Crystallization of Fluoramphiboles From Fluosilicate Glasses

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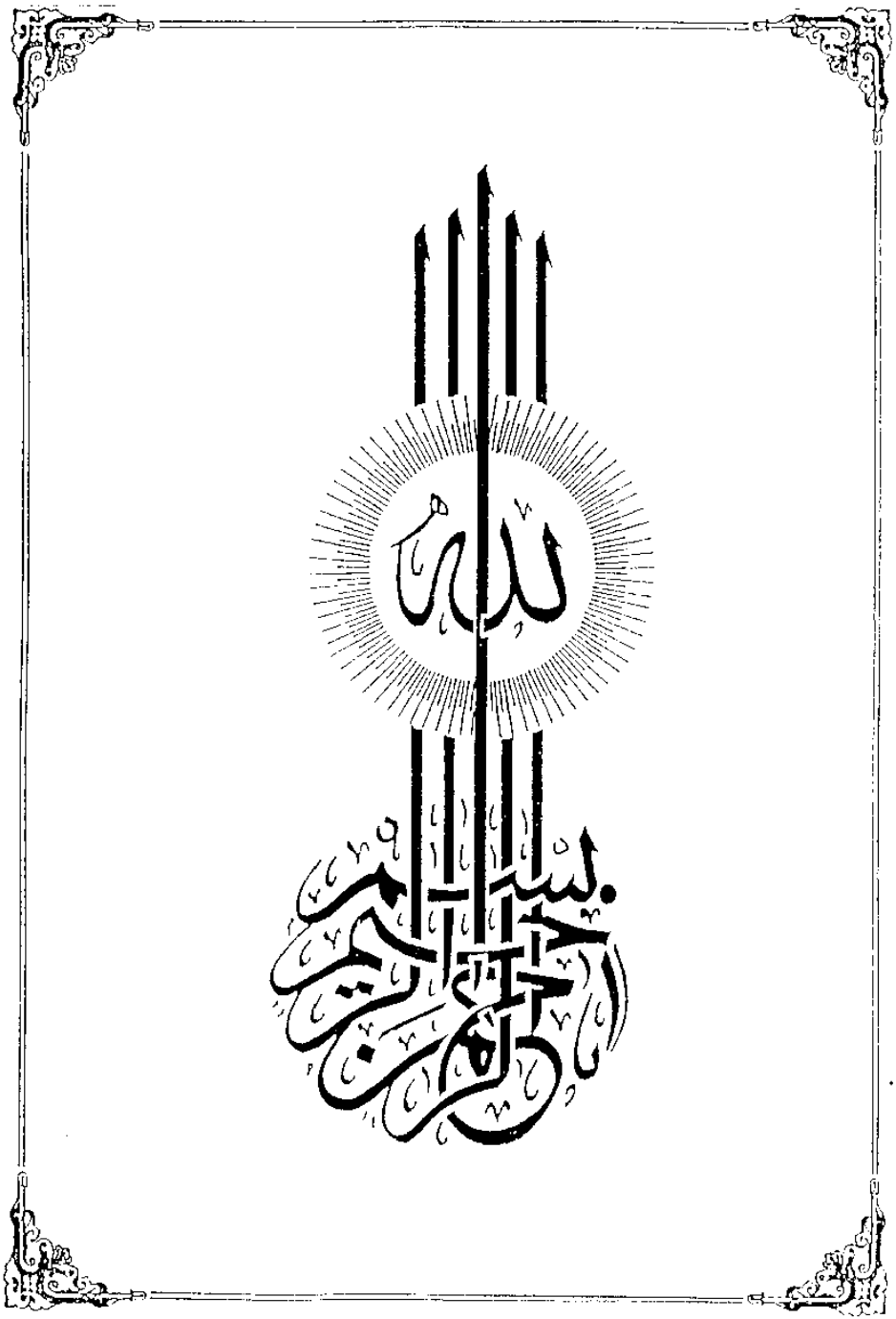

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Part II. Results and Discussion

ABSTRACT

The present investigation is concerned with the study of synthesizing fluoramphibole glass-ceramics , based on the fluorrichterite mineral by controlled crystallization of parent glasses of appropriate composion, and the effect of isomorphous substitution in its structure .

Differential thermal analysis , powder x-ray diffraction , polarizing and scanning electron microscope techniques were used for the study of the crystallization behaviour of the parent glasses and characterization of the obtained crystalline products .

The mechanism of fluorrichterite formation involves the first crystallization of pyroxene with or without mica and silica phases and then reaction of these phases with the present residual glass at higher temperatures .

Substitutions of one alkali cation in fluorrichterite ($Na\ Na\ Ca\ Mg_5\ Si_8\ O_{22}\ F_2$) by K or Li still lead to fluorrichterite crystallization : in case of substitution of one Na by K and the other by Ca a fluoramphibole phase of tremolitic composition is formed . On the other hand substitution of one Na by K and the other also by K or Li gives pyroxene and fluormica which persist till high temperatures without reactions to form richterite .

Isomorphous substitution of Ca by Zn in the K-fluorrichterite formula gives fluorrichterite , even upon complete substitution of Ca by Zn , together with Mg-rich phases such as roeddenite , fluorphlogopite , enstatite and forsterite . Ba could not substitute Ca , and Ba-Mg-silicate , forsterite , fluorphlogopite and enstatite were developed instead of fluorrichterite .

Coupled substitution in the tetrahedral position in K-fluorrichterite formula , of one Si by (Na+Al) delays the crystallization of fluoramphibole . Higher replacement [2 Si = 2(Na + Al)] enhances an early crystallization of aluminosilicates(nepheline and carnegieite) which are then joined by forsterite , fluorphlogopite , and enstatite without fluorrichterite formation even after long durations of heat-treatment .

The increase of fluorine content in the amphibole glasses leads to enhancing the formation and stability of fluoramphibole crystal phase , and diminishes the probability of crystallization of fluorine-free phases and vice versa . The addition of P_2O_5 to fluoramphibole glasses enhances the formation of the fluorine-free phase [roeddenite , $(K,Na)_2Mg_5Si_{12}O_{30}$] and diminishes the probabilities of fluorrichterite formation .

The microstructures developed in the obtained glass-ceramics are usually homogeneous and fine-grained in nature , composed of needle-like and acicular crystals . This is enhanced by positive effect of fluorine in creating a multitude of crystallization centers . Coarsening and nonhomogeneization of the microstructures take place after long duration heat-treatment at higher temperatures.The high aspect ratio of the amphibole crystals imparts a great toughness to the material .

Part 1

Introduction and Literature Review - Experimental methods

Chapter one
Introduction and Literature review

CHAPTER ONE

INTRODUCTION

1.1 GENERAL

Glasses are essentially highly viscous supercooled liquids that have amorphous or disordered structures , and can be obtained from a wide range of both inorganic and organic compounds (Pye, 1972) . Glass may be simply defined as a non - crystalline solid (Secrist and Mackenzie, 1960) .

Glass is thermodynamically metastable . Its formation is not only limited by viscosity but also by its liquidus temperature and rate of cooling of the melt . Below the liquidus temperature atomic rearrangements may occur leading to devitrification or uncontrolled crystallization of glass .

One of the few really new materials developed since 1950 , was a uniformally crystallized glass or " glass-ceramic " A glass-ceramic is a polycrystalline material obtained by controlled crystallization of glass The glass is melted , fabricated to shape , and then converted to a ceramic by specific heat-treatment . If the crystallization could be controlled then it might be possible to procure a good , strong , microcrystalline ceramic material from the glass (Stooky, 1959&1960) .

Glass-ceramics possess many superior properties such as wide ranges of thermal expansion coefficients , high thermal endurance , high hardness , high chemical durability ... etc. These properties depend upon the overall chemical composition , crystalline phases developed and the microstructure of the material .

Glass-ceramic materials have become technologically very important materials founding uses in many diverse applications ; in domestic , medical , military and many industrial fields (Berezhoni, 1970; McMillan , 1979 ; Beall , 1986 ; and Partridge 1994) .

The conversion of glasses by a well controlled heat-treatment to specific crystalline phases has become an ever increasing field of investigation and application The crystalline phases , or synthetic minerals , like amphiboles , feldspars micas , pyroxenes and olivines , .. etc have different sturctures and wide ranges of chemical compositions and consequently possess different proporties , which constitute the basis for tailoring of many valuable crystalline-glass materials (e.g. Omar and coworkers , 1971- 1993 ; Beall , 1986&1989)

The formation of uniform very fine-grained textures or microstructures (as technologist call them) is desired in glass-ceramic materials . To obtain uniform crystallization , an efficient suitable nucleating agent must be added in appropriate amount to the glass batch . The rates of nucleation and crystal growth can then be controlled during subsequent heat-treatment of the glass articles obtained .

1.2 CRYSTALLIZATION OF GLASS

Rapid crystallization takes place in most metals and some inorganic melts when they solidify . However silicate melts which have very high viscosites , solidify when cooled quickely to amorphous solids , called glasses , characterized by the absence of long-range atomic order

The rate of cooling of the liquid and its viscosity are the main parameters governing its solidification giving either glass or a crystalline material . For any