

INTRODUCTION

CHAPTER ONE

INTRODUCTION

According to the structure of materials, solids are classified into crystalline and non-crystalline (amorphous) materials¹¹.

The term 'amorphous' can be definite, as the materials do not possess the long-range order (periodicity) characteristic of a crystal. The randomness in amorphous can present in several forms, which topological, spin, substitutional and vibrational disorders are the most important. These types of disorder are illustrated in Fig. (1.1).

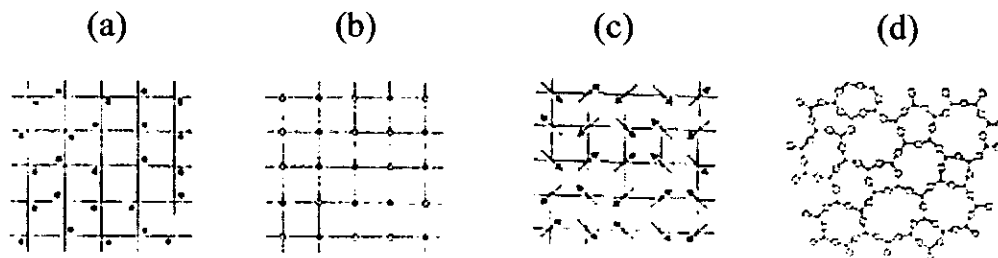


Fig. (1.1): Types of disorder (a) Vibration (b) Substitution (c) Spin
(d) Topological

A: Theoretical background

The inorganic oxide glasses (amorphous materials) consist of glass formers and glass modifiers. Generally, the inorganic oxides introduced in these oxide glasses can be classified into three types:

I: Glass Formers

These oxides have the ability to form glass network by themselves; such as SiO_2 , B_2O_3 , GeO_2 , and P_2O_5 . Nearly all-commercial glasses are based on these glasses. In addition, these oxides can also

form glasses when mixed (up to limiting percentage) with another oxide or oxides, which are not by themselves glass formers.

II: Glass Modifiers

These oxides cannot form glass by themselves but they can be accommodated in the glass matrix in interstitial positions and can lead to modify the glass matrix properties. Na_2O , Li_2O and CuO are examples of such oxides.

III: Intermediate Oxides

These oxides can take part either in the glass network structure or set in the interstitial positions, and can also play a role between the network formers and network modifiers. Al_2O_3 , PbO and V_2O_5 are examples of such oxides. According to this rule, the glass network would contain large holes (interstices) which would easily accommodate elements that cannot enter the glass structure. Based on these assumptions, a glass can be visualized as continues random network extending in three dimensions.

Silicate glasses exhibits the large area of oxide glasses, so the structure of silica glass is the simplest of all the glass structures, yet many of the details are not fully understood. The basic unit is shown in fig. (1.2a). Each oxygen acts as a bridge between neighboring tetrahedra (Bridging oxygen) fig (1.2b).

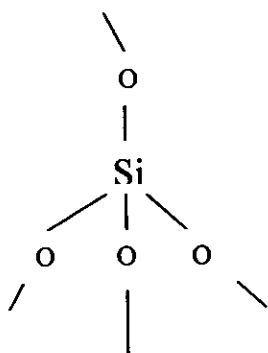


Fig. (1.2a)

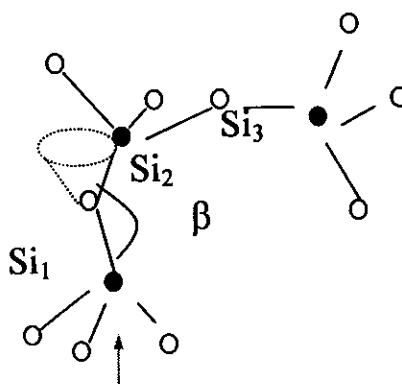
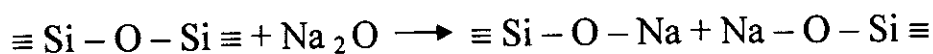


Fig. (1.2b)

Nearly 100% of the oxygens are bridging except for some defect sites and for those associated with impurities in commercial specimens.

The disorder of the glass structure is ascribed mostly to the variations in the bond angle β and the torsion angles α_1 and α_2 and to some extent to the variation in bond lengths, where β is the angle between neighboring tetrahedra and is called the bond angle. α_1 and α_2 are the angles between $\text{Si}_1\text{-O}_1$ and $\text{O}_4\text{-Si}_2$, respectively, when projected on the $\text{O}_1, \text{O}_2, \text{O}_3$ plane, and the rotation angle about the $\text{O}_4\text{-Si}_2$ axis, variable Si-O-Si combining angles is present with mean values about 145° . Generally, the vitreous silica structure has atomic defect sites arise, preminently through energy-rich radiation. These phenomena have been summarized by Griscom ⁽²⁾. In the alkali silicate glasses nonbridging oxygen occur adjacent to the alkali ions. According to the very simple reaction equation, a splitting of the network takes place, and nonbridging oxygen occur.



This formation of nonbridging oxygen represents the most important influence of the alkali oxides; the reason is that they cause a

weakening of the glass structure whose strength in these glass systems increases with the number of Si-O-Si bridges. With glasses containing alkalis a surprising behavior has been discovered; with gradual substitution of one alkali ion by another alkali ion, some properties display a distinctly non linear behavior, for example electrical conductivity and self diffusion. This effect is called "the mixed alkali effect or sometimes called the mixed oxide effect".

1.1 : D.C Electrical Conductivity of Glasses ⁽³⁾

The DC conductivity behavior at a finite temperature for the amorphous semiconductor glass can be written as:

$$\sigma = - \int \sigma_E [(\partial f(E) / \partial E)] dE \quad (1.1)$$

where σ_E is the conductivity for states with energy E and $f(E) = \{1 + \exp (E - E_F) / kT\}^{-1}$ is the Fermi-Dirac distribution function. Conduction involving localized states in the gap energy can only occur by phonon-assisted hopping and thus the only current-carrying states are the extended states beyond E_V and E_C in the valence and conduction bands, respectively.

In real materials, which may contain a high concentration of defects and consequently have a high density of states in the gap, electron transport can take place via such defective states, and the magnitude of this defect-controlled conductivity may greatly sidele that due to conventional band conduction. Moreover, the temperature dependence of this form of conduction can have a distinctive form, easily distinguishable from the simple activated behavior characteristic of the band conduction. Mott ⁽³⁾ considers two localized sites; one filled or slightly below the Fermi energy E_F and the other empty and above E_F ;