

Ultra low and negative expansion glass–ceramic materials produced from pyrophyllite and blast furnace slag

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Abstract. Ultra low and negative expansion glass–ceramic materials have been obtained from pyrophyllite and blast furnace slag. The batch composition was modified with the addition of lithium carbonate, hydrated alumina, boric acid and nucleating agent (titania). The batch was melted at 1400°C followed by casting in the form of bars and annealed at 510°C for 4 h. The annealed specimens were subjected to heat treatment at pre-determined temperatures selected from DTA study of the parent glass. Thermal expansion measurement and X-ray diffraction analysis revealed that the specimen nucleated at 545°C for 4 h and crystallized at 720°C for 2 h which resulted in negative coefficient of thermal expansion [$(-)$ 9 to $(-)$ $2 \times 10^{-7}/^{\circ}\text{C}$] over the temperature range (30–600°C) due to the formation of *b*-eucryptite while other heating schedule showed the formation of spodumene and lithium aluminium silicates. The samples showed excellent flexural strength value and varied in the range 120–200 MPa depending upon the phases present.

Keywords. Glass–ceramic; $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$; blast furnace slag; pyrophyllite.

1. Introduction

Lithia–alumina–silica ternary phase diagram (Eppler 1963) provides important information regarding phases useful for glass–ceramic material. Glass–ceramics are the ceramic material formed through the controlled nucleation and crystallization of the parent glass. This is one of the most important glass–ceramic system which has been extensively investigated and commercialized because of its low, zero or negative thermal expansion coefficients as well as excellent thermal and chemical durability. Several researchers reported their crystallization behaviour with different types of nucleating agents (Locsei 1962; Freimann and Hench 1971; Macmillan 1980; Hlavac 1983).

Various types of glass–ceramic materials are produced from conventional raw materials and there is a growing interest to produce glass–ceramic material from the industrial waste due to their great technological advantage and scientific importance with proper correction of the chemical composition (Wang and Hon 1990; Suzuki and Taraka 1997; Boccacini and Rawlings 2002; Khater 2002; Kneiss *et al* 2002; Rozenstrauha *et al* 2002; Park *et al* 2003).

The transformation of wastes into glass or glass–ceramic provided the opportunity for making useful marketable products out of hazardous waste like fly ash, iron and steel slag and other silicate and municipal wastes. Kneiss *et al* (2002) studied the development of $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-$

SiO_2 glass ceramic system from coal bottom ash. Lithium carbonate was used to promote glass melting and rutile as nucleating agent. Controlled heat treatment of this glass resulted in the formation of lithium alumino-silicate glass and *b*-eucryptite as crystalline phase with negative coefficients of thermal expansion. Lithium alumino-silicate phases are well known for their low linear thermal expansion coefficient over a wide range of temperature which permits the development of glass–ceramic material with a large range of interval of thermal expansion, $(-)$ to $43 \times 10^{-7}/^{\circ}\text{C}$. Almost similar large range interval of thermal expansion values have been reported by other workers also (Strand 1986; Kneiss 2002) for other $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ based glass–ceramic materials.

Suzuki and Taraka (1997) and Park *et al* (2003) reported the characteristics of glass–ceramics made of sewage sludge ashes from the municipal solid waste incinerator. Although glass–ceramics prepared from sewage sludge ash consisted of anorthite as main crystalline phase, control of crystalline phase formation was not possible due to complex composition of the waste. Khater (2002) reported that different types of slag viz. silicon manganese slag and steel slag, can be used successfully for the production of crystalline glass material of different microstructures and mineralogical constituents that have many valuable technological properties. He observed an increase in bulk crystallinity with the increasing content of bustamite phase in the glass. Preparation of glass–ceramics from blast furnace slag has been described by many workers (Yoshimi *et al* 1977; Strand 1986; Chang and Jung 1980) and the main crystalline phases identified

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by them were disopside, spinel, wollastonite and anorthite. Wang and Hon (1990) produced $\text{Li}_2\text{O}-\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ based glass-ceramic from blast furnace slag with addition of silica, alumina, lithium carbonate and rutile as nucleating agents. The major crystalline phase identified in this case was *b*-spodumene. Boccacini and Rawlings (2002) produced new glass-ceramic material in their recent work with interesting magnetic and constructive properties utilizing slag, fly ash and combustion dust waste materials. The heavy iron content of coal fly ash contributed towards the development of magnetic phases with well developed dendrite structure ascribed to magnetite, which offered soft magnetic properties to the materials. In another work (Mandal *et al* 2000), glass produced from a mixture of blast furnace slag and clay were studied for their crystallization behaviour with rutile and zirconia as nucleating agents. Formation of crystalline phases like *b*-spodumene and *b*-quartz solid solution was observed. However, controlling of the glass composition was found to be a major problem in this system.

The aim of this paper is to use waste material like quenched and granulated blast furnace slag with pyrophyllite, a hydrous aluminosilicate mineral ($\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$) for the development of ultra low thermal expansion material. Judicious selection of other additives were made in controlling the composition of the glass. Titania (TiO_2)

was used as the nucleating agent. The crystallization behaviour was studied at different time temperature schedules after DTA analysis of the parent glass powder. The resulting material was subjected to thermal expansion and flexural strength measurements. The phase assemblages were characterized by XRD studies.

2. Experimental

2.1 Preparation of parent glass

Quenched granulated blast furnace slag (collected from Indian iron and steel plant) and pyrophyllite (Maharashtra, India) were used as major raw materials to prepare the batch. The batch composition was modified in order to get the $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ glass-ceramics with addition of LR grade lithium carbonate (NICE Chemicals, India, 98% purity) and LR grade hydrated alumina of 99.45% purity. LR grade boric acid (NICE Chemicals, India, 99.5% purity) was added to the batch in order to accelerate the glass melting process. LR grade titania (NICE Chemicals, India, 98% purity) was added to the batch as nucleating agent. Around 0.5% arsenic oxide (As_2O_3) was also added as refining agent. The batch composition (table 1) was designed matching to the eutectic composition of $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system.

The following flow sheet (figure 1) was followed to prepare the parent glass.

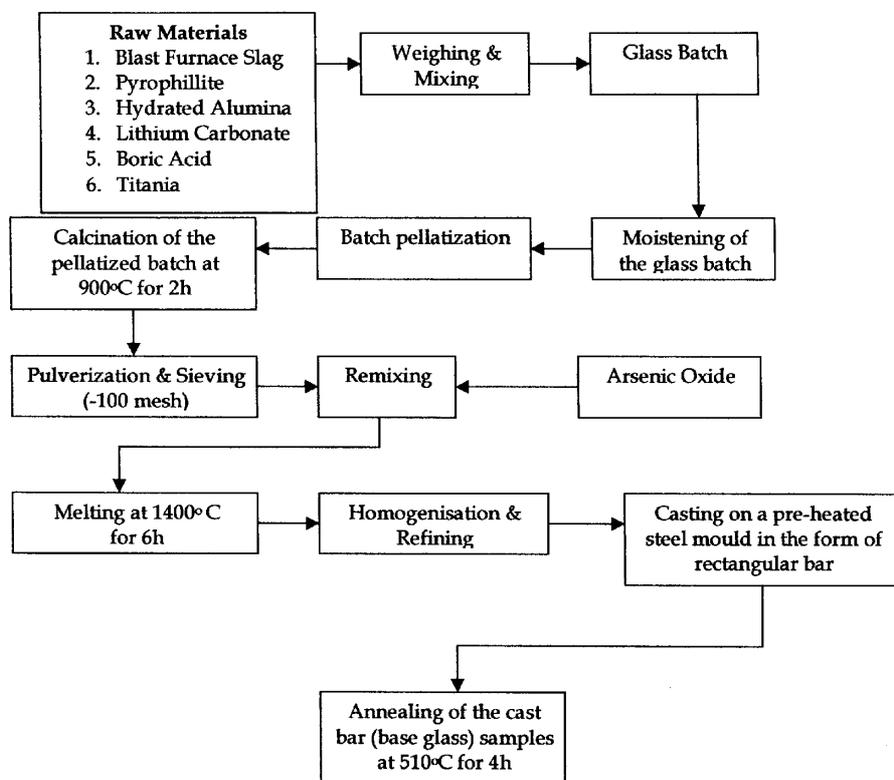


Figure 1. Flow sheet for preparation of parent glass.

Two kilograms of calcined batch was charged gradually into a re-crystallized alumina crucible placed inside an electric furnace at 1350°C. After charging, the temperature was raised to 1400°C and kept at this temperature for 6 h to undergo complete melting and refining process. The homogeneity of the glass was checked by physical inspection of a glass fibre drawn from the bulk of the molten glass. After melting and proper refining, the bubble and seed free melt was cast onto a preheated steel mould in the form of rectangular bar of dimension 60 × 10 × 10 mm³. The cast bar samples were immediately transferred to a preheated electric muffle furnace for annealing at 510°C for 2 h followed by controlled cooling at the rate of 15°C/h. Requisite quantity of the annealed samples was crushed into powder for the determination of crystallization order by DTA analysis, chemical analysis and XRD study.

TG/DTA study was conducted in an air atmosphere at the rate of 10°C/min using Netzsch 409C model. Powdered alumina was used as the reference material. Chemical analyses of the raw materials (blast furnace slag and pyrophyllite) and parent glass powder were carried out by conventional technique (Hillebrand and Lundell 1953). An annealed sample of 25 ± 0.1 mm in length and 6 ± 0.1 mm diameter was used for thermal expansion measurement as well as for determination of glass transition and softening temperature of the parent glass. Orton Automatic Dilatometer (DIL 402C) was used for expansion study.

2.2 Thermal treatment

The annealed glass bars were finally subjected to further heat treatment in a programmable electric furnace to study the effect on nucleation and crystallization at different

time temperature schedules. The schedule used in the present study for heat treatment is given in table 2. Finally, the heat-treated samples were cooled to room temperature and subjected to various characterizations.

2.3 Characterization of samples

Flexural strength (three-point bending) of the heat-treated samples was determined by Universal Mechanical Testing machine (Instron 5500R) and thermal expansion was measured by the technique as described earlier. The crystallization phases evolved in some of the selected samples were identified by X-ray diffraction analysis using a Philips PW-1730 with CuK α radiation and Ni filter, at a scanning rate (2θ) of 2°/min.

3. Results and discussion

The chemical analysis of the raw materials (blast furnace slag and pyrophyllite) is given in table 3.

Chemical analysis of blast furnace slag shows the presence of main components like SiO₂, CaO, Al₂O₃ and MgO and pyrophyllite is rich in SiO₂ and Al₂O₃. Use of pyrophyllite in the composition was found to be beneficial not only for its contribution towards controlling of SiO₂ and Al₂O₃ content of the glass but also in reducing the glass melting temperature. A vitreous melt obtained from the batch at 1400°C showed adequate viscosity and flowing characteristics. Table 4 gives the analysed oxide composition of the melted glass.

It may be seen from the melted glass composition that the molar ratio of Li₂O : Al₂O₃ : SiO₂ is 1 : 0.97 : 1.98 which is almost matching with the ratio as per required eutectic batch composition (1 : 0.997 : 1.99). Differential thermal analysis of the parent glass powder (figure 2) showed characteristic endothermic peak at 540°C (range 538–548°C). Accordingly, the temperature (545°C) closer to higher range i.e. 548°C, was ultimately chosen as the nucleation temperature in the present study. The formation of this peak may be due to molecular rearrangement phenomenon at the pre-calcination stage which is also observed by Shennawi (1983). Characteristic sharp exothermic peak was obtained at 653°C (range 652 indicating the crystallization temperature followed by

Table 1. Batch composition.

Raw materials	Mass (%)
Blast furnace slag	15.48
Pyrophyllite	35.04
Hydrated alumina	11.25
Lithium carbonate	23.36
Boric acid	8.68
Titania	6.19

Table 2. Heat treatment schedule for nucleation and crystallization of annealed samples.

Sample no.	Nucleation temperature (°C)	Soaking time (h)	Crystallization temperature (°C)	Soaking time (h)
GC-1	545	1	650	2
GC-2	545	2	650	2
GC-3	545	4	720	2
GC-4	545	4	825	4

another small exothermic peak at 720°C. Accordingly, in the present study the crystallization temperature was fixed at 650°C closer to 652°C. Finally, the TG/DTA results were utilized for the selection of nucleation as well as crystallization temperature towards the fixation of controlled heat treatment schedule for subsequent ceramization of the parent glass samples.

Table 3. Chemical composition of blast furnace slag and pyrophyllite (mass%).

Oxide component	Blast furnace slag	Pyrophyllite
SiO ₂	32.97	63.51
Al ₂ O ₃	20.47	28.73
Fe ₂ O ₃	0.83	0.35
TiO ₂	1.20	1.00
CaO	35.47	tr
MgO	8.13	tr
K ₂ O	0.75	0.86
Na ₂ O	0.18	0.27
LOI	–	5.30

Table 4. Analysed oxide composition of the melted glass.

Oxide component	Mass (%)
SiO ₂	35.81
Al ₂ O ₃	33.73
Fe ₂ O ₃	0.59
B ₂ O ₃	4.47
TiO ₂	4.07
CaO	8.02
MgO	1.88
K ₂ O	1.13
Na ₂ O	0.23
Li ₂ O	10.08

Linear thermal expansion coefficient (LTEC) of the parent glass in the temperature range 30–300°C was found to be $80 \times 10^{-7}/^{\circ}\text{C}$ (figure 3). The comparison of LTEC value of the ceramized samples, heat-treated at different schedules is graphically exhibited in figure 4. It is evident from figure 4 that the LTEC value in all the ceramized samples lies in the range of (–) to $43 \times 10^{-7}/^{\circ}\text{C}$ and this is significantly lower than the value obtained in parent glass ($80 \times 10^{-7}/^{\circ}\text{C}$). It is very interesting to observe that sample GC-3 showed negative thermal temperature coefficient in the temperature range 30–600°C. Therefore, it may be said that low expansion glass–ceramic may be synthesized by utilizing blast furnace slag and alumino–silicate mineral like pyrophyllite.

The XRD results of all the crystallized samples are summarized in table 5 and their XRD patterns are shown in figure 5.

Table 5 showed that the principal crystalline phases evolved from the present samples corresponded to *a* and *b*-spodumene ($\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$), *b* and *g*-eucryptite ($\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) and lithium aluminium silicate. Formation of *b*-eucryptite as only the major phase in sample GC-3 is responsible for the negative thermal expansion over the temperature range 30–600°C. Higher thermal expansion values in sample GC-1 compared to others is probably due to the presence of other associated lithium aluminium silicate phases with somewhat larger value of linear coefficient of thermal expansion. Formation of *b*-spodumene as principal crystalline phase in such type of $\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ based glass ceramic material produced from blast furnace slag was also observed by Wang and Hon (1990). No formation of *b*-eucryptite was noticed by them in their system. As a result, they observed that the average coefficient of linear thermal expansion in the temperature range 25–600°C is in the order of $40\text{--}50 \times$

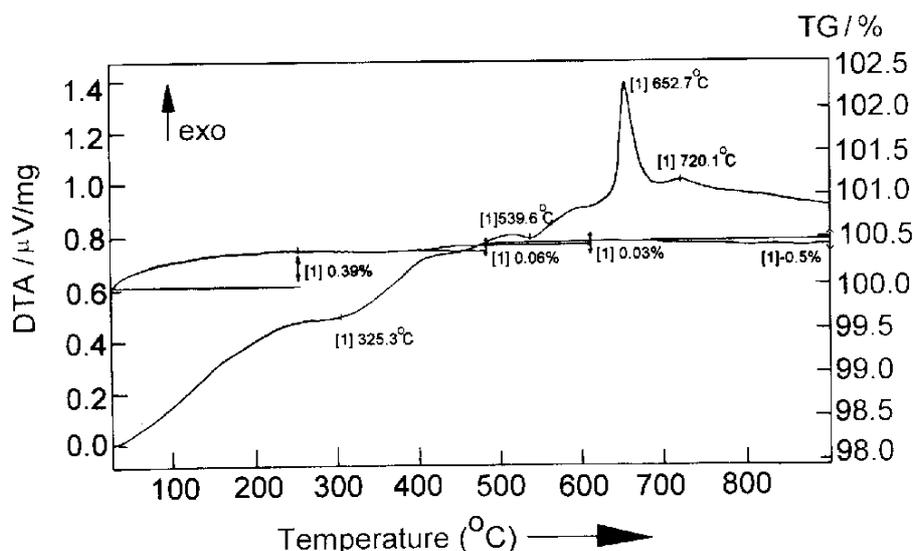


Figure 2. Differential thermal analysis curve of the parent glass powder.

$10^{-7}/^{\circ}\text{C}$ which is significantly higher than the values obtained in the present study. As the crystalline phases depend on the initial glass composition, heat treatment schedule and type and amount of nucleating agents, it is possible to formulate appropriate glass composition to achieve the desired properties. Considering commercial applications of glass ceramic the present glass composi-

tion was formulated and studied here which presented a value of negative coefficient of linear thermal expansion over the entire temperature range (30–600°C).

It is evident from table 6 that GC-1 sample shows the flexural strength value as high as 201.45 MPa. Decrease in strength value in GC-2 sample may be due to the presence of *b*-spodumene phase which is likely to result in

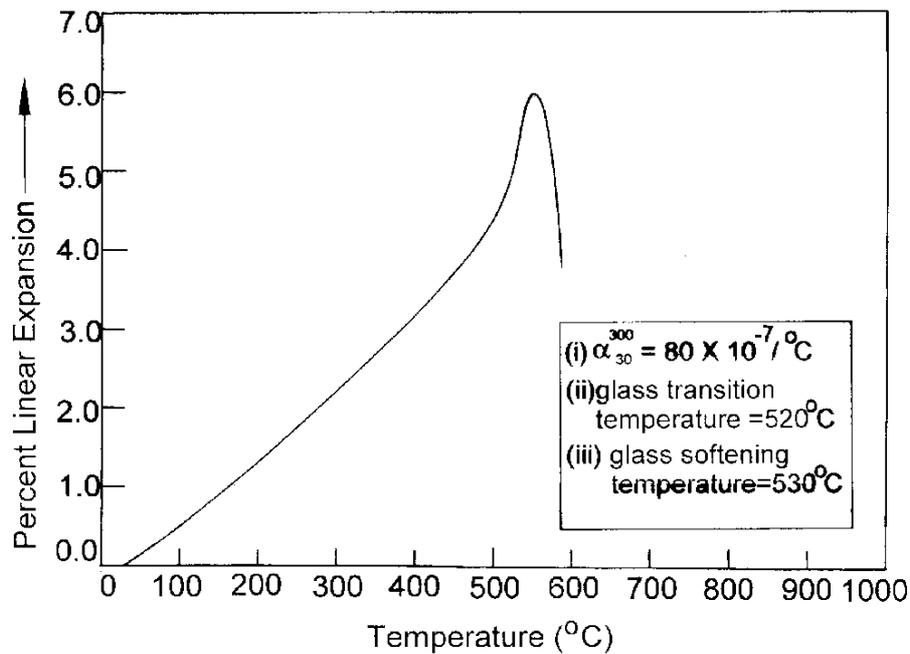


Figure 3. Dilatometric thermal expansion curve of the parent glass.

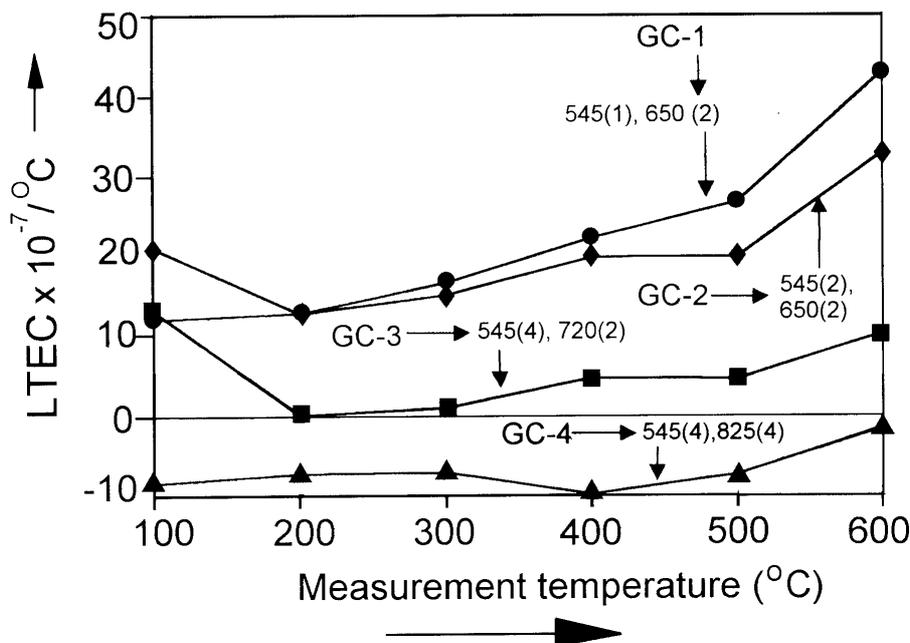
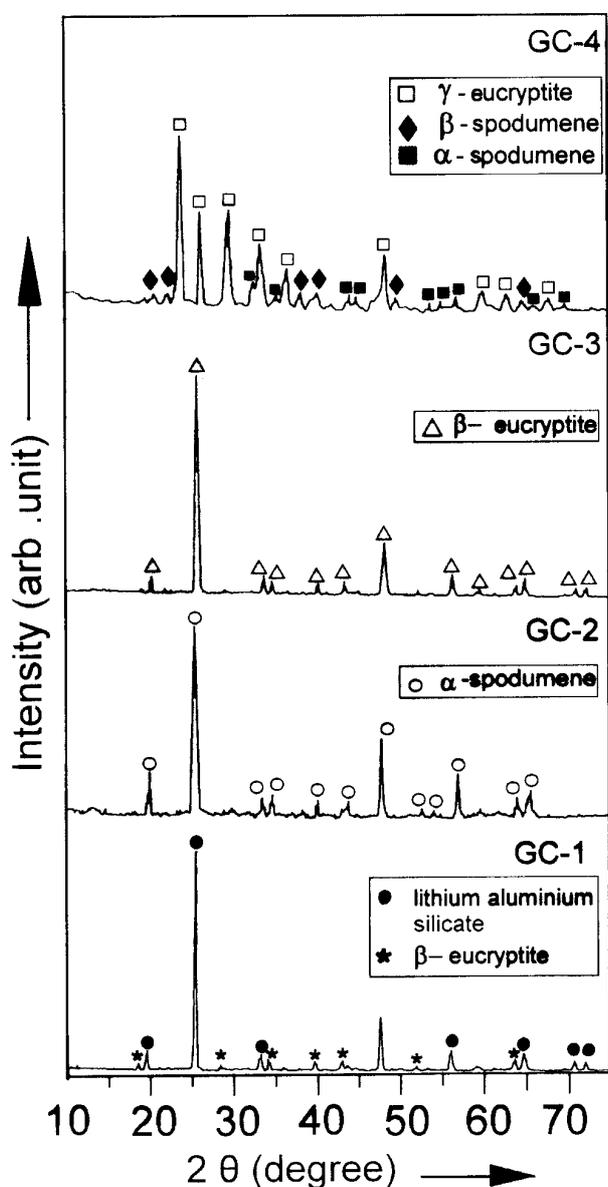


Figure 4. Linear thermal expansion coefficient (LTEC) values of the samples heat-treated at different time temperature schedules.

Table 5. Phases developed in thermally crystallized samples.

Sample code	Heat treatment schedule		Major phases developed	JCPDS (PDF#)
	Nucleation temperature (°C)	Crystallization temperature (°C)		
GC-1	545 (1)	650 (2)	Lithium aluminium silicate, <i>b</i> -eucryptite	26-0840 (standard <i>hkl</i> 112) 17-0534 (standard <i>hkl</i> 102)
GC-2	545 (2)	650 (2)	<i>a</i> -spodumene	33-0786 (standard <i>hkl</i> 221)
GC-3	545 (4)	720 (2)	<i>b</i> -eucryptite	17-0534 (standard <i>hkl</i> 102)
GC-4	545 (4)	825 (4)	<i>g</i> -eucryptite, <i>b</i> -spodumene & <i>a</i> -spodumene	47-27 (standard <i>hkl</i> 003 & 121) 35-0797 (standard <i>hkl</i> 201) 33-0786 (standard <i>hkl</i> 221)

**Figure 5.** X-ray diffraction pattern of the samples heat-treated at different time temperature schedules.**Table 6.** Mechanical strength values of the samples heat-treated at different time temperature schedules.

Sample code	Mechanical strength (MPa)
GC-1	201
GC-2	145
GC-3	120
GC-4	155

circumferential tensile stresses in the residual glass phase around the crystal. This phenomenon is also reported by Macmillan (1980). Further decrease in strength values in the sample GC-3 is due to the presence of *b*-eucryptite crystalline phase as this crystal is anisotropy in nature and exists in the form of a polycrystalline aggregate which has a highly negative coefficient of linear thermal expansion (Macmillan 1980). GC-4 sample showed higher strength than GC-2 and GC-3 samples but lower than the sample GC-1 and this is attributed towards the formation of both spodumene and eucryptite at higher crystallization temperature.

4. Conclusions

(I) Lithium aluminosilicate glass was prepared from blast furnace slag by modifying the composition with addition of pyrophyllite (a major source of SiO_2 and Al_2O_3), hydrated alumina, boric acid (H_3BO_3), lithium carbonate (Li_2CO_3) and titania (TiO_2).

(II) The introduction of pyrophyllite, a hydrous aluminosilicate material to blast furnace slag decreases the glass melting temperature, melt viscosity and results in the formation of desired glass-ceramic phases on subsequent ceramization.

(III) Crystallization at 720°C favours the formation of *b*-eucryptite which has a highly negative coefficient of thermal expansion.

(IV) The glass-ceramic materials obtained at different heating schedules showed varying thermal expansion values, ($-$) to $43 \times 10^{-7}/^\circ\text{C}$. By controlling the composition

of the glass, nucleating agent, crystallization temperature and time schedule, it is possible to optimize thermal expansion coefficient of the final product which permits for its application in specific areas including kitchen stove, hot plates etc. Due to use of inexpensive raw materials and lower melting temperature, the cost of production of such items is expected to be low.

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