PHYSICo - CHEMICAL STUDIES OF SOME LEAD SILICATE GLASSES

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Physico-chemical Studies of Some Lead Silicate Glasses

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بسم الله الرحمن الرحيم

TO

MY HUSBAND
AND
MY FAMILY
WHO GAVE ME HELP AND
ENCOURAGEMENT

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CONTENTS

Abstract

Physico chemical investigations, namely infrared absorption spectra, chemical durability and density of some lead silicate glasses were carried out with the aim to throw some light on the structure of these glasses.

All glasses were melted in platinum -2% rhodium crucibles in an electrically heated furnace at temperature ranges from 1100 to 1200 °C, depending on the glass composition. The duration of each melt was four hours. After complete melting, the molten glass was annealed at the appropriate temperature.

The quantitative analysis obtained, by the infrared absorption spectra in the range of (4000-200) cm^{-1}, were studied using the alkali-halide disc-technique. The effect of monovalent, divalent, trivalent or tetravalent metal oxides on the deformation of SiO_4 tetrahedra was investigated, and it has been found that their behaviour depend on their mobility and their respective field strength.

The chemical durability of some glasses were investigated using hydrochloric acid or sodium hydroxide as the immersion solution. Different factors were studied such as the glass composition, concentration of the immersion solution and conditions of the immersion process. The experimental results obtained revealed that the change in the weight loss may be mainly attributed to the change of the corrosion rate and the pH value of the immersion solution.

Also, the results obtained from the density measurements and molar volume calculations were explained, by considering the glass system studied, type of the incorporated cations and their arrangements in the glassy network.

I. INTRODUCTION

I- INTRODUCTION

Glass is a general term for a number of special materials of varying compositions and properties. In our time, glass is of considerable importance for the production of scientific, technical, architerial and decorative objects and many articles used in the daily life. Without a thorough knowledge of the relationship between the structure and glass properties, no important progress is any longer possible. This has been recognized and the modern glass research establishments are being set up all over the world.

I.1. Glassy state:

In order to understand the relation between the glassy, liquid and solid states, it is useful to recall the volume-temperature relationship for a substance which can exist in all three states, Fig.(1).

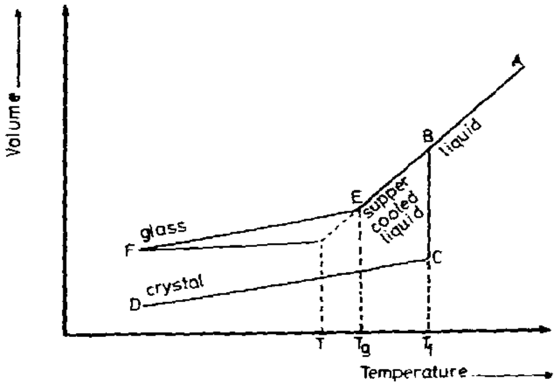

Fig.(1): The relation between the glassy, liquid and solid states.

On cooling such a substance from the liquid state, the volume of a given mass will decrease along the line AB. If the rate of cooling is sufficiently slow, crystallization will take place at the normal freezing temperature (T_f) accompanied by a sharp decrease in the volume from B to C. On further cooling, the resulting crystalline material will contract along the line CD. On the other hand if the rate of cooling is sufficiently rapid, crystallization cannot take place at T_f; and as cooling continues, the volume decreases linearly along the line BE which is a smooth continuation of the line AB. At a certain temperature, however called the glass transformation temperature Tg, the volume-temperature curve will undergo a significant change in its slope, being almost parallel to the contraction line CD of the crystalline form. Only below Tg, the material will be in the glassy state. The value of Tg, usually varies with the change in the rate of cooling, and thus it is called the transformation range(1&2). Therefore, if the rate of cooling is fast, the configurational change takes place at higher temperatures; while if it is very slow, the transformation temperature is correspondingly lower. If the glass in the transformation range is heated long enough at atmospheric pressure and at constant temperature, it reaches a state at which its volume no longer varies with time. This is called the equilibrium state or the stabilized condition.

I.2. Definition and characteristic of glass:

Many authors define the glass as "a material formed by cooling from the normal liquid state, which shows no discontinuous change in properties at any temperature, but become more or less rigid through a progressive change in its viscosity(3); while ASTM standards for glass define it as "glass is an inorganic product of fusion which has been cooled to a rigid condition without crystallization". The difficulties of these two definitions are:

1 . Glass can be prepared without cooling from liquid state, e.g., the deposition or chemical reaction from vapour.
2 . There are many types of glasses, not only inorganic oxides but also metallic glass and polymer.

The correct definition of glass is "an amorphous solid". A material is amorphous when it has no long-range order, that is, when there is no regularity in the arrangement of the molecular constituents on the scale larger than few times the size of these groups. From the definition, it can be seen that glass is a solid material from mechanical view and a liquid material from structural view, but there are many differences which the glass differentiates from the solid and liquid states such as brittleness and transparency.

I.3. Structure of glass:

Many theories dealing with the glass structure and formation have been put forward. The first real advance in the theory of glass structure was due to Zachariasen(4) who proposed the random network theory, i.e., a structure lacking symmetry and periodicity in contrast with the crystalline state.

I.3.1. Zachariasen random network theory:

Zachariasen(4) illustrated that atoms in glass must be linked by forces essentially the same as crystals and that atoms are oscillating about definite equilibrium positions. This conclusion has been attributed to the fact that the glass strength is of the same order as that of the corresponding crystalline phase. As in crystals, atoms in glass must form an extended three dimensional network, but the absence of sharp X-ray diffraction spectra reveals that this network is not a periodic one. The network cannot be entirely random, however, since the interatomic distances cannot be observed below certain minimum values. Zachariasen(4) proposed that atomic or molecular arrangement in the glass-like state is an extended network which lacks symmetry and periodicity, with an energy content comparable with that of the corresponding crystalline network. Therefore, the coordination number of the atom in glass must be approximately the same as in crystal. Zachariasen(4) also proposed the following simple rules for the glass formation.

1 . The anions in the glass structure cannot be linked to more than two cations. If more than two cations are bonded to an anion, the rigidity of bonding prevents the linkage distortion required for glass formation.
2 . The coordination number of cations must be small, being either three or four, i.e., the positively charged ions in glass forming oxide must be small in size.
3 . The oxygen polyhedra must share corners with each other, not edges or faces, since the highly charged cations tend to be as far apart as possible.
4 . At least three corners of each polyhedron must be shared to form three dimensional network.