Chapter (1)

Introduction and Literature survey

Solids are classified either as crystalline or non-crystalline (amorphous). The crystalline substance consists usually of atoms arranged in a periodic repeatition in three dimensions while a non-ctystalline one does not show like periodical repeatition .

A distinctive class of amorphous solids are glasses, which are defined as amorphous solids obtained from the melt by solidification. Since the distinction between glasses and other amorphous solids is not strictly defined by the above statement, another definition was given here in which glasses are known to be characterized by the following three points[1]:

(i) *Brittleness:* i.e. they are unable for stress and strain in contrast to metallic bonds.

(ii) *Transparency:* i.e. they permit approximately all the optical spectrum to transmit through them.

(iii) *Gradual softening:* i.e. they have not a definite temperature for changing from solid to liquid state.

1.1 The glassy state[1,2]:

In order to understand the relation between the glassy state and the normal solid and liquid states, the dependdence of the volume on temperature will be considered for a substance which can exist in all three states, see Fig. (1.1).

Starting at the high-temperature, end of the diagram, the liquid is cooled through the freezing point T_f it may either freeze into a crystalline solid, with discontinuous change in volume, or it may continue as a super-cooled liquid below this temperature. At lower temperatures, it will be seen in Fig. (1.1) that, at a certain temperature the curve of volume against temperature for the super-cooled liquid show a " bend" and then continues with a new slope, which is often nearly the same as that of the corrresponding curve for the crystal. The temperature region over which this change occurs is located roughly by ' the glass transition temperature' T_g.

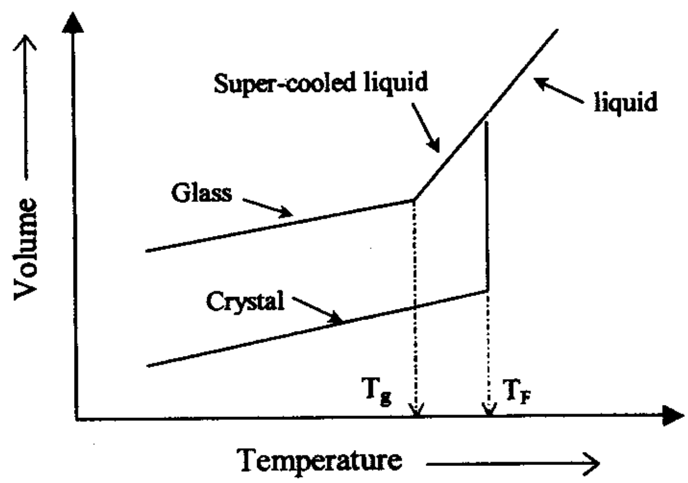

Figure (1.1) :Relation between the glassy , liquid and solid states.

If the substance is cooled still further it continues to contract, but now at a slower rate. Its viscosity continues to increase- also at a slower rate. Any liquid or super-cooled liquid whose viscosity is greater than about 10^{13} poise is called a glass. This value of viscosity, or equally, the transformation temperature, T_g , defines the boundary between the liquid and the glass states.

1.2 The structure of glasses:-

Glasses, like ordinary liquids posses only short-range order, and from X-ray diffraction patterns it is known that, both glasses and liquids have the same structure. The difference between crystalline and non-crystalline (amorphous) states is that, in the case of crystalline state peaks appear in the X-ray pattern but in the case of non-crystalline (amorphous) is not, because the crystalline substance has a parallel planes of atoms and non-crystalline substance has not.

On the other band, as the temperature is lowered the degree of order in a liquid increases whereas in glass it does not approach the crystalline state as the temperature is lowered.

Zachariasen[3] began with the idea that the atoms in glass must be linked by forces essenitially the same as in crystals, as well as they oscillate about a difinite equilibrium positions. This was deduced from the fact that the strrength of the glass is of the same order as the strength of the crystal. Also as in crystals, the atoms in glass must form an extended three-dimensional network, but not periodic. This was shown by the absence of sharp X-ray diffraction spectra.

Zachariasen then proposed the following condition for glass formation, " the substance can form extended three- dimensional network lacking periodicity with an energy content comparable with that of the corresponding crystalline network". It follows that the coordination number of the atom must be approximately the same in both the crystalline and glassy forms. For example, in crystalline SiO_2 and silicates, the silicon atoms are almost surrounded by four oxygen atoms forming SiO_4 tetrahedra.

Zachariasen requirements which must be satisfied by the crystalline oxides in order to able to form glasses, are :

(1) Each oxygen ion is linked to no more than two cations.

(2) The oxygen polyhedra share corners with each other,not edges or faces.

(3) The number of oxygen atoms surrounding the positive ion must be small (3 or 4)

(4) At least three corners of each oxygen polyhedron must be shared with another polyhedron.

It is found that, all crystalline oxides which are suited to form a glass satisfy the conditions of Zachariasen and reversely that each oxide satisfying the conditions can appear in the vitreous state. Figure [1.2 (A,B)] represents the structure of an imaginary oxide in both crystalline or glassy forms respectively with AO_3 traingles in both cases.

In phosphate glasses[4], the basic building block is the phosphorus-oxygen tetrahedron. The phosphorus has a double bond to one of its surrounding oxgen atoms. Thus it seems likely that the structure of glassy P_2O_5 is a three - dimensional network of these phosphorus-oxygen tetrahedra, each tetrahedra being bonded to three other tetrahedra. It shows that in phosphate glasses, the most common structural units are chains of rings of PO_4 tetrahedra.

1.3 Glass formation:

Glass formation becomes more probable if : *(1)* The cooling rate is great, *(2)* the sample volume is small, and *(3)* the crystallization rate is slow. It was found also that all crystalline oxides which are suited to form a glass satisfy the conditions of Zachariasen and reversibly each oxide satisfying Zachariasen conditions can appear in the vitreous state. These oxides are usually classified as oxide glass formers. The other oxides which can not readily form glasses are either intermediate or modifiers.