CRYSTALLIZATION OF SOME SILICATE GLASSES

Thesis Submitted

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By

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ABSTRACT

The effect of compositional variation, thermal treatment and nucleation catalysts TiO_2 and ZrO_2 on the nature, type and stability of the crystallizing phases as well as the resulting microstructures is described for some stoichiometric glass compositions within the systems Li_2ZnSiO_4-$LiAlSi_2O_6$ and Li_2MgSiO_4-$LiAlSi_2O_6$ to obtain glass-ceramic materials. Differential thermal analysis, X-ray diffraction, dilatometry, polarizing and electron-microscopy were used for studying the crystallization process and characterization of the resulting materials.

Fine-grained glass-ceramic materials with favourable thermal properties were resulted from glasses rich in Li_2ZnSiO_4 or Li_2MgSiO_4 components. Transparent glass ceramics with ultrafine microstructures could also be obtained from glasses within the Li_2ZnSiO_4-$LiAlSi_2O_6$ system .

The crystallization of Zn-containing glasses begins with the formation of proto β-and/or β'_{II}-Li_2ZnSiO_4 followed by, or concomitant with, β-eucryptite ss. The proto β-phase was formed over a narrow temperature range (600-700°C) and rapidly transformed into its β'_{II}-modification which showed a wider stability range upto 1040°C and then transformed into the stable γ_0-Li_2ZnSiO_4 modification. The metastable B-eucryptite ss was

first formed instead of β-spodumene and starts its transformation into β-spodumene around 800°C.

γ_0-lithium magnesium orthosilicate, β-eucryptite ss , β-spodumene, lithium metasilicate and forsterite were encoutered during crystallization of Li_2MgSiO_4-$LiAlSi_2O_6$ glasses.. The γ_0-Li_2MgSiO_4 phase showed a limited and narrow stability range and dissociated rapidly around 800°C. The β-eucryptite ss ⟶ β-spodumene transformation was delayed with increasing the lithium magnesium component in the glass.

TiO_2 exhibits a catalytic effect on the formation of the proto β-Li_2ZnSiO_4 phase, the transformation of β-eucryptite ss to β-spodumene and the decomposition of the γ_0-Li_2MgSiO_4. ZrO_2 showed a retarding effect on the formation of these phases.

The type, stability and compatibility relations of the crystallized phases are discussed in relation to glass composition and thermal treatment applied. Glass-ceramic with favourable properties could be obtained by controlled crystallization of glasses in these investigated Li_2ZnSiO_4-$LiAlSi_2O_6$ and Li_2MgSiO_4-$LiAlSi_2O_6$ systems.

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PART ONE

INTRODUCTION AND EXPERIMENTAL

CHAPTER I

SCIENTIFIC BACKGROUND AND LITERATURE REVIEW

1.1. INTRODUCTION :

When glasses are cooled from the liquid state, they pass through a temperature range wherein devitrification may occur. This uncontrolled crystallization (devitrification), which arises at interfacial glass boundaries or from a small number of nucleation sites in the interior, may result in coarse-grained microstructures that may be accompanied by planes of wheakness and gross distortion leading to low strength resultant materials. Glass formation implies the avoidance of such uncontrolled crystallization during cooling of the melt.

On the other hand, if the crystallization process could be controlled by adopting special glass formulations, suitable nucleation catalysts and proper heat treatment schedules, a new class of engineering materials (glass-ceramics) with desirable chemical, physical and mechanical properties could be obtained. Glass-ceramics are characterized by uniform fine-grained microstructures with randomly oriented crystals and some residual interstitial glassy matrix with no voids or microcracks. Such structural characteristics provide improved performance and reliability of the glass-ceramics over traditional ceramics$^{(1-4)}$. As a result of this unique microstructure, glass-ceramics with properties such as translucency, high strength and very low and uniform thermal expansion can be routinely produced. Thus controlled crystallization has a number of key advantages.

Glass-ceramics, therefore, are primarily silicate-based materials formed by the usual glass-forming processes and converted through controlled crystallization into polycrystalline ceramic-like products by the proper heat-treatment. These glass-ceramics, which are also referred to in the technical literature as pyroceram, vitroceram, devitroceram, sitall, and melt-cast ceramics, generally have a crystal content greater than 40-50%.

The choice of glass composition, raw materials, and processing methods of glass manufacture and the final properties are to some degree variable so as to suit particular applications. The choice of composition for a glass-ceramic must depend not only on the ease with which the glass can be prepared and nucleated, but also on the properties expected for the subsequent crystalline phases developed(3). A type of these phases, with a very low thermal expansion, is that based on the β-quartz structure. A variety of names has been proposed to identify the family of phases based on the β - quartz structure. The name " β-eucryptite ss"* is one of them used to indicate that Li^+ ions are the main stuffing ions present. Another type of the crystallization products which may yield useful glass-ceramics are the orthosilicate Li_2O. (ZnO,MgO) . SiO_2 phases. These orthosilicate phases are sensitive to the phase composition and can crystallize readily from a wide range of compositions. Complexities usually arise from their extensive polymorphism and wide ranges of solid solutions. For instance, Li_2ZnSiO_4 exhibits ten polymorphs. Phase transformations could be affected in reasonable times at low temperatures, although the transformations were often metastable.

Moreover, different varieties of metastable and stable polymorphs such as B-eucryptite ss, β-spodumene could also be eouncterd in the complex $Li_2O.Al_2O_3$.(ZnO, MgO).SiO_2 system.

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* ss = Solid solution(s).

On the other hand, as the number of possible phases in a system increases, the probability of production of fine-grained textures increases as well, because the complex nature of the chemical composition hinders the diffusion of ions over large distances. Therefore, the formation of many fine crystals is more favourable than the formation of few coarse crystals of the same phase. In addition, compositions crystallizing to give solid solutions are of importance with regard to the physical properties of the resultant materials. Crystallization of a glass to yield one or more solid solution series leads to a reduction in the grain-boundary energies and elimination of the stresses found at these boundaries consequently an increase in the strength of the material would result(5). However, the more complex the composition of the glass is, the greater will be the diversity of the expected stable and metastable phases and the higher is the probability of a successful combination of properties in the resultant glass-ceramic (6).

In order to increase the relevance of our studies to the chemically more complex commercial glass ceramics, a number of compositions within the systems spodumene ($LiAlSi_2O_6$)-lithium zinc orthosilicate (Li_2ZnSiO_4) and spodumene-lithium magnesium orthosilicate (Li_2MgSiO_4), were selected for study.

1.2. SCIENTIFIC BACKGROUND :

1.2.1. Crystallization of Glass :

Crystallization is the process by which the regular lattice of the crystal is generated from the less ordered liquid or glassy states (3). It is generally considered as consisting of more or less two independent processes:

i) Nucleation, or formation of crystal centres, and ii) crystal growth on the formed centres (7).

i) Nucleation :

For crystallization to begin, crystal nuclei must be present. Nucleation involves the intiation of regions of longer range atomic order, known as embroys, than are normally present in the molten state or in the supercooled liquids (8). When these embroys attain a critical minimum size capable of developing spontaneously into gross particles of the stable phase they are known as nuclei.

Nucleation may take place either homogeneously, i.e. freely in the volume of the original phase, or heterogeneously on the surfaces of the container, surfaces of foreign particles or on structural imperfections(9). In homogeneous nucleation, the composition of the primary nuclei does not differ from that of the main crystalline phase, whereas in heterogeneous nucleation the crystallization of the glass is induced by introducing foreign nuclei. The nucleant, which is generally a metal, oxide or fluoride, is incorporated in the batch and becomes an integral part of the glass during melting.

However, despite considerable research, the mechanisms by which nucleating agents induce crystallization are not yet completely clear. A generalized picture of the nucleating mechanism cannot be developed, since the role of nucleating agents in catalyzing the formation of nuclei and the major crystalline phases undoubtedly differs from one nucleant to another. However, it is more safe to say that, by a mean or another, the nucleant causes a disproportionation of the binding forces(10) which, in turn, introduce sites of lower thermodynamic stability.

Stookey(1) listed some of the requirements of an effective nucleating agent, viz. a) it should be readily