

CRYSTALLIZATION AND CHARACTERIZATION OF SOME CABAL GLASSES CONTAINING Li_2O AS NUCLEATING AGENT

A.A. EL-KHESHEN, M.A. AZOOZ

Glass Research Dept., National Research Centre, El-Tahrir St., Dokki, Cairo, EGYPT

(Received Oct. 12, 2001; Revised Feb. 21, 2002; Accepted March 12, 2002)

ABSTRACT

The behavior of cabal glasses, based on the $\text{CaO-B}_2\text{O}_3\text{-Al}_2\text{O}_3$ compositions towards crystallization, their chemical durability and thermal expansion coefficients as well as derivative glass ceramics have been investigated. The base glass composition was modified by replacing part of CaO by Li_2O to initiate crystallization. The glass ceramics were found to have higher chemical durability and lower thermal expansion coefficients than the precursor glass, that can be correlated with the formation of $\text{Li}_2\text{B}_8\text{O}_{13}(\text{Li}_2\text{O}.4\text{B}_2\text{O}_3)$, $\beta\text{-CaAl}_2\text{B}_2\text{O}_7$ and LiAlO_2 .

1. INTRODUCTION

Cabal glass is one of the earliest types of manufactured glass. Its importance is due to its resistance to weathering and its relative low melting point. The name "cabal" was firstly given by Sir Herbert Jackson to non-alkali, non-silica glasses with lime, boric oxide and alumina as basic constituents. The structure of these glasses is very different from that of silicate glasses. However, this ternary glass system can be regarded as a binary system, with lime as the modifier oxide and the boric oxide and alumina serving jointly as the network formers (Bishop et al 1966)⁽²⁾.

Early study on the leaching of borate glasses by Mazelev⁽¹⁵⁾ had indicated that the chemical stability of such glasses was closely connected with their structure, especially with the ratio of $\text{BO}_4:\text{BO}_3$ in the glass and also with the degree of binding of B_2O_3 in borates.

The durability of lithium borate glasses was investigated by Velez et al⁽²³⁾. They pointed out that these glasses dissolved at a constant rate, and the decrease in weight was found to vary linearly with time. The minimum observed in the dissolution rate with varying Li_2O content was correlated with a change in structure.

Glass ceramics are polycrystalline solids prepared by controlling crystallization of glasses⁽¹⁶⁾ and, since their discovery in 1959, have been used in a number of diverse applications. The crystallization is achieved by subjecting a

suitable homogeneous glass to a predetermined heat treatment schedule so nucleation and subsequent growth of the crystals occur in a satisfactory manner. The ability to control crystallization allows one to utilise glasses for high technology applications such as advanced ceramics for high temperature aerospace and automotive uses⁽¹⁶⁾, and for optical systems⁽¹⁷⁾. Of particular importance in many applications is the high uniformity of the microstructure of glass ceramics, the absence of porosity and the minor changes in volume attending conversion of glass into ceramics⁽¹⁰⁾.

The key to understand glass-ceramic formation is the knowledge of the kinetics of crystallization⁽²²⁾; this type of knowledge will enable the glass scientist to make better glass ceramics and design glasses to meet specific needs.

The objective of this work is to investigate the crystallization behaviour of some cabal glasses by replacing CaO, cation for cation, by Li₂O in order to initiate nucleation and crystal growth. In the course of this investigation, DTA, XRD, SEM, chemical durability measurements and thermal expansion behaviour were employed to investigate the effect of crystallization on properties.

2. EXPERIMENTAL PROCEDURE

All the glass samples under investigation were prepared from pure chemical reagents and their chemical compositions are summarized in Table (1). Boric oxide B₂O₃ was added as orthoboric acid H₃BO₃, Li₂O and CaO were added in the form of their respective anhydrous carbonates, but Al₂O₃ was added as alumina.

Table (1): The composition of the studied glass.

Glass No.	Composition (Wt.%)			
	CaO	B ₂ O ₃	Al ₂ O ₃	Li ₂ O
1	30	40	30	--
2	29	40	30	1
3	25	40	30	5
4	20	40	30	10

The melts were made in platinum 2% Rh crucibles in an electrically-heated furnace at a temperature $\cong 1350^{\circ}\text{C}$ for 3 hours and stirred from time to time to achieve homogeneity. The glass was then cast in stainless steel moulds. The molten masses were subjected to normal annealing in a muffle furnace at $\cong 400^{\circ}\text{C}$, which was cooled to room temperature at 30°C/hr .

Differential thermal analysis (DTA) was carried out on finely powder glass samples up to 800°C in a standard Perkin-Elmer 7 series thermal analysis system instrument using powder alumina as a reference with a heating rate of 10°C/min .

The observed endothermic and exothermic peak temperatures were used to characterise the glass-ceramic conversion process.

From DTA data, the glass samples were subjected to heat treatment at 500°C for 5 hours, then raised to 700°C for another 5, 10 or 15 hours to study the effect of time on crystal growth, then left to cool to room temperature. This procedure is believed to give satisfactory glass ceramic products.

Identification of crystalline phases was carried out by X-ray diffraction (XRD) using a Philips powder camera (type CPM 9920/05) through the examination of fine powder of the glasses after thermal treatment. CuK_α radiation with Ni filter was used. A Philips scanning electron microscope (SEM: XL30) was used for the investigation of microstructure.

To study the leaching process, a regulated water bath was used to heat the water. The temperature of the bath was controlled to be $95 \pm 0.5^\circ\text{C}$. Silica beakers (250ml) with covers were suspended in the bath through adjusted holes in the water bath lid, then 0.5 gm of the sample tested was accurately weighed in a sintered glass crucible (G_4) Jena type, then placed into the silica beaker. Then 150ml of 0.1N HCl or 0.1N NaOH was introduced as leaching solutions to cover the glass grains, and the rest of the solution placed into the beaker. After 1 hour, the sintered glass crucible was fitted on a suction pump to remove the whole solution, then washed with distilled water, and transferred to an air oven at 120°C for 1 hour. The glass crucible was then removed and left to cool in a desiccator, then reweighed to calculate total weight loss.

The thermal expansion coefficient (TEC) of the samples was measured using a dilatometer system, Linseis model 76/1250, between 25°C and 700°C .

3. RESULTS AND DISCUSSION

Fig.(1) shows the weight loss percent of the parent cabal glass containing different proportions of lithium oxide, in both acid and base, it appears that:

1. The weight loss values obtained by using leaching solutions 0.1N HCl or 0.1N NaOH progressively increase with increasing Li_2O content.
2. All the glasses showed minor weight loss in sodium hydroxide, while hydrochloric acid gave the highest corrosion values.

The chemical durability of the glass is its resistance towards the attack by aqueous solutions, so it is necessary to study the structure of the cabal glass which consists essentially of lime, alumina and boric oxide. The oxygen ions donated by lime will be largely bonded to the Al^{3+} and B^{3+} ions. Most or all of the alumina present is previously assumed⁽¹²⁾ to be present as AlO_4 tetrahedra, and some of the boron ions become tetrahedrally coordinated till one-fifth of the boron ions have formed tetrahedral groups, with the rest of the boron in three-fold coordination. The calcium, if present, will occupy bridging positions in the network.

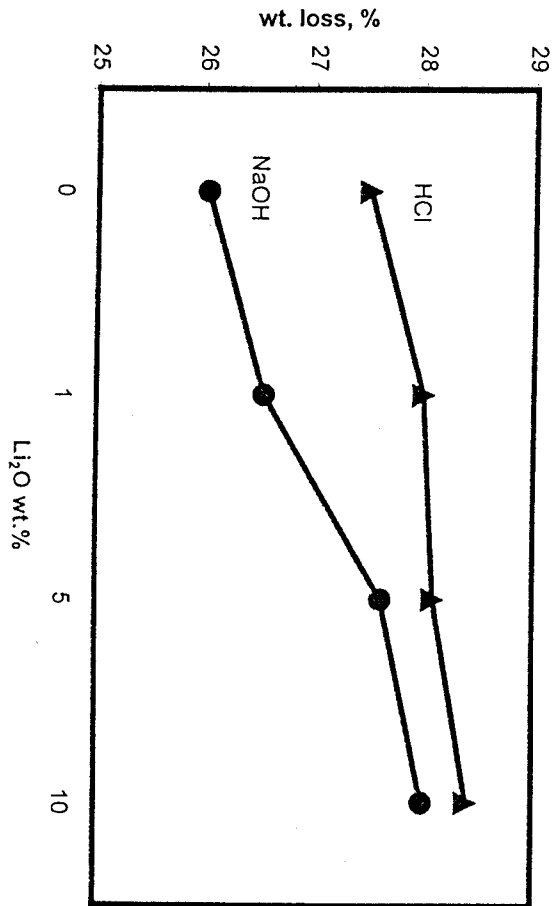


Figure 1. wt. Loss % of some cabal glasses as a function of Li₂O content, in different media.

Searstone and Isard⁽¹⁹⁾ investigated the solubilities of cabal glasses by the grain method. They found that boric oxide was preferentially leached into boiling water and that the rate of the reaction was generally limited by diffusion process through a residual coating of hydrated alumina is left on the grains.

Zhang et al⁽²⁵⁾ studied the water corrosion of borate glasses, and the dissolution weight loss increased linearly with time. The dissolution rate was found to decrease with the addition of Na₂O but increased when the Na₂O content exceeded 20 mole %.

Khedr et al⁽¹²⁾ studied the corrosion behaviour of some Zn-containing cabal glasses and found that the decrease in chemical durability in acidic or alkaline, as well as neutral media, is related to the role of zinc ions which are believed to occupy network interstices in octahedral symmetry. The priority in cabal glasses is for Al³⁺ and B³⁺ ions to assume tetrahedral coordination states, leaving less chance for Zn²⁺ ions to be present as ZnO₄ group.

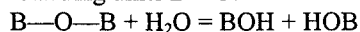
Ghoniem et al⁽⁹⁾ assumed that tetrahedrally coordinated boron is energetically more stable than a non-bridging oxygen.

Stallworth and Bray⁽²⁰⁾ concluded that, in cabal glasses six-fold coordinated aluminum could not be ruled out by Bishop and Bray⁽²⁾. If aluminum occurs purely in four-fold coordination, then for Al₂O₃-rich glasses there must be different four fold coordinated environments.

One possible description⁽¹²⁾ is that aluminum may be distributed among sites of charged AlO_{4/2} and neutral tricluster AlO_{3/2}(O_{1/3}) units (i.e. a combination of any three BO_{4/2}, AlO_{4/2} and/or AlO_{3/2}(O_{1/3}) units bound to a common oxygen).

In the glasses studied here, Li₂O cations which replaced CaO will occupy positions different from those of Ca²⁺ cations. Similarly, some of the bridging O²⁻ ions would be changed to non-bridging O²⁻ ions, so the structure will loosen and be easily attacked by aqueous solutions.

Attack by acid solutions leads to the penetration of protons (H⁺) or hydronium ions into the surface layer of the lattice and exchange with the easily bound ions (Ca²⁺ ions) in interstitial positions. Water accompanying the protons may react with the bonds of the structural building units B—O.



In basic solutions such as NaOH, the dissolution of the studied glass will be less and that can be understood when it is recalled that sodium hydroxide solution produces on ion exchange with the cabal glasses yielding hydroxides of aluminum and calcium. These hydroxides are known to be gelatinous and sparingly soluble in aqueous media.

Thermal expansion is one of the most important properties of glass and glass ceramics, the understanding of this property would permit the development of new material having desired properties and would lead to a better understanding of the structure of material itself.

Table (2) shows thermal expansion coefficients (TEC) of the glass samples. It reveals that the (TEC) increase with increasing lithium oxide content. The

transition temperature " T_g " and the softening temperature " T_s " decrease with change in composition.

Table (2): Thermal expansion coefficient values of the studied glass.

Glass No.	T_g °C	T_s °C	$\alpha \times 10^{-6}$ 25-200°C	$\alpha \times 10^{-6}$ 200-300°C	$\alpha \times 10^{-6}$ 300-400°C	$\alpha \times 10^{-6}$ 400- T_g
1	590.3	606	7.5	7.5	7.6	7.6
2	567.1	606	7.2	7.4	7.6	7.8
3	532.4	563	7.5	7.7	7.9	7.8
4	507.4	540	14.1	16.0	16.7	17.5

Uhlman et al ⁽²¹⁾ concluded that, the compositional variation of the thermal expansion coefficient of alkali borate glasses is not truly anomalous but rather seems to vary with structural variations in a generally predictable manner.

Ghoneim⁽⁸⁾ has studied the thermal expansion on glass of the system CaO-B₂O₃-Al₂O₃ and found that the change in coefficient of expansion of the glass could be discussed in relation to the mode of vibration of the atoms in the network, the mobility of the constituent ions and the ability of some cations to build glass forming unit.

Ghoniem et al ⁽⁷⁾ have found that the increase of lead oxide in lead silicate glass increased the thermal coefficient of expansion but to lesser extent than the alkaline fluxes, and that could be explained by considering the bond strengths and ionic sizes of the cations.

The increase in the thermal expansion of the glass in the transformation range was attributed by Weyl and Marboe⁽²⁴⁾ to the formation of defects such as vacant anion sites or incomplete coordination. These defects introduce asymmetries into the short range order of glasses and increase the amplitude of thermal vibration.

The thermal expansion of glass is not only a function of temperature but also depends on composition and it is sensitive to the structure, type of structural units, nature and contribution of the different cations, whether they occupy forming or modifying positions in the glass network⁽¹⁾.

In the studied glasses, the alkali ions are the most weakly bonded constituents, and as a result, they will be able to move easily (or become more mobile) with rising temperature. Increasing the glass temperature up to T_g increases the movement of constituent ions. As a result of such mobility they can move away from the non-bridging O²⁻ ions, and interact with the neighbouring bridging O²⁻ ions and contrapolarise it. This would weaken the M³⁺-O bonds more than one would expect from the increase in thermal vibration.

At higher temperatures⁽⁸⁾, the change of positions between the bridging and non-bridging oxygen ions become more pronounced, the O²⁻ ions become

sufficiently mobile and can move within the anion network and diffusion through the bulk is possible.

The decrease in T_g value when CaO is replaced by Li_2O could be attributed to the high polarizability of the introduced O^{2-} ions, which give good screening for the positive cations giving lower values for T_g .

CRYSTALLIZATION OF THE GLASSES

Glass ceramics can provide significant advantages over conventional glass or ceramic materials, by combining the ease and flexibility of forming and inspection of glass with improved and often unique physical properties in the glass-ceramic. They possess highly uniform microstructures, with crystal size on the order of 10 micrometers or less; this homogeneity ensures that their physical properties are highly producible. Unlike conventional ceramic materials, glass ceramics are fully densified with zero porosity.

Two types of crystallization occur: self crystallization or nucleated crystallization to promote volume nucleation.

Table (3) summarizes the X-ray diffraction results of the investigated samples at different thermal treatment periods. Three principal phases are obtained, $Li_2B_8O_{13}(Li_2O.4B_2O_3)$, $\beta-CaAl_2B_2O_7$ and $LiAlO_2$, in samples 2, 3 and 4 which contain 1, 5 and 10% Li_2O respectively. Sample 1 without lithium, remained amorphous when heat treated at 500 °C and 700 °C.

Table (3): XRD of crystallized glass-ceramic containing Li_2O as a nucleating agent.

Glass Ceramic No.	Temperature, °C	Time, hour	$Li_2B_8O_{13}$	$\beta-CaAl_2B_2O_7$	$LiAlO_2$
1	700	5	--	--	--
2	700	5	mature	mature	mature
3	700	5	LI	LI	LI
	700	10	MI	MI	MI
	700	15	HI	HI	HI
4	700	5	VHI	VHI	VHI

LI: low intensity, MI: moderate intensity, HI: high intensity and VHI: very high intensity

By increasing the time of the second step heat treatment, it is found that the intensity of all the phases increase.

El-Batal et al investigated⁽⁵⁾ the X-ray diffraction patterns obtained from the glass ceramic of the system $\text{Li}_2\text{O} \cdot \text{B}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$. The results indicate that the main phases separated out on controlled crystallization are lithium borate LiB_3O_5 and lithium diborate $\text{Li}_2\text{O} \cdot 2\text{B}_2\text{O}_3$. Without Al_2O_3 , the two phases are observed to form in equal ratios but on increasing the Al_2O_3 content, a new crystalline phase (beta- $\text{Li}_4\text{B}_2\text{O}_5$) is observed in which the ratio of Li:B is higher than in the diborate phase.

CHARACTERIZATION OF THE GLASS CERAMICS

The samples under investigation were examined using scanning electron microscope and we failed to resolve individual crystals which indicate that, the degree of fineness is too great to the extent that only an evenly homogeneous massive crystalline materials is indicated.

Fig (2) shows the weight loss percentage of the glass ceramics in both HCl and NaOH solutions. Generally, it reveals that the weight loss is lower than that for the parent glass. This seems to be due to better bonding in the ceramic network rather than the parent glass, due to the formation of new phases during crystallization.

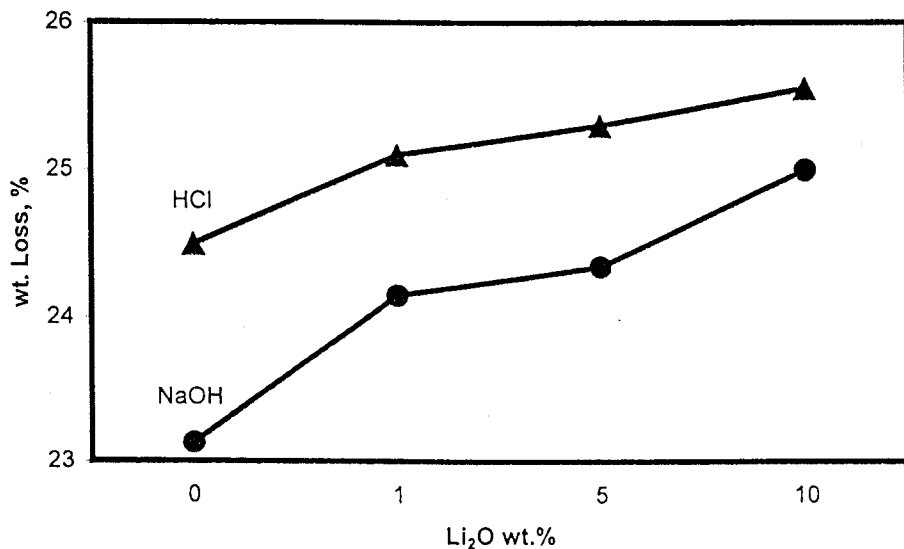


Figure 2: wt. Loss % of some glass-ceramics as a function of Li_2O content, in different media.

It is likely that when a glass-ceramic is chemically attacked, initial attack is upon the glass phase. This occurs because the early stages of attack involve ion exchange between hydrogen (or hydronium ions) and mobile cations (usually alkali metal ions) in the glass. The greater mobility of alkali metal ions (Li_2O) in the glass phase, as compared with that of similar ions incorporated in crystals, will lead to greater reactivity of the glass phase and hence to inferior resistance to chemical attack. This achievement of high chemical durability in glass ceramics indicates that, the chemical composition of the phases obtained favour good stability⁽¹⁶⁾. For the sample number 1, it was believed that, no crystallization occurred but the thermal treatment leads to more stable structure.

It was shown⁽¹⁶⁾, however, that a more complex glass-ceramic having low lithia content and containing in addition substantial amounts of alumina was very durable.

The resistance of material to chemical attack by water or other reagents is of considerably practical importance, McMillan⁽¹⁶⁾, had indicated that, glass-ceramic in general possess good chemical stability and that they compare favourably in this respect with other ceramic type materials.

Kay and Doremus⁽¹¹⁾ reported on the durability of a glass ceramic containing beta-spodumene crystals and it was only slightly susceptible to stress-enhanced reduction of strength by reaction with water.

Elmer⁽⁴⁾ studied the role of acid concentration on cordierite and alkali borosilicate and found that, the dissolution of Al and Mg in cordierite and of B, Na, Al in alkali borosilicate is brought about by interaction with H_3O^+ ions in the acid solutions. Since the concentration of the hydronium ions increases with acid concentration, the reaction rate is expected to increase, after reaching a maximum, there is a gradual decrease in chemical reaction.

Highly siliceous⁽¹³⁾ glass ceramics with low alkali residual glasses, such as glass ceramics based on β -quartz and β -spodumene have excellent chemical durability and corrosion resistance similar to that obtained in borosilicate glasses.

Table (4) indicates the thermal expansion behaviour of the glass ceramics. The glass ceramic samples show lower expansion coefficients rather than the respective amorphous glass.

The thermal expansion coefficient of glass ceramics can differ markedly from that of the glasses. Thermal treatment of the glasses generally introduces crystalline phase having expansion coefficients usually different from that of the parent glass. Therefore, the glass ceramic materials may have high or low coefficients of expansion depending on the crystal phases formed and the residual glass matrix^(16,18).

An extremely wide range of thermal expansion coefficients is covered by the different crystal types and the development of these phases in appropriate proportions forming the basis of the production of the glass ceramics with controlled thermal expansion coefficients.

Table (4): Thermal expansion coefficient values of the studied glass ceramic

Glass No.	T _g °C	T _s °C	$\alpha \times 10^{-6}$ 25-200°C	$\alpha \times 10^{-6}$ 200-300°C	$\alpha \times 10^{-6}$ 300-400°C	$\alpha \times 10^{-6}$ 400-T _g
1	579.5	609.0	6.9	7.2	7.3	6.8
2	555.3	603.0	7.2	7.4	7.5	-----
3	590.0	606.0	7.5	7.5	7.6	7.6
4	657.8	684.4	3.5	3.6	4.0	4.4

The effect of the phases obtained on the thermal expansion may depend on the size and field strength of the different cations present and also on the decrease in the mobility of alkali ion.

Drotning⁽³⁾ had measured the thermal expansion on a lithia aluminosilicate glass and glass ceramic from ambient to 1000°C. Using gamma densitometry, data were obtained on the solid-phase thermal expansion of the glass some 400°C higher than attainable with conventional push-rod dilatometry. This increase in temperature range allowed the quantitative investigation of the thermal expansion of crystalline phase in a glass matrix.

The thermal expansion of some ternary silicate was measured by Ezz-Eldin et al⁽⁶⁾ from room temperature to above the softening temperature, and deduced that, the increase in barium or zinc oxide content decrease the thermal coefficient of expansion of glass and gamma irradiation caused a remarkable decrease in thermal expansion due to the irradiation damage happened.

Salama et al⁽¹⁸⁾ concluded that, the thermal expansion property of the Li₂O-B₂O₃-SiO₂ glasses modified by CaO, MgO and/or Al₂O₃, was essentially correlated to the internal structure of the glasses and to the nature and role played by glass forming cations. On the other hand, the thermal properties of the crystalline products were mainly attributed to the phase assemblages developed. They also found that, the thermal expansion coefficient values obtained from the Al₂O₃-containing glass-ceramic materials were much lower than those obtained for the other investigated crystalline materials.

Little work has been carried out in the crystallization of cabal glass, but some frit-derived glass-ceramics based on alkaline-earth aluminoborate (RA₁₂B₂O₇) crystals have been investigated⁽¹⁴⁾. These nonsilicate glass-ceramics can yield thermal expansion coefficients of less than 10.10⁻⁷/°C.

CONCLUSION

The chemical durability and the thermal expansion properties of the CaO-B₂O₃-Al₂O₃-Li₂O glass were improved by the conversion of the glass to the corresponding crystalline product, by subjecting the glass to suitable thermal treatment, XRD patterns indicated the appearance of three phases, Li₂B₈O₁₃(Li₂O.4B₂O₃), β-CaAl₂B₂O₇ and LiAlO₂.

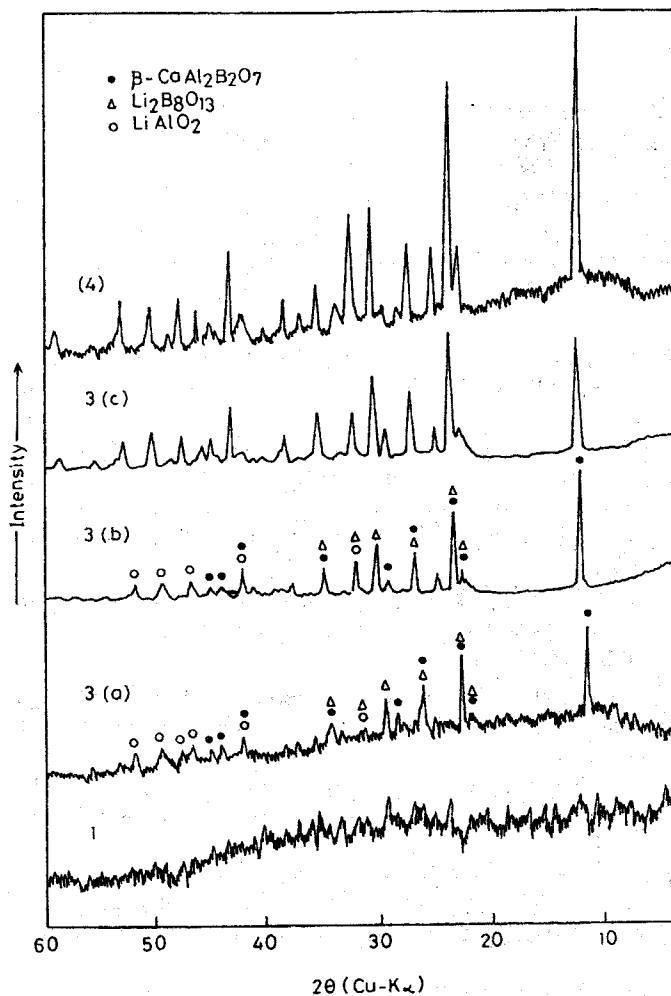


Figure 3 : XRD pattern of the phases formed:

1. No Li_2O content at 700°C for 5hrs (Amorphous).
- 3a. 5% Li_2O content at 700°C for 5hrs.
- 3b. 5% Li_2O content at 700°C for 10hrs.
- 3c. 5% Li_2O content at 700°C for 15hrs.
4. 10% Li_2O content at 700°C for 5hrs.

N.B. The batch number 2 with 1% Li_2O content has mature peaks and it nearly has the same pattern as number 1 (Amorphous), so it was not shown in the Figure.

REFERENCES

1. Ahmed, A. A., Abbas A. F. and Salman S. M., "The Thermal Expansion of Mixed Alkali Borate Glasses", *Phys. Chem. of Glasses*, 36, 1, (1985).
2. Bishop S. G. and Bray, P. J., "N.M.R. Studies of Calcium Borosilicate Glasses", *J. Phys. Chem. Glasses*, 7, (1966).
3. Drotning W. D., "Thermal Expansion of Glasses in The Solid and Liquid Phases", *International Journal of Thermophysics*, 6, 6, (1985).
4. El Mer, Thomas H., "Role of Acid Concentration in Leaching of Cordierite and Alkali Borosilicate", *J. Am. Ceram. Soc.* 68, 10, (1985).
5. El-Batal H. A., Khalifa F. A. and Azooz M. A., "Gamma Ray Interaction, Crystallization and Infrared Absorption Spectra of Some Glasses and Glass Ceramics From The System $\text{Li}_2\text{O} \cdot \text{B}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$ ", The 15th Egypt. Chem. Conference, 20-25 Nov., (1999).
6. Ezz-El din F. M. and El-Batal H.A. "Radiation effects on Thermal Expansion of Some Ternary Alkali-Silicate Glasses", *J. Non-Cryst. Solids* 152, (1993).
7. Ghoneim N. A. and El-Badry Kh., "Thermal Expansion of High Lead Silicate Glasses in Relation to Structure", *Thermochimica Acta*, 60, (1983).
8. Ghoneim N. A., "Thermal Expansion Studies on Glasses of The System $\text{CaO} \cdot \text{B}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$ ", *Central Glass and Ceramic Bulletin*, 24, 4, (1977).
9. Ghoneim N. A., El-Batal H. A. and Nassar A. M. H., "Microhardness and Softening point of Some Alumino-Borate Glasses as Flow Dependent Properties", *J. Non-Cryst. Solids*, 55, (1983).
10. James P. F., "Glass Ceramics: New Compositions and Uses", *J. Non-Cryst. Solids*, 181, 1, (1995).
11. Kay, J. F. and Doremus, R. H., "Strength and Durability of a Glass Ceramic Containing Spodumene Crystals", *J. Am. Ceram. Soc.* 57, 11, (1974).
12. Khedr A. A. and El-Batal H. A., "Corrosion of Zinc Containing Cabal Glasses by Various Leaching Solutions", *J. Am. Ceram. Soc.*, 79, 3, (1996).
13. Kirk-Othmer, *Encyclopedia of Chemical Technology* 4th ed., volume No. 12, (1994).

14. MacDowell. J. F. , "Alumino Borate Glass Ceramic With Low Thermal Expansivity", *J. Am. Ceram. Soc.* , 73, 8, (1990).
15. Mazelev L. Ya, "Borate Glasses", translated from Russian Consultants Bureau, New York, (1960).
16. McMillan P. W., "Glass-Ceramics", 2nd Ed., Academic press, London, (1979).
17. Ovshinsky S. R. and Klose P. H., "Imaging in Amorphous Materials by Structural Alternation", *J. Non-Cryst. Solids*, 8-10, (1972).
18. Salama S. N., Salman S. M. and Darwish H., "Thermal Expansion of Some Borosilicate Glasses and Their Crystalline Solids", The 15th Egypt. Chem. Conference, 20-25 Nov., (1999).
19. Searstone K. and Isard J. O., "The Chemical Durability of CaO-B₂O₃-Al₂O₃-SiO₂ Glasses", *Glass Technol.*, 6, 6, (1985).
20. Stallworth P. E. and Bray P. J., "Glass Science and Technology", Vol. 4B. Edited by Uhlmann D. R. and Kriedle, N. J. , Academic Press, Boston, MA, (1990).
21. Uhlmann D. R. and shaw R. R, "The Thermal Expansion of Alkali Borate Glasses and The Boric Oxide Anomaly", *J. Non-Cryst. Solids* 1, (1969).
22. Uhlmann D. R., "Glass Formation, a Contemporary View", *J. Am. Ceram. Soc.*, 66, 2, (1983).
23. Velez M. H., Tuller, H. L. and Uhlmann D. R., "Chemical Durability of Lithium Borate Glasses", *J. Non-Cryst. Solids*, 49, (1982).
24. Weyl, W. A. and Marboe E. C., "The Constitution of Glasses", A Dynamic Interpretation, Academic Press, N. Y. Vol. 1, (1962).
25. Zhang Z., Hirao K. and Soga N., "Water Corrosion Behaviour of Densified Glass: II Borate Glasses", *J. Non-Cryst. Solids*, 135, 62, (1991).