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Review Article

Categorization of oxide glasses along with its uses and advancement in its journey: A review

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ABSTRACT

Glass is an inorganic solid material that is usually transparent, hard, brittle, and has high structural disorder i.e., it belongs to amorphous solids. It is one of the most antique materials originated by human beings. Among several materials, the research on glasses has been very active because of their controllable physical properties, easy mass production at low cost, excellent homogeneity in a variety of shapes and sizes, and their tremendous applications in the field of optics and electronics, etc. The most recent development in this field is glass-ceramic materials which lead to enormous applications in the future. In this paper, we will become familiar with different classes of glass and their applications and different glass theories, although this empirical hypothesis describes glass formation in some co-related manner, a uniform approach capable of satisfying all the well-known explanations is yet to be developed.

1. Introduction

Glass is an amorphous material it is usually transparent, hard, brittle, and has a highly disordered structure [1-3]. It is one of the most antique materials formulated by human beings. At 1st the glass was used only for decorative purposes. The word glass has been derived from the Latin word “Glaseum” which means shiny and transparent material. The naturally made glass is occurred due to the rapid cooling of lava or molten rocks (i.e. obsidian), due to impacts of meteorites on rocks (i.e. impactites and tektites), and also due to lightning discharge into the ground (i.e. fulgurites). This natural glass was used 1st time as tips for weapons and as a tool for other activities by prehistoric men. Among several materials, the research on glasses has been very active because of their tuneable physical properties, easy mass production at lower cost, excellent homogeneity in a variety of shapes and sizes, and their tremendous applications in the field of optics and electronics, etc. Today approximately 500 different glass compositions are in commercial use, Indian glass industry has made the greatest development all over the globe. The most recent development in this field is glass-ceramic materials which lead to enormous applications in the future [2].

Over the 20th century, the definition of glass has changed by different scientists from time to time as they gain better scientific knowledge from previous research work and due to the advancement of technology. In 1930, glass was described as an amorphous solid. These solids are clarified by an irregular arrangement of atoms or molecules inside any substance. Randall, in 1931, notified that glass is made up of finely divided crystals. Tamman, in 1933, started his book with the line “In the glassy state, there is solid, uncrystallized material”. This was a general classification. Warren, in 1937,

proposed that crystal size in the glass would be of the order of a few angstroms. Most traditional glasses are inorganic and non-metallic. In 1949 American Society for Testing and Materials (ASTM) defined glass as ‘An inorganic product of fusion, which has been cooled to a rigid condition without crystallization’ [4]. This definition declares glass is a non-crystalline hard material formulated by a melt-quenching process. In 1960 glass was defined as a non-crystalline solid.

There are two major definitions of glass. One is based on the preparation techniques and the 2nd definition is focused on the glass structure, i.e. glass is an amorphous solid, in which atoms are arranged randomly. Neither definition appears to be ideal since today glasses can be prepared by those techniques in which cooling of molten substance is not required i.e. by drying of aqueous gels or by vapor deposition. The definition of Morey and ASTM confines the glass to be an inorganic product, which in general form is arguable. In 1996, the national research council advisory committee (NRCAC) observed that glass can't be described only based on the chemical nature of the material used. Based on an infrared transmitting materials study, NRCAC defined glasses as “glass is an amorphous solid which exhibits the glass transition”. In 1994, Varshneya clarify the glass as “solid with liquid-like structure”. Each glass inorganic or organic found to date follows two usual features.

- (1) Display no long-range, periodic atomic arrangement.
- (2) Exhibits the time-dependent glass transformation behavior.

This behavior arises over a temperature range known as the glass transformation region. Any substance organic, inorganic, or metallic created by any technique that displays glass transformation behavior is glass. The materials which have to lack long-range periodic atomic arrangement and don't



exhibit glass transition are amorphous but not glass [3]. Thus, all the glasses are amorphous but all amorphous materials are not necessarily glasses. Therefore, scientists redefine the term 'glass' as material covering all amorphous solids that show the glass transition phenomenon, regardless of the preparation method.

2. Objectives of the study

The objective of this review paper is to obtain an idea about the growth of the glass industry from ancient to recent times in different fields, the factors on which glass is categorized, its preparation methods, characterization tools, different glass theories and the importance of its applications.

3. Preparation method and characterization techniques

For glass preparation normally we use two methods one is melt quenching and the other is vapor quenching. Melt Quenching is the oldest and most reliable method for the preparation of amorphous solids. In this method, molten material is cooled rapidly to prevent nucleation and crystal growth. This process includes the melting of material in a suitable crucible made of alloy. Effective cooling can be achieved by quenching the melt immediately after removing it from the furnace. The oxide glasses prepared by this method are SiO_2 , P_2O_5 , B_2O_3 , etc [5]. This technique has limitations for the preparation of ultra-high pure glasses.

Vapor condensation techniques are used to prepare glasses that can't be prepared by melt quenching and are generally used for the preparation of amorphous films. It relies on the fact that atoms, once vapourised and propelled on a cold substrate, do not have time to reach a crystallographic order. Thermal evaporation, electron beam, ion bombardment, and plasma-induced decomposition are used for this purpose. Depending on the method to vaporize the material to be amorphized, vapor quenching is termed thermal evaporation, sputtering, glow discharge, chemical vapor deposition. In this method the powdered material to be amorphized is placed inside an evacuated chamber, having a substrate material kept at a lower temperature and is heated. Due to the lower temperature of the substrate, the mobility of atoms that are reaching the surface of the substrate is significantly reduced and are randomly frozen resulting in thin films. Thin films of amorphous semiconductors like Si, Ge, GaAs, chalcogenides, etc, are prepared by this method.

XRD and Raman Spectroscopy are the preferred tools for glass characterization. X-Ray Diffraction technique is widely used to confirm the glass phase formation. It helps to identify the structures, phase purity, degree of crystallinity, unit cell parameter, crystallite size, etc. A phase is assumed to be pure when the x-ray pattern matches with that of the reported one, and some or all peak positions are differing from those of the known structures in the case of the latest structures. A fixed wavelength is chosen for the incident radiation and the diffraction pattern is obtained by observing the intensity of the scattered radiations [6]. Raman Spectroscopy informs about molecular vibrations that can be utilized for sample detection. A monochromatic light from a laser source is allowed to fall on a sample, during this process energy is exchanged between the photon and the molecule, as a result, the scattered photon is of either higher energy or lower energy in comparison to the

incident photon. This scattered light is detected. The Raman Spectrum of the sample is obtained by plotting the intensity of shifted light versus frequency.

4. Categorization of glasses

Based on chemical composition and nature of bonding between adjacent particles, glasses are mainly divided into the following two groups- Oxide Glasses and Non-oxide glasses. Moreover, they are further divided into various systems like single, binary, ternary, quaternary, etc. Oxide glasses are used by humans since ancient times and this glass is one of the most important industrial glasses. Oxide glass contains oxygen as an anion, which acts as bridging oxygen during glass formation. These glasses are further subdivided into various categories as discussed below.

Silicate glasses: Silicate glass is compositionally simplest and technologically one of the most valuable glasses. These glasses contain SiO_2 (~72%), Na_2O (~13%), CaO (~11%) as the major components and MgO (~2%), Al_2O_3 (~2%), BaO , K_2O etc [7] as the minor components. Aluminium and CaO are used to improve durability; MgO is used to bypass the crystallization. This glass is very cheap in price due to easily availability of raw materials and effort less formation condition. The structure of silicate glasses satisfies all the Zachariasen rules. The basic building block of these glasses is a silicon-oxygen tetrahedron (silicon with four oxygen atoms forms a tetrahedral arrangement) with a coordination number of four. The short-range order of glass is conserved by these tetrahedra as they have a high degree of internal order. The continuous three-dimensional network in these glasses is occurred by corner sharing of tetrahedral units. The disorder in the structure is mainly caused by variations in the bond angles between the adjacent tetrahedral units, torsion angles α , and only to a minor extent by the distortion of the tetrahedral. Silica is geometrically representative of the CRN model formed by corners connecting tetrahedra. X-ray diffraction of vitreous silica discloses that each silicon is surrounded by four nearly equidistant oxygen atoms at an average spacing of $1.608 \pm 0.004 \text{ \AA}$. Between two adjusted oxygen atoms the bond distance is 2.626 \AA and the mean bond angle is of the order of $109.7 \pm 0.6^\circ$. The Si-O-Si angle allotment in silica glass was achieved by ^{29}Si magic angle spinning (MAS) nuclear magnetic resonance (NMR) studies and the result of this study was reinforced by XRD. NBO atoms cause the rigid and covalent Si-O-Si bond to less rigid Si-O-M⁺ linkages, here M is an NWM metal ion. So diffusion of network modifying (NWM) oxides to silica cause the destruction of the extended Si-O-Si network and generates non-bridging oxygen atoms, hence a change in the structure occurs or structure is modified due to which thermo-physical properties like micro-hardness (MH), glass transition temperature (T_g), etc. going to decrease by increasing the non-bridging oxygen atoms. The various silicon structural units available in modified silicate glasses have been sketched as Q_n units, where n indicates the no. of bridging oxygen atoms joined to silicon. The modification results in the formation of meta, pyro, and ortho silicates in the order; $[\text{SiO}_{4/2}]^0$, $[\text{SiO}_{3/2}\text{O}]^-$, $[\text{SiO}_{2/2}\text{O}_2]^{2-}$, $[\text{SiO}_{1/2}\text{O}_3]^{3-}$ and $[\text{SiO}_4]^{4-}$ which are formulated as Q^4 , Q^3 , Q^2 , Q^1 and Q^0 units, respectively [8]. ^{29}Si MAS-NMR studies of Na_2O - SiO_2 glasses verified that glasses having Na_2O (33.3 mol%) display only Q^3

structural units of Si; as we made further increment in Na²O (50 mol%) generally Q² structural units are present. The addition of alkali oxides to SiO₂ leads to network modification and hence grows the range of glasses. Silicate glasses containing transition metal ions have been subjected to recent studies due to their many fold applications. These glasses are utilized in making glass plates, glass bricks, tubes, glass bottles, glass bends, window glass, jars, eye lenses, electric lamps, test tubes, beakers, etc.

Borate glasses: Over the last few decades borate glasses have been rigorously analyzed from technological and academic points of view. The unusual structural characteristic of these glasses attracted the researcher's attention towards them. These glasses are characterized by high transparency, low melting point, high thermal stability, and high mechanical strength. Under usual conditions, it is very tough to create a moisture-free intrinsic borate glass. Due to water solubility, these glasses are of little importance in pure form. Poch prepared water-free borate glass by melting orthoboric acid for several hours at a pressure of 1 mm of Hg. B₂O₃ is one of the biggest glass formers, used as a flux material in different kinds of glasses, and has the largest glass formation tendency because it does not crystallize by itself even at the slowest cooling rate. It crystallizes only under pressure. Boron is the 1st member of the periodic table's 13th group. B³⁺ ion is very small in size so it easily fits inside the trigonal void made between mutually connected three oxygen ions and a [BO_{3/2}] unit is created. In all borate glasses [BO_{3/2}] unit serves as the basic building block. In the glass structures, these building blocks are joined in the form of a hexagonal arrangement of six B-O bonds which consists of three [BO_{3/2}] units, known as borax ring or boroxol group. The arrangement in B₂O₃ is significantly composed of boroxol units. The doping of modifiers such as alkali or alkaline earth oxides alters the boron co-ordination number in boroxol structure and transforms one of [BO_{3/2}] unit to a tetrahedral [BO_{4/2}] unit that vanishes planarity of the boroxol ring. This change in boron coordination was 1st observed by Biscoe and Warner on the basis of an X-ray diffraction study. These trigonal and tetragonal borate units can be arbitrarily joined to generate various B_xO_y structural units like triborate, ditriborate, penta-borate, diborate groups, etc[9]. On the basis of some experimental studies like NMR, IR, and Raman spectra and on behalf of physical properties Krogh-Moe concluded that the boroxyl group is an important element in the structure of borate glass. The non-bridging oxygens are present in the form of ortho-borate, pyroborates, ring, and chain-type meta-borates at higher concentrations of alkali oxides. B₂O₃ in practice is a common ingredient of chemically resistant and thermal shock-resistant glasses. The existence of few transitional metal ions in these glass structures makes them semi-conducting and superparamagnetic. Borate glass having higher availability of rare earth oxides is used to fabricate optical and optoelectronic devices, because of its low melting point, high transparency, and higher thermal stability [10]. With the addition of heavy metal oxide the density of these glasses increases. These glasses are generally used for manufacturing insulating and dielectric materials. These glasses have wide applications in the fields of radiation, shielding, photonic switches, 3rd order harmonic light

generation, glaze, etc. In the presence of silica, borate glass becomes more applicable rather than as a single compound.

Phosphate glasses: Glass containing phosphorous pentoxide (P₂O₅) as one of the principal constituents are known as 'phosphate glasses' [11]. Phosphorous-oxygen tetrahedra (PO₄) serve as the primary building block for these glasses, here each unit's three oxygen atoms are joined to nearby PO₄ units and the remaining fourth non-bridging oxygen is doubly bonded to the central phosphorous atom. It was analyzed that the bond length of P=O is smaller than that of the single-bonded P-O length. Pure P₂O₅ glass is highly hygroscopic (water absorbing) in nature due to the presence of NBO atoms that immediately react with water and due to this are of weaker chemical stability. Hence these glasses are less important; research on their structure, properties, and applications is very limited. The chemical stability of these glasses can be improved by mixing some heavy metal oxides such as lead oxide and bismuth oxide. Dehydrated P₂O₅ are manufactured in sealed silica ampoules (a small bottle) in moisture-free boxes by using P₂O₅/P₄O₁₀ crystal. Similar to silicate glasses phosphate glasses are made up of corner-sharing tetrahedra, with the major difference that these are three-fold rather than four-fold coordinated. Phosphate tetrahedral units exist in phosphate glasses. In neutron diffraction study, two types of bonding are disclosed between P and O; i.e. (P-O_B): bonding between phosphorous and bridging oxygen and (P-O_{NB}): bonding between phosphorous and non-bridging oxygen. Similar to binary silicate glasses, the modifying oxides in phosphate glasses cause the conversion of bridging oxygen to non-bridging oxygen. In phosphate glasses, band gap is generally higher than in silicates so these are better options for UV transmission. Phosphate glasses possess a high coefficient of thermal expansion, low ultraviolet cutting edge, fast photonic conduction, and low transition temperature. The durability of these glasses is improved by suitable materials like Al₂O₃, In₂O₃, and Fe₂O₃ etc. All alloys are dominant materials for space applications due to their low weight, less price, and desirable strength. Phosphate glasses containing fluoride and rare earth are used in optical high-power laser applications. These glasses have high ionic conductivity along with thermal and electrochemical stability so are of great importance in solid-state ionic devices. These glasses also serve as nuclear waste hosts. These glasses with lanthanide ions like neodymium, erbium, holmium, and thulium are employed as laser glass materials.

Germanate glasses: The irregular arrangement of germanium-oxygen tetrahedra develops the germanate glasses, which are arranged similarly to silicate glasses in structure. GeO₂ by itself can generate the glass network that contains tetrahedra and octahedra of germanium surrounded by oxygen atoms. Mixing of alkali oxide to germanate glass transforms a few of germanium atoms from four to six coordination without disturbing the Ge-O-Ge bonds, this allows some variation in properties which are not possible within silica glass. Vergano et al. broadly studied the kinetics of glass formation. These glasses have lower melting points, higher refractive indices, and greater densities in comparison to silicate glasses. These glasses also exhibit larger dispersion and lower chemical resistivity. GeO₂ and silica are mixed with calcium aluminate glasses to enlarge the optical transmission. Bismuth-

germanates are usually explored for application in optical devices [12]. To increase the refractive index of optical devices GeO_2 is added to silicates as minor ingredients. Technologically pure GeO_2 glasses have less significance because of their property's similarity with silicate glass and their overpriced raw materials. The specific utilization of this glass system is the invention of glass capable of infrared transmission.

Tellurite glasses: Starwort, in 1952, first time created tellurite glasses and examined them. These glasses are characterized by higher thermal co-efficient (approx. $25 \times 10^{-6} / ^\circ\text{C}$) and their higher order of refractive index (approx. 2.3). Under suitable conditions, a lot of tellurite glasses offer better stability. In these glasses tellurium (Te) is available in two types of configurations, one is a trigonal by-pyramid (tpp) having structural unit $[\text{TeO}_{4/2}]^0$ which leads to three-dimensional composition and 2nd one is a trigonal pyramid (tp) with the structural unit $[\text{TeOO}_{2/2}]^0$ which make chains. In a trigonal by-pyramid unit, all oxygen atoms set up bridging bonds within the domain. In a trigonal pyramid; one oxygen atom forms a bridging bond with the surrounding, the other oxygen atom forms a double bond with tellurium and one oxygen atom forms no bond i.e. acts as a terminal atom. Tellurium dioxide (TeO_2) is the most durable oxide of tellurium. The field influence of Te^{4+} lies in between that of network formers and modifiers. The characteristic features of these glasses like high refractive index, low transition temperature (approx. 733°C), chemical stability, high conductivity, high homogeneity, high dielectric constant, and superb infrared transmission, etc. specify them exceptional materials, having extreme importance in scientific study and technological area [13]. Tellurite glasses having rare earth ions, achieved universal awareness because of their capability in manufacturing fibers and lasers.

Chalcogenide glasses: These glasses contain one or more chalcogen elements (i.e. periodic table's 16th group elements like sulfur, selenium, tellurium, etc.) intermixed with 14th or 15th group elements (like Si, Ge, Sn, P, As, Sb, etc.). To create chalcogenide glasses the suitable composition of the above elements is melted in an oxygen-free (or in vacuum) atmosphere to avoid the raw materials reaction with oxygen. Sulfur and selenium on heating create viscous liquids which on rapid cooling transform into glass. In such type of glasses, the nature of bonding is fairly covalent and the molten material carry rings or chains of sulfur and selenium atoms. By using the vaporization quenching techniques thin films are developed over a large composition range and by using the melt quench technique glass in rich amounts are obtained within a limited composition range. The band gap of these materials lies between 1eV to 3 eV, hence these glasses show semi-conducting behavior. Their conductivity values (10^{-3} to 10^{-13} $\text{ohm}^{-1} \text{cm}^{-1}$) change sharply when the magnitude of voltage exceeds a fixed threshold voltage. In pure chalcogens, the conductivity rises with increasing atomic weight and for example, the electrical properties of tellurium melt are very similar to a liquid metal. Ternary chalcogenide glasses have been considerably investigated due to their potential technological applications in the fields of infrared optics, infrared optical fiber, switching devices in computer memories, multifunctional photonic materials, IR sensors, and many other

solid-state devices [14]. These glasses are opaque in the visible region but begin to transmit in the near IR region. These glasses modified with halogens are called 'chalcogenides'.

Metallic glasses: Metallic glasses are amorphous materials made up of either intrinsic metals or a mixture of metal and metalloids. Molten metals generally do not create glasses because they display a big tendency towards crystallization even at slow cooling or annealing, but currently, certain combinations of metal and metalloids have been exposed to do so at higher quenching rates of the order of 10^6 to 10^8 kelvin/second. To create such a glass, the presence of two elements is a must, in the melt. Out of these two, one element belongs to conventional metal (i.e. a transition metal element) and the 2nd one is an element on the metal-insulator border lines. The glasses are designed in the form of thin ribbons or fibers. The features of these glasses alter over a wide range. Some glasses exhibit high tensile strength, high corrosion resistance, and easy magnetize-ability, etc. The electric, magnetic (low hysteresis and high value of magnetization), and optical properties of these glasses are very similar to metals. These glasses are used in transformer laminations and inside thermonuclear reactors to protect from radiation [15].

5. Advancement of glass

We are not sure exactly when, where and by which technique glass was originated by humans in ancient times. The origin of 1st synthetic glass is lost in antiquity. Before people learned to make glasses, they had found naturally formed glasses like obsidians. According to legends, the credit for glass creation goes to a Roman sailor, who cooked the food on a beach and set the pots on the top of stones of natron (a naturally occurring mixture of sodium carbonate decahydrate and sodium bicarbonate along with small quantities of sodium chloride and sodium sulfate). The fire heated the stones and the sand below, then an unfamiliar solution began to flow and that was the origin of human-manufactured glass. Archaeologists informed glass transformation was discovered in earliest Egypt and Mesopotamia as far back as 3500 BC [16]. Egyptians considered glass as a precious material, as exhibited by the glass beads found in the jewelry, tombs, and golden death masks of ancient pharaohs. During the excavation of Harappa, archaeologists found glass bangles, which belong to the period of 3000 BC, which shows that ancient Indians knew the glass-making techniques before the Christian Era.

Prehistoric persons prepared glasses from different inorganic materials to yield the commonly known silicates, borates, phosphates, and other types of oxide glasses containing light and heavy elements as additives in the final glass. The glass matrix was not composed until 1500 BC by covering a sand core with a layer of molten glass. From 1500 BC onwards, trading helped to spread glass-making knowledge to Europe and Eastern Asia. The temple of Belus was constructed with colored bricks containing glass about 2000 years ago in Egypt. Around the 1st century BC, the invention of glass roared in Syria. Romans established few glass factories in their country [17]. During this time glass containers were made, which were highly colored due to impurities. In the 1st century AD, doping of certain inorganic compounds into

glasses was done. Nearby the 3rd century Lactantius mentioned the 1st time use of glass for windows.

By the 15th century, glass was used in architecture. In the 15th and 16th centuries England, France, and Germany started glass manufacturing. In 1612, an Italian priest named Antonio Neri published a book “L’ Arte Vetraria” which is now the most famous book in the history of glass making. In this book, he reported the use of lead oxide and borax, and of arsenic oxide as a fining agent. This exceptional work by Neri was the beginning of a scientific approach to glass technology. After this, the growth of glass technology goes on increasing. By the end of the 17th century, Ravenscroft invented lead glass which is a combination of silica with potash and lead oxide, up to this time glass manufacturing was industrialized in England. In the 18th century, a long-range telescope was constructed having the lead glasses. At present, this telescope is still widely used because of its radiation-shielding properties. In 1854, Germans prepared the 1st scientific glass in Jena. At the beginning of the 19th century, Faraday and others started the scientific study of glasses. It is still today a rapidly growing subject. In 1959 Pilkington Brothers developed flat surface glass sheets having uniform thickness by the process of float glass. This development revolutionized the architecture industry. A real advance was made in the selection and purification of raw materials. In the 20th century, the existence of a broad variety of glass, the quick expansion of new glasses, and the evolution of glass manufacturing processes made a historical time for material science physics. In the last 60-70 years, the utility of glass fibers in many applications like automobile, space, and marine technology, etc. has grown up tremendously. Most commercial glass production is now part of heavy industrial complexes [18].

6. Structural theories of glass formation

The theories to explain the process of glass formation are known as the structural theories of glass formation.

Goldschmidt’s Theory (1926): Goldschmidt on the basis of his observations suggested that the 1st structural theory of glass in 1926. According to him compounds (or oxides) having the general formula A_nO_m form the glasses most easily if the ratio of ionic radius of the cation (A) to oxygen (O) lies in the range 0.2 to 0.4. Metal oxides whose radius ratio belongs to this range favor the creation of tetrahedral arrangement.

Table 1: Limiting radius ratio for glass formation according to Goldschmidt’s criteria [19].

Polyhedra	CN	Radius ratio
Triangle	3	0.155
Tetrahedron	4	0.225
Trigonal bipyramid	5	0.414
Square pyramid	5	0.414
Octahedron	6	0.414

Hence, Goldschmidt concluded that for any material to be a glass former it must have tetrahedrally co-ordinated cations. Goldschmidt did not explain why tetrahedral coordination should be so supportive of glass generation. This theory was not sufficient to explain a variety of systems completely.

Zachariasen Theory (1932): W.H. Zachariasen extend Goldschmidt’s proposal. On the basis of the continuous random network (CRN) hypothesis, he made an effort to describe why certain coordination no.’s support the glass generation [20]. CRN model is based on the existence of polyhedra, that are joined together to develop an overall random network. He suggested that oxide in crystalline and glassy forms is made up of a similar type of oxygen polyhedra but they differ in their atomic arrangement, in a crystal polyhedral units have periodic and symmetric alignment but in the case of glass polyhedral units have enough variation in bond angles and bond lengths and are randomly arranged. Because of this random network, the internal energy of glass is slightly higher than that of the corresponding crystal, this clarifies that crystal polyhedral units must be grouped together in a similar way to that of glass polyhedral units. Hence using the random network theory he investigated the structure of glasses by applying some rules to the relevant oxide from which the glass may or may not be formed. This consideration was suitable because both the crystalline and liquid states have similar bonding, coordination polyhedral, etc. A review of rules proposed by Zachariasen for glass formation is described as:

- (1) An oxygen atom should not be linked with more than two cations.
- (2) The no. of oxygen atoms in the neighborhood of any specific cation must be small (typically 3 or 4).
- (3) The oxygen polyhedral share only corners with each other, neither edges nor faces.
- (4) At least three corners in each polyhedron must be shared.

From the above rule 1 and 2 we understand that glasses are brittle (i.e. we can easily break them). 2nd rule clears that cations (Si, B, P, Ge, As, etc.) are surrounded by oxygen tetrahedra or triangles (because CN = 3 or 4). From the 3rd rule, we have to know that glasses have asymmetric structures with varying bond lengths and bond angles. 4th rule makes it clear that glass formers have a three-dimensional network. Hence the role of cations depends on their valency, CN, and the corresponding bond strength. From the above points we can conclude that these rules are satisfied for compounds of the form A_2O_3 if the shape of oxygen atoms is triangular around each atom A and for compounds of the form AO_2 and A_2O_5 if the shape of oxygen atom is tetrahedra around atom A. The basic structural units of the form AO_3 and AO_4 yields short-range order in glassy materials. So the compounds, which satisfy Zachariasen’s rules are known to be glass formers like SiO_2 , B_2O_3 , P_2O_5 , GeO_2 , Sb_2O_3 , As_2O_3 , Ln_2O_3 , SnO_2 , TiO_3 , PbO_2 , P_2O_3 , Nb_2O_3 and Ta_2O_5 . We have two more compounds that are non-oxide but are glass formers like As_2S_3 and B_2F_2 . Compounds of the form A_2O and AO do not satisfy Zachariasen’s rules, these oxides are not glass formers but are known as network modifiers, these oxides interact with the structure of glass former and result in an extreme change in several properties of glasses. An another category of oxides also exists which do not create glasses by themselves easily but do so when mixed with other oxides, such oxides are called intermediate glass modifiers or conditional glass formers like TeO_2 , WO_3 , MoO_3 , Al_2O_3 , Ga_2O_3 and V_2O_5 etc. Zachariasen in his rules had also mentioned that proper cooling conditions are a must for any glass formation, this was later supported by the

kinetic theory of glasses. The experimental data of x-ray diffraction given by Warrant et al. supports Zachariasen's theory. Random network theory is an accepted structural theory of glass today. Some glass-forming oxides are obtained in recent years which do not follow the Zachariasen rules, hence there are certain limitations in his rules, but these limitations can not take over the usefulness of Zachariasen rules.

Sun Theory (1947): Sun suggested the theory of glass generation based on single bond strength. According to him when molten material is rapidly cooled down to form a glassy state then reforming and breaking of bonds take place. The strong bonds yield enough viscosity to resist the conversion of molten structure into crystalline and support the glass formation. On this basis, it is believed to have a connection between bond strength and glass formation. According to Sun glass formation is effortless if the cation-anion bond strength is stronger in molten material. He explained the bond strength as the dissociation energy of oxides into their component atoms. The strength of the single bond is achieved by dividing the dissociation energy by the total no. of cation-anion bonds in the coordination unit. In this way, single bond strength was calculated. On the basis of bond strength Sun, divided the oxides into three classes. The oxides possessing a single bond strength greater than 80 kcal/mol were labeled as glass network formers and oxides having a single bond strength smaller than 60 kcal/mol were defined as glass network modifiers. The oxides whose single bond strength lies between 60 to 80 kcal/mol were justified as intermediates [20].

Smekal Theory (1951): According to Smekal "only those melts could form glasses which contain bonds that are intermediate in pure covalent or pure ionic character". This theory favors the fact that stronger covalent bonds usually yield invariable bond angles but is inadequate to clarify the deviations in bond angles for a continuous random network of the glass structure. On the other side, purely ionic bonds do not have directional characteristics; therefore they are unable to form network structures.

Rawson Theory (1967): Rawson modified the Sun's criteria by introducing the concept of melting temperature as a mandatory parameter to determine the nature of bond strength. He clarified the high melting temperature as the availability of sufficiently high energy to break bonds between different atoms, while low melting temperature suggests that less energy is occupied. Here it should be clear that, at higher temperatures, more bonds are disturbed or broken which causes low viscosity & low viscosity means it is tough to form glass materials [20]. From this assumption, he concluded that the materials which are at low melting temperatures and have a large single bond strength will be a better glass former than one with similar single bond strength but kept at a much higher melting temperature.

Kinetic Theory (1983): This theory was introduced by Unlmann and Hinnon (1983) and is based on the free volume and entropy model [23]. This approach suggests that the rate of cooling is the biggest factor that affects the transition of melt to crystal or glass. The melts which cooled instantly support the glass formation, but the melt which have sufficient nucleation and is cooled slowly have enough time to arrange atoms in a well-mannered structure like a crystal. Hence to create a glass

(an irregular arrangement or motion of atoms or molecules), melt should be cooled fast enough to avoid crystallization. In this way, the glass production process is a kinetic phenomenon associated with a quenching rate and depends on kinetic constants.

7. Conclusions

In this paper, we become familiar with different classes of glass, their uses, and different theories, although these empirical hypothesis describes the glass formation in some correlated manner, but a uniform approach capable of satisfying all the above explanations is yet to be developed. In the 20th century, the existence of a broad variety of glass, the quick expansion of new glasses, and the evolution of glass manufacturing processes made a historical time for material science physics. In the last 60-70 years, the utility of glass fibers in many applications like automobile, space and marine technology, etc. has grown up tremendously. Most commercial glass production is now part of heavy industrial complexes.

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References

- [1] M. Zhang, et al., Influence of oxidation on structure, performance, and application of metallic glasses, *Adv. Mater.* **34** (2022) 2110365.
- [2] S. Urata, et al., Atomistic to continuum simulations of fracture and damage evolutions in oxide glass and glass-ceramic materials: A critical review, *J. Non-Cryst. Solids* **15** (2022) 100102.
- [3] L. Berthier, G. Biroli, Theoretical perspective on the glass transition and amorphous materials, *Rev. Mod. Phys.* **83** (2011) 587.
- [4] ASTM standards on Glass and Glass products, prepared by ASTM Committee C14, American Society for Testing Materials, April 1955.
- [5] J.E. Shelby, Introduction to Glass Science and Technology, The Royal Society of Chemistry, UK (1997).
- [6] U. Shmueli, Theories and Techniques of Crystal Structure Determination, Oxford University Press, London (2007).
- [7] T. Sasaki, Y. Mori, M. Yoshimura, Y.K. Yap, T. Kamimura, Recent development of nonlinear optical borate crystals: key materials for generation of visible and UV light, *Mater. Sci. Eng. Rep.* **30** (2000) 1–54.
- [8] K.J. Rao, Structural Chemistry of Glasses, Elsevier Science Technology Books (2002).
- [9] D. Xue, K. Betzler, H. Hesse, D. Lammers, Nonlinear optical properties of borate crystals, *Solid State Comm.* **114** (2000) 21–25.
- [10] A. Edukondalu, et al., Synthesis, thermal, optical, mechanical and radiation-attenuation characteristics of borate glass system modified by Bi₂O₃/MgO, *Appl. Phys. A* **128** (2022) 331.
- [11] K.S. Shaaban, et al., Mechanical, structural and crystallization properties in titanate doped phosphate glasses, *J. Inorg. Organom. Poly. Mater.* **30** (2020) 4655–4663.

- [12] B.V. Padlyak, V.T. Adamiv, Ya. V. Burak, M. Kolcun, Optical harmonic transformations in borate glasses with $\text{Li}_2\text{B}_4\text{O}_7$, LiKB_4O_7 , CaB_4O_7 , and LiCaBO_3 compositions, *Physica B* **412** (2013) 79–82.
- [13] F. Desevedavy, Review of tellurite glasses purification issues for mid-IR optical fiber applications, *J. Am. Ceram. Soc.* **103** (2020) 4017-4034.
- [14] S.K. Pal, et al., Insights into the physical aging in chalcogenide glasses: A case study of a first-generation As_2Se_3 binary glass, *Coord. Chem. Rev.* **442** (2021) 213992.
- [15] H. Liu, et al., Crystallization in additive manufacturing of metallic glasses: A review, *Add. Manuf.* **36** (2020) 101568.
- [16] H. Tait, *Five Thousand Years of Glass*, British Museum Press, London (1991).
- [17] M. Bimson, I.C. Freestone, *Early Vitreous Materials*, British Museum Occasional Papers N°56, British Museum, London (1987).
- [18] C. Vakif Ahmetoglu, T. Semerci, G.D. Soraru, Closed porosity ceramics and glasses, *J. Am. Ceram. Soc.* **103** (2020) 2941-2969.
- [19] V.M. Goldschmidt, *Skrifter Norske Videnskaps Akad (Oslo)*, I. *Math Naturwiss Kl*, **8** (1926) 7.
- [20] G. Kaur, *Solid Oxide Fuel Cell Components: Interfacial Compatibility of SOFC Glass Seals*, Springer Cham Heidelberg New York Dordrecht London (2016) p. 181.

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