Women's College
For Arts, Science & Education
Chemistry Department

Physico-Chemical Studies On Some Types Of Boro-Phosphate Glasses Containing Two Transition Metals

A Thesis submitted to

Chemistry Department
Women's College for Arts, Science & Education
Ain Shams University

By

Taha Mohamed Abd-Alla Mostafa
(M.Sc. ١٩٩٤)

For
THE DEGREE OF DOCTOR OF PHILOSOPHY

In
Physical Chemistry
(٢٠٠٨)

Women's College
For Arts, Science & Education
Chemistry Department

Physico-Chemical Studies On Some Types Of Boro-Phosphate Glasses Containing Two Transition Metals

Board of Advisors
Approved
١- Prof. Dr.\ Ahmed Abdel-Rehim Taha
Prof. of Physical Chemistry,
Chemistry Department
Women's College for Arts, Science and Education
Ain –Shams University

٢- Prof. Dr. \ Zeinb Abdel-Hady Zaky
Prof. of Physical Chemistry,
Chemistry Department
Women's College for Arts, Science and Education
Ain –Shams University

٣ - Prof. Dr.\ Ahmed Gamal El-Din Mostafa
Prof. of Glass Technology, Faculty of Science, Al- Azhar University,

Head of Chemistry Department
Prof. Dr. Samia M. Mokhtar

Women's College
For Arts, Science & Education
Chemistry Department

Student Name**: Taha Mohamed Abd-Alla Mostafa**

(M.Sc. Chemistry, ١٩٩٤)

Department: Chemistry
Faculty **:** Women's College for Arts, Science & Education
University **:** Ain Shams, Cairo, Egypt.

B.Sc. Graduation : May ١٩٨٠
M.Sc. Graduation Date : ١٩٩٤
Ph. D. Graduation Date: ٢٠٠٨

Acknowledgement

I would like to express my heart-felt thanks to **Prof. Dr \ Ahmed Abdel-Rehim Taha,** prof. of physical chemistry, Chem. Dept., Women's College for Arts, Science and Education, Ein Shams University, for suggesting the plain of this work, supervision, continuous encouragement and sincere help during this research, as well as for revising the manuscript.

I would like to express also my heart-felt thanks to the late **Prof. Dr \ Zinab Abdel-Hady Zaky**, prof. of physical chemistry, Chem. Dept., Women's College for Arts, Science and Education, Ein-Shams University, for her continuous encouragement and help, cooperative supervision, sincere help. I am always praying for her.

I would like to express my deepest thanks to **Prof. Dr \ Samia M. Mokhtar,** Head of chem. Dept., Women's College for Arts, Science and Education, Ein Shams University, for her continuous encouragement and sincere help during the work of this thesis.

I am grateful to **Prof. Dr. \ Ahmed Gamal El-Din Mostafa**, Prof. of glass technology, Faculty of Science, Al-Azhar University, for his sincere help in allowing me to use his laboratory for preparing the solid samples and for making some measurements.

I am also indebted to all the staff members of chem. Dept., Women's College for Arts, Science and Education, Ein-Shams University, for their continuous encouragement and help as well as their useful cooperation during this work.

Abstract

Glasses doped with transition metal ions become now of high interest because of their various applications in both science and technology. Accordingly the study of these glasses has drown the interest of most solid-state physicists, chemists and material science researchers. Also, the change of the physical properties of these glasses is directly connected to their structural transformations. On other hand, IR spectroscopy was found to be an effective tool for investigating glass structure. In addition ME spectroscopic analysis was established now to be a good technique which was successfully used long time age to investigate the hyperfine structure of glasses containing iron or any Mossbauer isotope. However, in this work the structure and the physico-chemical properties of some boro-phosphate glasses containing iron and zinc oxides were thoroughly investigated, under the effect of replacing $P_{٢}O_{٥}$ by $B_{٢}O_{٣}$ in the glass networks.

The prepared glasses were selected to obey the following molecular composition:

$$(٦٠\text{-}x)\ B_{٢}O_{٣} + x\ P_{٢}O_{٥} + ٢٠\ Na_{٢}O + ١٠\ Fe_{٢}O_{٣} + ١٠\ ZnO$$

(Where x = ٠, ٥, ١٠… ٦٠)

These samples were structurally studied firstly applying IR spectroscopy and Mossbauer Effect. Then density, molar volume, magnetic susceptibility and dc electrical conductivity were all measured and all results were discussed.

The glass batches were melted at ١٠٠٠ °C for two hours in porcelain crucibles and were casted on a copper plate in air and were then annealed at ٣٠٠ °C for ١٢ hours.

All the obtained results and the proposed discussion can be summarized as follows:

١. The IR spectroscopic analysis showed the presence of different structural building units such as $FeO_٤$, $FeO_٦$, $PO_٣$, $PO_٤$, $BO_٤$ and $BO_٣$ as well as many different bonds in the glass networks.

٢. The analysis of the ME spectra indicated the presence of iron ions in two different oxidation states ($Fe^{٢+}$ and $Fe^{٣+}$). It indicated also that all $Fe^{٢+}$ ions occupied the tetrahedral coordination state, while $Fe^{٣+}$ ions occupied the octahedral coordination in two different states, one is of low distortion and the other is of high distortion. This mains that the ferric ions act as glass network modifier (GNM), while all ferrous ions act as glass network former (GNF).

٣. The measured density and the calculated molar volume values indicated that the structure changed from random three dimensional boron network to layer and chain phosphate structure.

٤. The electrical conductivity measurements showed that all the studied glasses represent semiconducting properties. In addition to this all samples exhibit an ohmic behavior.

٥. The magnetic susceptibility measurements indicated that all the studied glass samples exhibit paramagnetic character.

Contents

CHAPTER ONE

AN INTRODUCTION TO GLASS STRUCTURE

Introduction

Glasses and Glassy State:

The study of glasses is now of great scientific interest due to their unique position among the states of aggregation of matter. As a matter of fact, glass structure 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 science and technology in the study of glass structure. However, during the last few decades, many 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 word glass, as well as about a substance in the glassy state. The term glass can be commonly defined as the product of fusion of a material 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 **(Rawson, ١٩٦٧)**.

According to the above speech, 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 about glass, one should speak now about the glassy state, just like the crystalline, liquid or gaseous states.

Amorphous and Crystalline States:

Solids are defined according to their mechanical behavior as materials whose viscosities exceed $١٠^{١٤.٦}$ poise, while fluids (liquids and gases) have viscosities less than $١٠^{١٤.٦}$ poise **(Condon, ١٩٥٤)**.

Structurally, solids can be classified either crystalline or non-crystalline (amorphous). A crystalline substance consists usually of atoms arranged in a periodic repetition in three-dimensions **(Barret, ١٩٥٢)**. When the periodicity of structure is interrupted in order to form grain boundaries, poly-crystalline materials are obtained, while when the pattern extended throughout the whole matrix, a single crystal is obtained.

In polycrystalline materials the dimensions of a grain in which the structure is periodic, may vary from one-angstrom to several angstroms. When the size of the grains or crystallites becomes comparable to the size of the pattern, the definition of the crystalline state lost its meaning and irregular structure is then appeared forming what is known as the non-crystalline state. For most solids, the crystalline state is naturally obtained since the energy of an ordered atomic arrangement is lower than that of irregular packing of atoms. However, when the atoms are not given an opportunity to arrange themselves, their amorphous state may then be obtained.

Amorphous Solids:

Amorphous or non-crystalline solids represent a class of materials lacking long-rang periodic order of their constituent atoms. They have short rang-order, i.e. an order observed over distance commensurate with molecular size. There are different types of disorder, such as:

١-Topological or geometric disorder, which arises from the random arrangement of the molecules in the solid matrix, that is there is no transitional periodicity (Fig. ١-a). Some amorphous materials have considerable short- range order while some others have little, but both have no long range order, however all amorphous or glassy solids are therefore distinguished by their lack of periodicity.

٢- Spin or magnetic disorder, in which the crystalline lattice is preserved, but the spin or the magnetic moment of each atomic site is oriented randomly (Fig. ١-b).

٣- Substitutional disorder, (Fig. ١-c) in which the crystalline lattice is preserved also but the material is in fact an alloy with one type of atoms randomly substituting by another in the lattice.

٤- Vibrational disorder, of a crystalline lattice (Fig. ١-d). Of course the concept of a perfect crystal is only valid at the absolute zero temperature (if zero-point motion is ignored) and at any finite temperature the random motion of atoms about their equilibrium positions destroys the perfect periodicity.

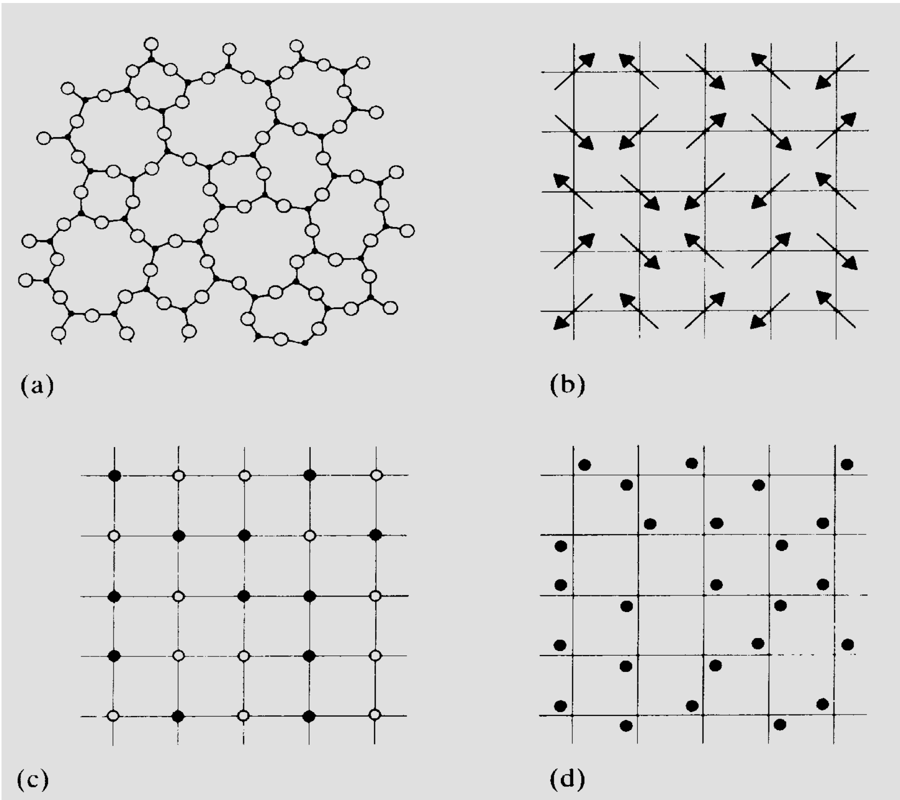

Fig. (١)

A distinctive class of amorphous solids is glasses, which is defined as amorphous solids obtained from melt by fast solidification **(Morey, ١٩٥٤)**. 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 characterized by the following three points; **(Jones, ١٩٥٦):**

١- Brittleness:

The majority of crystalline solids, specially the metallic ones show a high resistance when they are subject to either external pressure or tensile stress i.e. they behave as elastic solids. In contrast, nearly all glasses are easy to break on compressing or when exposed to tensile. So glasses seem to be hard but they are still easily broken.

٢- Transparency:

The crystalline solids appear to be opaque for the incident light while glasses are transparent. When the light falls on crystalline solids, the energy of each photon is absorbed instantly and then suddenly reradiated by the excited electrons in such solids. On the other hand, glasses absorb light only at particular wavelengths, dependent on their constituents **(Robert, ١٩٧٣)**. So they transmit approximately the majority of the incident light.

٣- Gradual softening:

On heating, glasses usually show a progressive and continuous change in their softening properties in contrast to the crystalline solids which show a well defined melting temperature. Such property of glasses is mainly due to the gradual change in their viscosities, which in turn depends on both the composition and the rate of cooling. The gradual change in viscosity appears as a result of the wide spread range of the strengths of the cation–oxygen bonds in the glass random network.

Glass formation (Glassy state):

A glass is generally obtained by rapid cooling from a liquid below its freezing point. The classical explanation for the formation of a glass is that when a liquid is cooled rapidly, its fluidity decreases gradually and at certain temperature below its freezing point it becomes nearly zero, and the liquid becomes rigid **(Steval, ١٩٤٨)**.

In order to understand the relation between the glassy, liquid and solids state, it is useful to recall the volume temperature relationship for a substance which can exist in all the three states (Fig. ٢).

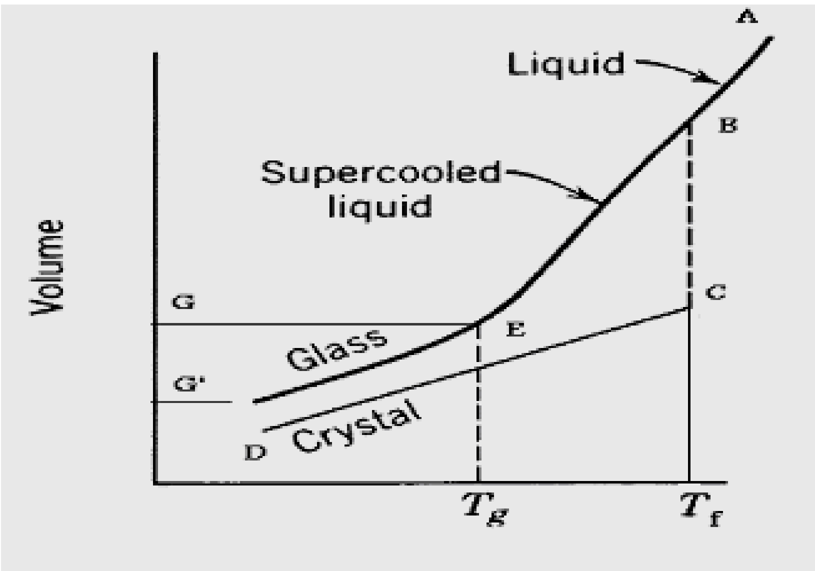

Fig. (٢)

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