of glasses containing zinc, lead, potassium, calcium, fluorine, and phosphate amended via various rare earth elements (Pr^{3+} , Sm^{3+}) can present a significant potential for nonlinear, linear optical switching and optical fiber, as well as for photonics and optoelectronics due to their high spectroscopic value, according to the study's overall optical findings.

As the concentration of rare earth ions (Pr^{3+} , Sm^{3+}) in the multicomponent phosphate glasses increases ($0 \leq x \leq 1$, x in mol%), the fluorescence characteristics also improve.