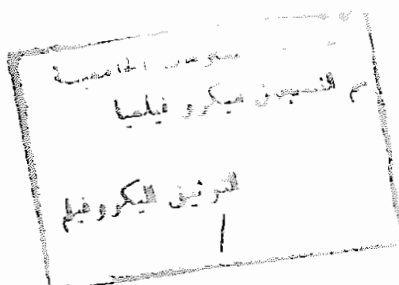
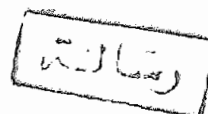


# SPECTRAL STUDIES ON THE STABILITY OF SOME METAL BORATES

A THESIS  
Submitted



The University College For Girls  
Ain Shams University  
Heliopolis, Cairo



By  
TAHA MOHAMMED ABDALLA  
B.Sc.

In Partial Fulfilment of the  
Requirements for the Degree  
of  
MASTER OF SCIENCE

٨٨٨٨



1994

541.3687  
T-M

## ACKNOWLEDGEMENTS

The author of this thesis wishes to express his gratitude to Professor Dr. Ahmed, A. Taha, Dean of the University College For Girls, Ain-Shams University, Cairo, for his supervision, valuable guidance and continuous encouragement in the course of this work.

Thanks are indebted to Dr. Zeinab, A. El-Hadi, Assistant Professor of physical chemistry at Department of Chemistry, University College For Girls, for her valuable help and continuous supervision during the progress of this work.

Thanks are also due to Dr. Ahmed, G. Mostafa, Faculty of Science, Aswan, Assiut University, for supervision during the the progress of this work.



**To  
My Parents With love .**

## Contents

Abstract	i
I.INTRODUCTION	1
I.1.Glassy state	1
I.2.Structure of glass	2
I.3.Condition for glass formation and the principles governing the ionic structure of glasses and crystals	6
I.4.Origin of spectra	8
I.5.Absorption of radiation by matter	8
I.6.Origin of infrared spectra	9
I.7.Infrared spectroscopy and glass structure.	11
I.8.Chemical durability of glass	12
I.9 Density and Molar Volume of Glass	14
II.LITERATURE REVIEW.	15
II.1.Infrared studies...	15
II.2.Chemical durability studies	17
II.3.Density and molar volume studies	19
III.EXPERIMENTAL	21
III.1.Spectrophotometric measurements	21
III.2.Chemical durability measurements	22
III.3.Density measurements and molar volume calculation	22
IV.RESULTS AND DISCUSSION	24
IV.1.Infrared absorption	24
IV.1.1.Results obtained from infrared absorption measurements	24
IV.1.2.Discussion of the results obtained from infrared absorption measurements	28

IV.2.Chemical durability	36
IV.2.1.Results obtained from chem. durability measurements	36
IV.2.2.Discussion of the chemical durability measurements	47
IV.3. Density measurements and molar volume calculation	53
IV.3.1.Results obtained from the density measurements	53
IV.3.2.Discussion of density measurements	60
V.Summary	64
VI.References	69
VII.Papers from the thesis	76
VIII.Arabic summary	

# ABSTRACT

## ABSTRACT

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

All glasses were melted in Pt-2% crucibles in an electrically heated furnace at  $1100^{\circ}\text{C}$  for four hours.

The effect of introducing one of the mono, di., tri., tetravalent metal oxides, cation for cation, on the infrared absorption spectra of glasses studied was found to depend on their molability and respectively field strength.

The chemical durability of some glasses were investigated using  $\text{HCl}$  or  $\text{NaOH}$  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  $\text{pH}$  value of the immersion solution.

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



# I. INTRODUCTION

# I. INTRODUCTION

The study of the glass structure is potentially of great scientific interest and importance of unique position of the glass state among the states of aggregation of matter. As a matter of fact, glass technology has grown up largely on empirical bases, separated some how from the scientific approach. But the workers in this field found themselves forced to fill the apparent gap between the science and technology in the study of the glass structure. However, during the last three or four decades, efforts have been made in order to investigate and identify glasses from the scientific point of view. Therefore, it is easy now to speak in scientific terms about the world glass, as well as about a substance in the glassy state.

The term glass can be commonly defined as being the product of fusion of some materials which have been cooled to a rigid condition without crystallization, i. e., glass is a material which can be obtained by cooling from the normal liquid state without any discontinuous change in its properties at any temperature, but it has become more or less rigid through the continuous change in its viscosity<sup>(1)</sup>. Substances of quite diverse chemical composition can be normally obtained now as glasses and they become widely recognized. Thus, the word " glass " is a generic term, and instead of speaking of glass, one should speak now about the glassy state, just like the crystalline state, liquid state or gaseous state.

## 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. (1.1) 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,

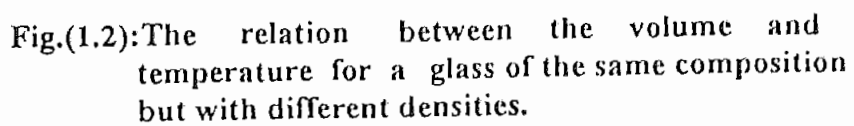
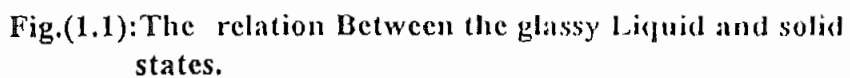
crystallization will take place at the normal freezing temperature  $T_f$ , accompanied by a sharp decrease in the volume from B to C. On further cooling, the resulting crystalline material will contract along the line CD. On the other hand if the rate of cooling is sufficiently rapid, crystallization 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  $T_g$ , 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  $T_g$ , the material will be in the glassy state. The value of  $T_g$  usually varies with the change in the rate of cooling, and thus it is called "transformation range"<sup>(2,3)</sup>. Thus, 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. Therefore a glass with the same composition but with different densities can be obtained (Fig 1.2.). If the glass in the transformation range is heated long enough at atmospheric pressure and 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 Structure of glass:**

As a result to the great efforts, previously done to investigate and identify the glass structure and glass forming process, several theories have been developed for the structure of the glass. Two of them are the most recognized ones, the random network theory developed by Zachariasen<sup>(4)</sup> and the crystallite theory by Lebedev<sup>(5)</sup>.

### **I.2.1. Zachariasen random network theory:**

The theory is based on four concepts, depending on the fact that the strength of glasses



is of the same order as that of crystals. Therefore, it was supposed by Zachariasen that the atoms in glasses are linked by forces essentially the same as those in crystals. The four concepts are:

- a- Not more than two cations can be linked to an oxygen ion.
- b- The oxygen polyhedra share only corners with each other not edges or faces.
- c- The number of oxygen atoms surrounding the positive ions must be small (three or four only).
- d- Each oxygen polyhedron share at least three corners with other polyhedra.

According to the above criteria, all cations which participate in a glass network can be divided into three main groups:

i. The network formers:

These cations have the ability to form the glass network by themselves, such as ( $\text{Si}^{+4}$ ,  $\text{B}^{+3}$ ,  $\text{P}^{+3}$ ,  $\text{Ge}^{+4}$ ,  $\text{As}^{+5}$ ). They are acidic in nature and have low coordination number of about three or four.

ii. The network modifiers:

These cations cannot form glass alone but they can be accommodated in the glass matrix in interstitial position and they can result in modifying glass matrix properties. They have high coordination numbers and the mutual forces with their adjacent oxygens will be small. The oxides of Na, K, Ca and Ba are good examples of such modifiers.

iii. The intermediate oxides:

These oxides play a role between the network formers and the network modifiers. They have

a relatively high coordination number of about 4, 5 or 6. Good examples of these oxides are Al, Mg, Zn, Pb or Fe.

Sun<sup>(6)</sup> has shown that a glass forming tendency of an oxide is directly related to the strength of the bonds between its oxygen and metal atoms. He showed also that the oxides which form glasses have high bond energies (119 to 80 K. Cal.), where as the glass modifiers show low values of the M-O bond energy (60 to 10 K. Cal.). Oxides with bond energies between 80 and 60 K. Cal., such as  $\text{Al}_2\text{O}_3$ , are grouped as intermediate.

Stanworth<sup>(7)</sup>, suggesting the following criteria, made a correlation between the glass formation and the oxides:

1. The cation valency must be three or more.
2. The tendency of glass formation increases with decreasing cation size.
3. The electronegativity should be between about 1.5 and 2.1 on pauling scale.

By applying these criteria, Stanworth<sup>(7)</sup> classified four groups of oxides:

- a. Strong glass formers.
- b. Intermediate glass formers.
- c. Other oxides that do not form glasses on rapid cooling, but do form them on oxidized surfaces of their metals or in binary combination with non glass forming oxides.
- d. Other oxides that do not form glasses.

Rawson<sup>(8)</sup> has modified Sun's relation between bond strength and glass- forming

tendency of oxides to a comparison of the ratios of the bond strength.

Ermolenko<sup>(9)</sup> concluded that many metal oxides which are regarded as glass modifiers, when present in large concentration in different types of glasses, may exist as network formers such as lead oxide in boric oxide- alumina-lime system with up to 80% mole% lime.

### **I.2.2. Lebedev's crystallite theory<sup>(5)</sup>:**

The crystallite theory was originally regarded as the direct contradiction to the network theory, since the characteristic feature of the network theory is a statistical distribution of the cations (modifiers) over a disordered network, while the crystallite theory is characterized by the high ordering of the cations position in the matrix and this yields microcrystalline compounds. These microcrystals are optically undetectable either by visible or ultraviolet spectroscopy and could be imagined as greatly deformed structural units which possess some degree of ordering towards the crystalline structure of the normal lattice. These structural formations are called crystallites.

The crystallite theory, as was the case with the network theory, also was developed by a great number of researchers. Valenkov and Porai-Koshits<sup>(10)</sup> concluded from theoretical calculations and x-ray studies that the structure of a crystallite is most regular at the center, where it is practically the same as that of a crystal. The regularity of a crystal lattice decreases towards the periphery and this produces the greatly amorphous intermediate layers which bind the crystallite together having a diameter between 8 and 15 Å.

Despite these differences in the basic concepts of the glass structure, Zachariasen's network theory<sup>(4)</sup> and Lebedev's crystallite theory<sup>(5)</sup> have been subjected to certain modifications which brought them nearer to one another, yet they still remain basically different.