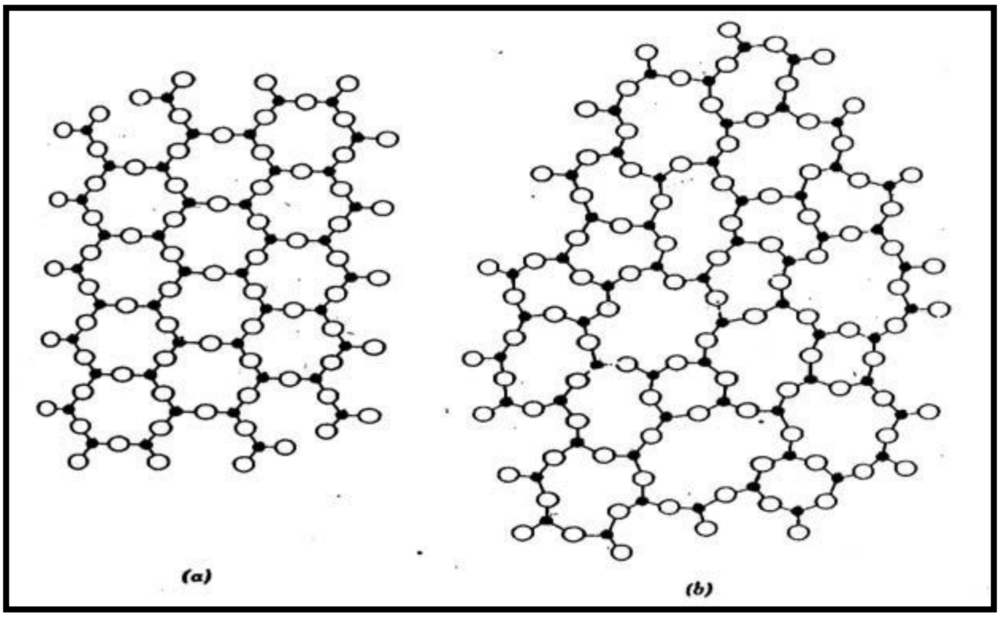
# Chapter One
# Introduction

## 1.1. Physical States of Matter:

Solids are classified into two main groups according to their structure:

(a) Crystalline solids which consist of a regular arrangement of atoms in a repeated three-dimensional pattern. When solids exhibit such regularity or periodicity, they are said to form a crystal lattice .i.e. exhibit long range-order.

(b) Amorphous (or non-crystalline) solids which consist of atoms or molecules tightly bound to one another, but having little or no geometric regularity or periodicity in their arrangement i.e. exhibit short range-order .Glass is an example of amorphous solids. Many solids can be found in both crystalline and amorphous forms [7].



○ ⟶ Oxygen
● ⟶ Boron

**Figure 1.1:** *(a) Ordered crystalline form and, (b) Random network glassy form of the same oxide* [12].

## 1.2. Amorphous Structure:

The amorphous materials possess randomness to some extent. Randomness can occur in several forms as topological, spin, substitution, and vibration disorder. That can be defined in figure 1.2 as;

- Topological (or geometric) disorder, in which there is no transnational symmetry , certain amorphous materials have considerable short – range order while others have a little, both still have no long- range order.
- Spin disorder; in which the underlying perfect crystalline lattice is preserved, but each atomic site possesses a spin or magnetic moment so it is said to be randomly oriented.
- Substitutional disorder, in this form although the underlying crystalline lattice is preserved, the material is in fact an alloy (solid solution say Cu-Au) with one type of atom randomly substituting the other in the lattice.
- Vibrational disorder, the concept of a perfect crystal is only valid at the absolute zero of temperature and at any finite temperature the random motion of atoms about their equilibrium position destroys this perfect periodicity. And that not consider of course a topological disorder [8].

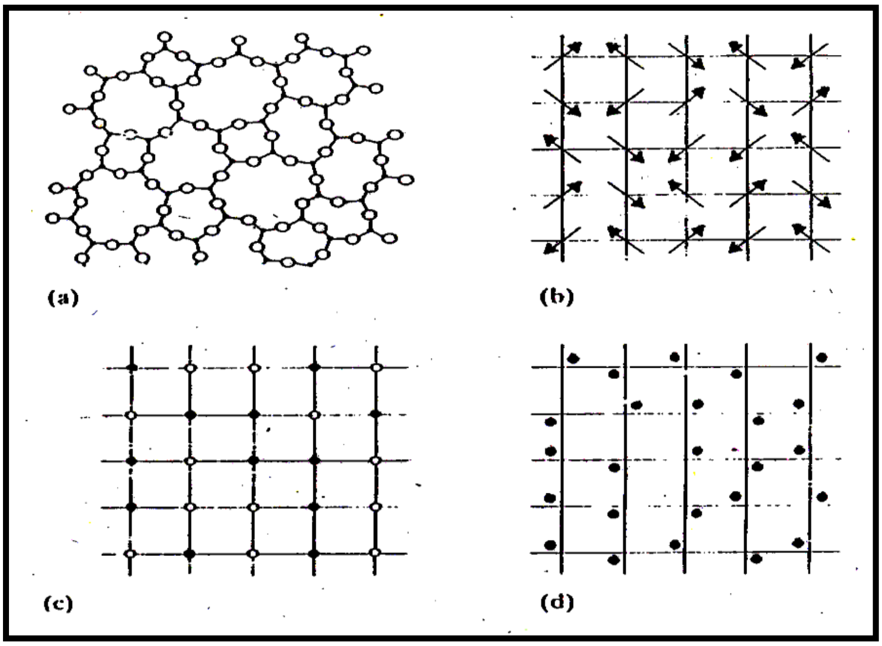


**Figure 1.2:** *Types of disorder: (a) Topological, (b) Spin (c) Substitution and (d) Vibrational disorder [8].*

## 1.3. Definition of Glass:

The term glass is more restricted and as a consequence varies most in its definition. All glasses found to date share two common characteristics. Firstly, no glass has a long range, periodic atomic arrangement. Secondly, every glass exhibits time-dependent glass transformation behavior. This behavior occurs over a temperature range known as the glass transformation region.

A glass can thus be defined as; "An amorphous solid is completely lacking in long range, periodic atomic structure, and exhibiting a region of glass transformation behavior." So all glasses are amorphous but not all amorphous solids are necessarily glasses. The most important question comes to mind. Does glass formation require melting? No, we can form glasses by (a) vapor deposition, (b) sol-gel processing of solutions, (c) irradiation of crystalline materials [9]. More succinctly "glass is an inorganic product of fusion which has been cooled to rigid condition without crystallization" [10] .

## 1.4. Volume-Temperature Diagram:

We traditionally discuss glass transformation behavior, the relation between crystal, liquid and glass, on the basis of volume- temperature diagram figure 1.3 considers a small volume of a material at a high temperature in the liquid form whose state is given by the point (A) on the V-T diagram .On cooling, the volume gradually decreases along the path "AB" where point B represents the melting point ($T_m$) of the corresponding crystal, If the rate of cooling is slow, crystallization occurs and the volume will decrease sharply along BC, upon further cooling the crystal so formed shrinks along the crystal line to point "D". If the rate of cooling is high, crystallization does not occur and the liquid mass moves into the supercooled liquid state along the line ABE which is an extrapolation of the line AB. No discontinuities in the V-T are observed the volume, however, shrinks continuously i.e., the structure of the liquid rearranges itself into a smaller volume along the line ABE. As cooling continues, the molecules become less and less mobil, i.e., the viscosity of the system rapidly increases. At sufficiently low temperature ,the molecular groups cannot rearrange themselves fast  enough to reach the volume characteristic of that temperature .the state line then starts a smooth departure from ABE and soon becomes a near-straight line (often roughly parallel to CD ,ending at point G, when cooled fast , or at G' , when cooled slowly . The material in the near-straight, low-temperature part of the curve behaves essentially as a solid. This is glassy state. The smooth curve between the onset of the departure from the supercooled liquid line and the completion to a seemingly rigid condition is termed as glass transition region or the glass transformation range and occur over a range of temperature. So it must be emphasized that the transition to glass state does not occur at a single, well defined temperature. In the glassy state the viscosity is very high to qualify for appearance as solids. The intersection of the extrapolated glass line and the supercooled liquid line is termed as fictive temperature ($T_f$). One may imagine that $T_f$ is the temperature at which the structure of the supercooled liquid is instantly frozen into the glass. The departure from the supercooled liquid line is depending upon the rate of cooling, slower cooling allows the structure to rearrange itself to stay on ABE .Some what longer, and hence the more slowly cooled glass at G' would be expected to have a smaller volume (higher density) and a lower fictive temperature than more quickly cooled glass at point G [12]. Finally, it is needed to define a term, which, while commonly used, has only a vague scientific meaning. As indicated above, the glass transformation occurs over a range of temperatures and cannot be characterized by any single temperature. It is, however, convenient to be able to use just such a single temperature as an indication of the onset of the glass transformation region during heating of a glass. This temperature, which is termed either the glass transformation temperature, or the glass transition temperature, $T_g$, is rather vaguely defined by changes in either thermal analysis curves or thermal expansion curves. The values obtained from these two methods, while similar, are not identical. The value obtained for $T_g$, is also a function of the heating rate used to produce these curves. Since $T_g$, is a function of both the experimental method used for the measurement and the heating rate used in that measurement, it cannot be considered to be a true property of the glass. We can, however, think of $T_g$, as a useful concept of approximate temperature where the supercooled liquid converts to a solid on cooling, or, conversely, of which the solid begins to behave as a viscoelastic solid on heating [9].

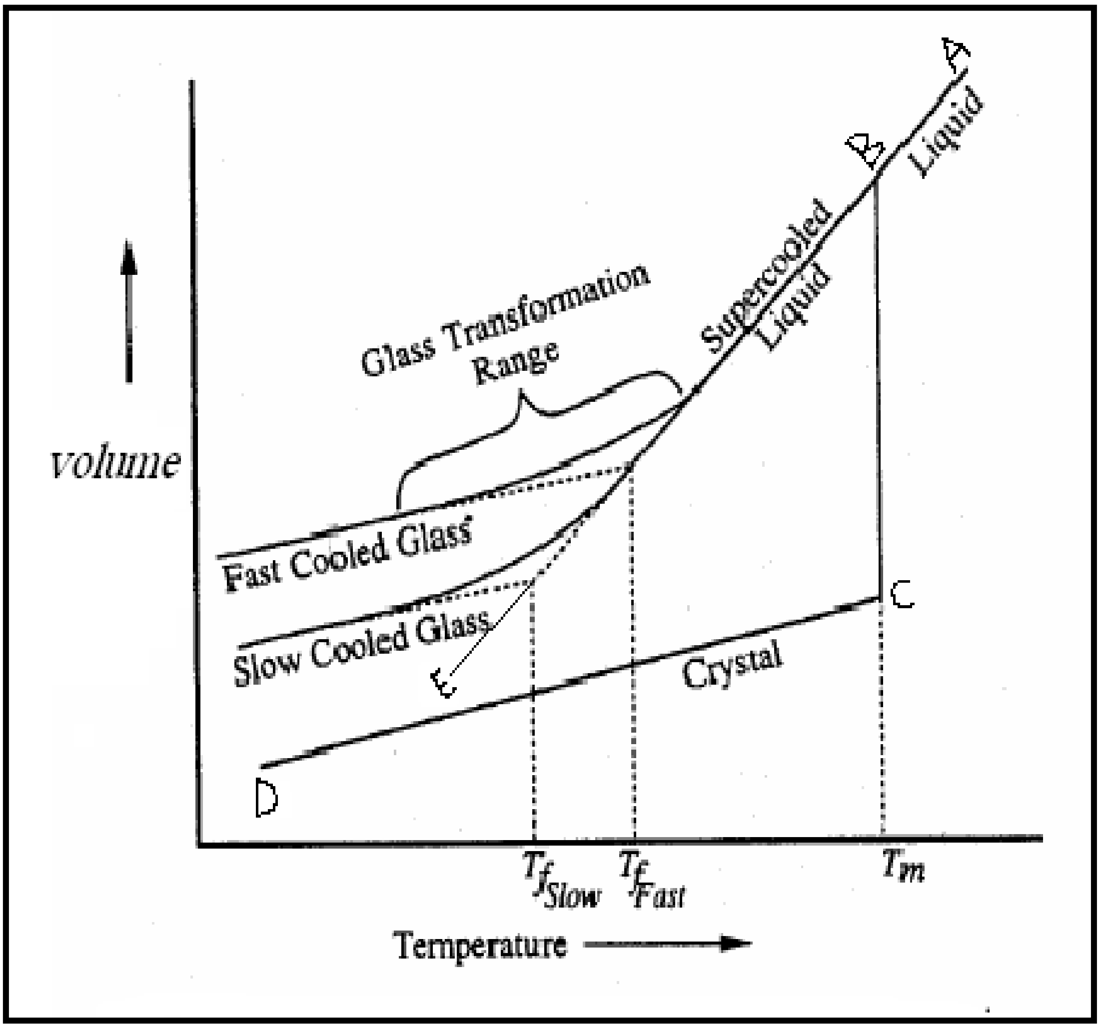


**Figure 1.3:** *Relationship between glassy, liquid, and solid states* [9].