

CRYSTALLIZATION CHARACTERISTICS OF SOME BOROSILICATE GLASSES

A THESIS

**Submitted in Partial Fulfillment of the
Requirements of the M.Sc. Degree in Chemistry**

By

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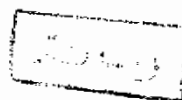
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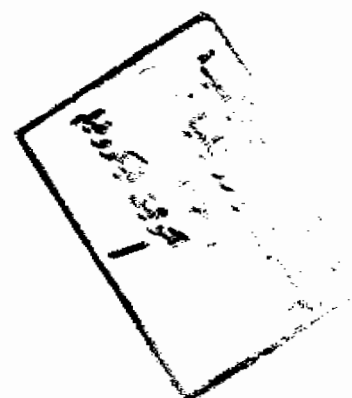
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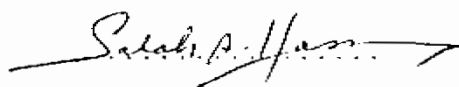
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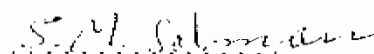
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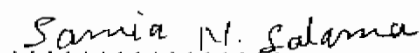
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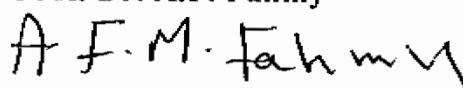






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To My Family

Hussein . . .

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ABSTRACT

A systematic study on the crystallization characteristics of some $\text{Li}_2\text{O-B}_2\text{O}_3\text{-SiO}_2$ glasses was carried out. The base glass composition was modified by replacing B_2O_3 by CaO , MgO or Al_2O_3 and, in some cases, Li_2O was replaced by MgO or Al_2O_3 . The thermal behaviour of the base-and modified-glasses was studied by differential thermal analysis technique and the glasses were heated through different heat-treatment schedules based on the DTA data. The crystalline phase assemblages and the resultant microcrystalline structures of the heat-treated glasses were investigated in relation to their basic chemical compositions and heat-treatment parameters by using X-ray diffractometry and scanning electron microscopy. The dilatometric thermal expansion and chemical durability against different aqueous solutions of the glasses and their crystalline solids were determined.

Different crystalline phase assemblages, including lithium meta-and di-silicate, lithium meta-, di-, tetra-, and pyro-borate, wollastonite (calcium metasilicate), calcium borate, diopside, clinoenstatite (magnesium metasilicate), magnesium borate, α -quartz and β -quartz solid solution (β -eucryptite ss), were formed under heat-treatment conditions. The formation of these crystalline phases was also studied depending on the ratios of $\text{Li}_2\text{O/B}_2\text{O}_3$, $\text{CaO/B}_2\text{O}_3$, $\text{MgO/B}_2\text{O}_3$ and $\text{Al}_2\text{O}_3/\text{B}_2\text{O}_3$ in the base glass. The type, stability and compatibility of the crystallized phases

were accordingly discussed in relation to glass composition and thermal treatment.

The physical and chemical properties of the studied glasses were essentially correlated to the internal structure of glasses and to nature and role played by glass-forming cations. On the other hand, the properties of the crystalline products were mainly attributed to the phase assemblages developed.

The present study revealed that the crystallization was greatly enhanced on replacing B_2O_3 by CaO , MgO or Al_2O_3 , thus fine-grained glass-ceramic materials were obtained therefrom. Also, a wide range of thermal expansion coefficient values of the modified glasses and their crystalline solids were obtained and their chemical durability towards the attack with acid and water was markedly improved.

PART ONE

INTRODUCTION, LITERATURE REVIEW AND EXPERIMENTAL TECHNIQUES

CHAPTER (I)

INTRODUCTION

PART ONE
INTRODUCTION, LITERATURE REVIEW AND
EXPERIMENTAL TECHNIQUES
CHAPTER (1)

INTRODUCTION

I.1. The Structure of Glass

Glasses are essentially non-crystalline solids obtained by freezing supercooled liquids(1). To understanding the structure of glass, it is very important to know the coordination numbers and types of bonding of the atoms. These coordination numbers and types of bonding are primarily determined by the kind of atoms present. Differences in the structure of glasses also mean differences in their physical and chemical properties. Therefore, in order to predict the properties of glass, the type of the coordination number and nature of bonding of the atoms present in the glass structure must be considered(1,2).

Up to now a good deal is known about the structure of many glasses(2), however, the current difficulty to describe the structure of glasses in details as fine as for crystals, had led to different approaches to describe the structure. Two main approaches may be observed, viz. the random-network hypothesis and the crystallite hypothesis. In the random-network hypothesis, it is thought for instance, that the SiO_4 tetrahedra in vitreous silica are bonded irregularly to each other. In the crystallite

hypothesis, it is suggested that in vitreous silica, submicroscopically small areas with an ordered structure are present, and are connected to each other by areas with a disordered structure. Today, the crystallite hypothesis finds but little support. On the other hand, the random-network hypothesis is also in discussion. Usually it is assumed that there is a certain short-range order in glass, somewhat similar to the order as observed in crystals but there is a definite absence of long-range order(2).

For the study of the structure of crystalline solids, the use of X-ray diffraction has been of vital importance. Due to the absence of long-range order in glass, X-ray diffraction can not reveal the complete structure. Other experimental techniques are used to study the molecular structure of glass, for instance, infrared and Raman spectroscopy, nuclear magnetic resonance and measurements of viscosity, thermal expansion, electrical conduction, dielectric and mechanical losses, density and refractive index. Study of the nature of colour centres in glass by electron spin resonance and optical absorption measurements has also been very helpful in understanding the structure of glass(2).

Certain oxides such as SiO_2 , B_2O_3 , P_2O_5 , GeO_2 and As_2O_5 are essential for glass formation, since they are able to form amorphous materials. These oxides are called "network-former", other oxides can associate with the glass former in a glassy structure, but can not by themselves form glass, they are called "network modifier" and whose presence have a great effect on the properties of the glass, these oxides are Na_2O , K_2O , Li_2O , and CaO . Intermediate oxides such as Al_2O_3 and
