

PROJECT REPORT ON

**Study of the Effect of Different Nucleating Agents**  
**On**  
**Lithium Alumino-Silicate Glass-Ceramic System**

SUBMITTED BY

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**ODISHA**  
**2013**

# DECLARATION BY THE CANDIDATE

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I **Shashwat Singh**, a student of Department of Ceramic Engineering, National Institute of Technology Rourkela bearing Roll Number 109CR0610 hereby certify that my B.Tech Project Report entitled “**Study of the Effect of Different Nucleating Agents On Lithium Alumino-Silicate Glass-Ceramic System**”, under the guidance of **Prof. Sumit Kumar Pal** at National Institute of Technology Rourkela, is being submitted under the requirement for the Degree of Bachelor of Technology in **Ceramic Engineering**. This is a record of bona fide work carried out by me and the results presented in the Project Report have not copied from any source. The results presented in this Project Report have not been submitted to any other University or Institute for the Award of any other certificate or degree.

**Rourkela**

**DATE:** 10-05-13

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## NATIONAL INSTITUTE OF TECHNOLOGY ROURKELA

### CERTIFICATE

This is to certify that the Project Report entitled “**Study of the Effect of Different Nucleating Agents On Lithium Alumino-Silicate Glass-Ceramic System**”, being submitted by **Mr. Shashwat Singh**, Department of Ceramic Engineering, National Institute of Technology Rourkela, under the requirement for the Degree of Bachelor of Technology in **Ceramic Engineering** is a record of bona fide work carried out by him, under my guidance and supervision. The results enclosed in this report have been verified and found to be satisfactory.

The results presented in this Project Report have not been submitted to any other University or Institute for the Award of any other certificate or degree.

Rourkela

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# ABSTRACT

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Lithium AluminoSilicate (LAS) Glass ceramic (GC) finds use in kitchenware, cooktop panels and telescope mirror because of its characteristic of very low and sometime zero thermal expansion coefficient (TEC) in the application temperature range. In this project work, conventional melt-quenching technique has been used for the development of the LAS base glass. After controlled crystallization, LAS GC has been developed using titania and/ zirconia as a nucleating agent and their effect has been studied in the presence of yittria. Here the yittria content has been varied from 1-3 wt% with corresponding variation in titania (2-4 wt%) or zirconia (2-4 wt%). Effects of temperature and time on crystallization have also been studied followed by the effect of crystallization on thermal expansion co-efficient of the developed glass ceramics. Developed crystalline phases were  $\beta$ -Spodumene and  $\beta$ -quartz solid solution (ss) which has been authenticated by X-ray diffractometer. TEC of the GC has been measured and studied using Dilatometer in the temperature range of 25°C to 750°C and its surface hardness has been measured at 0.5Kgf using Vickers indentation method.

# List of FIGURES

S.NO.	TITLE	PAGE NO.
1	Schematic of double push-rod dilatometer	13
2	Indentation made on a ceramic sample	14
3	Base glasses containing TiO <sub>2</sub> as nucleating agent	16
4	Base glasses containing ZrO <sub>2</sub> as nucleating agent	16
5	DSC curve at heating rate of 10°C/min for a glass containing titania as nucleating agent.	17
6	DSC curve at heating rate of 10°C/min for a glass containing zirconia as nucleating agent	18
7	DSC curve at different heating rates for Y2Z3 base glass.	19
8	DSC curve at different heating rates for Y3Z2 base glass	19
9	Glass ceramic samples of BY1T4 heat treated at different temperature	20
10	Glass ceramic samples of BY2T3 heat treated at different temperature	20
11	Glass ceramic samples of BY3T2 heat treated at different temperature and time	21
12	Glass ceramic samples of BY2Z3 heat treated at different temperature	21
13	Glass ceramic samples of BY3Z2 heat treated at different temperature	22
14	Bulk Density vs temperature graph of BY1T4 GC	23
15	Bulk Density vs temperature graph of BY2T3 GC	23
16	Bulk Density vs temperature graph of BY3T2 GC	24
17	Bulk Density vs time graph of BY3T2 GC	24
18	XRD plot of BY1T4 GC heat treated at 880-2h and 920-2h	25
19	XRD plot of BY2T3 GC heat treated at 920-2h	26
20	XRD plot of BY3T2 GC heat treated at 920 for 2,4 and 6h	27
21	dL/L <sub>o</sub> versus Temperature curve of BY2T3 GC ceramized at 920°C-2h	28
22	dL/L <sub>o</sub> versus Temperature curve of BY3T2 GC ceramized at 920°C-2h	29
23	dL/L <sub>o</sub> versus Temperature curve of BY3T2 GC ceramized at 920°C-4h	30
24	dL/L <sub>o</sub> versus Temperature curve of BY3T2 GC ceramized at 920°C-6h	31
25	Vickers Hardness of GC surface vs temperature of ceramization	32

## List of Table

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<b>S.NO.</b>	<b>TITLE</b>	<b>PAGE NO.</b>
1	Composition range possible for $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ glass formation	2
2	Composition of glasses containing $\text{TiO}_2$ as nucleating agent	9
3	Composition of glasses containing $\text{ZrO}_2$ as nucleating agent	10
4	Composition of glasses containing $\text{TiO}_2$ as nucleating agent	10
5	Composition of glasses containing $\text{ZrO}_2$ as nucleating agent	10
6	Vickers Hardness of GC measured at 0.5Kgf with a dwelling time of 2s	33

# INDEX

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S. No	TITLE	PAGE NO
I	<a href="#"><u>DECLARATION BY THE CANDIDATE</u></a>	i
II	<a href="#"><u>CERTIFICATE</u></a>	ii
III	<a href="#"><u>ACKNOWLEDGMENT</u></a>	iii
IV	<a href="#"><u>ABSTRACT</u></a>	iv
V	<a href="#"><u>List of FIGUREs</u></a>	v
VI	<a href="#"><u>List of Tables</u></a>	vi
1	<a href="#"><u>Introduction</u></a>	1-4
2	<a href="#"><u>Literature Survey</u></a>	5-7
3	<a href="#"><u>Objective</u></a>	8
4	<a href="#"><u>Experimental Procedure</u></a>	9-14
	4.1: <a href="#"><u>Preparation of batch</u></a>	9
	4.2: <a href="#"><u>Batch melting, casting and annealing</u></a>	11
	4.3: <a href="#"><u>Thermal analysis</u></a>	11
	4.4: <a href="#"><u>Ceramization of glass</u></a>	11
	4.5: <a href="#"><u>Density measurement</u></a>	11-12
	4.6: <a href="#"><u>Phase Identification</u></a>	12
	4.7: <a href="#"><u>Thermal Expansion coefficient Measurement</u></a>	12-13
	4.8: <a href="#"><u>Hardness testing</u></a>	13-14
5	<a href="#"><u>Results and Discussion</u></a>	15-33
	5.1: <a href="#"><u>Physical Observation Of Base glass</u></a>	15-16
	5.2: <a href="#"><u>Differential Scanning Calorimetry analysis</u></a>	17-19
	5.3: <a href="#"><u>Ceramization of LAS glass</u></a>	20-22
	5.4: <a href="#"><u>Bulk density</u></a>	23-25
	5.5: <a href="#"><u>Phase analysis</u></a>	25-27
	5.6: <a href="#"><u>Dilatometry analysis</u></a>	28-31
	5.7: <a href="#"><u>Vickers Hardness Analysis</u></a>	32-33
6	<a href="#"><u>Conclusion</u></a>	34
7	<a href="#"><u>Reference</u></a>	35-36



# 1. INTRODUCTION

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Glass-ceramics (GC) are generally developed to achieve special properties of conventional sintered ceramics with the characteristics of glasses. By developing desired crystal phases in the glassy matrix through controlled heat treatment properties can be modified. Among various GC systems, Lithium Alumino-Silicate (LAS) GC holds a special interest due to its low thermal expansion coefficient (TEC).

Major application of LAS GC includes cook-ware. They are subjected to frequent thermal shock when placed directly onto the hot stove from refrigerator. This application requires low TEC as well as aesthetic look. Another application of LAS GC is as cooktops (range top) for kitchen stoves which is required to withstand steep thermal gradient and frequent thermal shocks. The low thermal expansion glass ceramics is very well suited for such an application due to their low TEC values in the range of  $10^{-6}$  to  $10^{-7}$  /K or even less for the temperature interval 20–700 °C. Cooktop made from LAS GC has an edge over electrically heated kitchen stoves as it is made from one flat piece (monolithic) without gaps between heating zone and remaining area which can eliminate the pot tilting problem on placing them over heating zone. Research interest regarding GC is nowadays focused towards enhancing strength of the GC. Average flexural strength values for newly delivered samples have been reported around 150MPa for the keatite (ss) GCs and 100MPa for the  $\beta$ -quartz (ss) GCs. Product which are subjected to frequent thermal shock and thermal gradient may have keatite (ss) or  $\beta$ -quartz (ss) embedded in glassy matrix. Corning Inc. and PPG have developed white, opaque one with keatite glass ceramic while Schott, Corning Inc. together with Saint

Gobain have developed a strongly tinted partly transparent GC (Ceran®), based on  $\beta$ -quartz (ss) glass ceramic. Another advanced application of LAS GC is in astronomy. Telescope mirrors needs glassy material with high dimensional stability to resist any change in dimensions which otherwise may bring aberration in the mirror. Application temperature interval is smaller than in cookware or cooktops and is in the range of 50-150°C. In this interval TEC should be as low as possible. Schott has made LAS GC product for this particular application which is known as Zerodur® having TEC lower than  $0.5 \times 10^{-6}/K$ . New areas which have huge scope for LAS GC are radiation shielding in space and EUV lithography.

Most of the GC generally has some nucleating agent which aid in developing desired crystalline phases by nucleation as well as crystallization followed by growth from mother glass. Various nucleating agents which are generally used are  $TiO_2$ ,  $ZrO_2$ ,  $P_2O_5$ ,  $Y_2O_3$  and other rare earth oxides.  $TiO_2$  acts as a very efficient nucleating agent in LAS based GC, whereas a similar effect has been observed with  $ZrO_2$ . When nucleating agents are used simultaneously then ceramization temperature tend to decrease, this can be useful in commercialization of LAS-GC.

LAS glasses are generally formed using composition (wt%) tabulated in the following table no 1.

$LiO_2$		$Al_2O_3$	$SiO_2$	Other oxide
				$Na_2O+K_2O+TiO_2+ZrO_2+Y_2O_3+As_2O_3$
Wt%	3-6	18-25	60-75	6.5

**Table No 1:** Composition range possible for  $Li_2O-Al_2O_3-SiO_2$  glass formation.

For commercialization of GC with desired properties a controlled crystallisation of LAS glass is an essential process, therefore, the choice of nucleating agents plays a very crucial role. The properties of LAS GC largely depend on the concentration and crystallite size of the developed crystalline phases which are as follows.

1.  $\beta$ -Quartz solid solution (ss)
2.  $\beta$ -Spodumene (ss) or keatite (ss)
3.  $\beta$ -eucryptite (ss)

**$\beta$ -Quartz (ss)** is a hexagonal type structure with 6 and 8- membered ring of  $\text{TO}_4$  tetrahedron, where T = Si or Al. In a silica network structure (quartz structure), Al ions substitute some of the Si ions giving rise to a net charge in the system. This charge is neutralised interstitial substitution of Li ions by addition of corresponding oxides. Li ions occupy channel formed in hexagonal structure of  $\beta$ -Quartz. In the silica network, up to 30-50 wt% Si can be substituted by Al and Li. During this replacement, a solid solution is formed. It is a metastable phase and transforms to  $\beta$ -Spodumene (ss) or keatite (ss) around 800-900<sup>0</sup>C. When n, as in  $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-n.\text{SiO}_2$ , is in the range of 5 to 7 then  $\beta$ -Quartz (ss) is developed on ceramization of the mother glass. Corning Inc manufactures a product of LAS GC (Vision®) containing  $\beta$ -Quartz (ss) as the major phase. They are transparent or tinted and similar have properties to borosilicate ware.

**$\beta$ -Spodumene (ss)** (or keatite ss) has composition as  $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-n.\text{SiO}_2$ , where n can have value between 4 and 10. Keatite is the name of a  $\text{SiO}_2$  modification which does not occur in nature but has been synthesized under hydrothermal conditions. Keatite (ss) have a tetragonal type structure and consist of 5- to 7- membered rings of

TO<sub>4</sub> tetrahedra where T = Si or Al. Li ions occur near each pair of TO<sub>4</sub>. Due to characteristics negative TCE of this phase, LAS GC will have a negative or only small positive TCE as it is counter balanced by the positive TEC of the glassy matrix. This phase is stable up to 1100<sup>0</sup>C. Commercial product containing β-Spodumene (ss) phase is Pyroceram® which is used as cooktop panel has white and opaque appearance due to the large crystalline phase.

**β-eucryptite (ss)** has ordered distribution of AlO<sub>4</sub> and SiO<sub>4</sub> tetrahedra leading to doubling of the C lattice parameter. Temperature dependant ordering of the Li ions has been observed in the channel which has been formed by stacking of interstitial positions. This allows β-eucryptite (ss) GC to be the candidate for a superionic conductor, in which Li ions will act as the charge carrier.

This investigation will try to find out the relation between the increase in the content of nucleating agent and yttria and the corresponding changes in the Bulk density, TEC and Vickers Hardness of the LAS GC ceramized at different temperatures and soaking time. Phase evolution of β-Quartz (ss) and β-Spodumene (ss) will also be studied.

## 2. LITERATURE SURVEY

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Effects of various nucleating agents on the evolution of crystalline phases in LAS GC have been reported in the literature. It has been reported that most used nucleating agents for LAS GC is titania ( $\text{TiO}_2$ ) and zirconia ( $\text{ZrO}_2$ ). For best results they were used simultaneously by **Sack et al.** <sup>1</sup>**Aumin Hu** et al reported that on adding 2.36 wt% of  $\text{TiO}_2$  bulk crystallisation can be obtained. They optimized the two nucleation agents at 2%  $\text{ZrO}_2$ +2.36%  $\text{TiO}_2$  for maximum value of Vickers hardness, flexural strength, fracture toughness and optical transmission.

<sup>2</sup>**Hu et al**, reported that on using  $\text{CeO}_2$  as nucleating agent, decreases in viscosity of the melt occurred thereby promoting crystallisation at relatively lower temperature. However,  $\text{CeO}_2$  has little influence on the TEC of the LAS GC.

<sup>3</sup>**Kangguo Cheng** reported that carbon can effectively affect crystallisation kinetics of LAS glasses and  $\beta$ -eucryptite (ss) is the main phase in all GCs irrespective of their crystallisation temperature. Carbon lowered the crystallisation activation energy by increasing the viscosity or decreasing the diffusion rate. He has also reported that eucryptite content increases with ceramization temperature and soaking time.

<sup>4</sup>**Yu-Han et al**, reported that on addition of  $\text{B}_2\text{O}_3$  and  $\text{P}_2\text{O}_5$ , when nucleating agents used in glass were  $\text{TiO}_2$  and  $\text{ZrO}_2$ , phase transformation temperature from  $\beta$ -Quartz to  $\beta$ -Spodumene got lowered due to the destruction of glass network and distorted bonding as Si-O bond was replaced by B-O or P-O bonds. He also concluded that GC having only  $\text{B}_2\text{O}_3$  had higher flexural strength than when only  $\text{P}_2\text{O}_5$  was present.

<sup>5</sup>**Shyu et al**, found that 4mol %  $Y_2O_3$  and 8mol %  $La_2O_3$  improved the control over crystallisation of  $Li_2O-Al_2O_3-4SiO_2$  GC.  $Y_2O_3$  reduced surface crystallisation but didn't induce any bulk crystallisation, on the other hand,  $La_2O_3$  completely suppressed surface crystallisation and promoted bulk crystallisation with increase in kinetics for  $\beta$ -Quartz to  $\beta$ -Spodumene (ss) phase transformation compared to undoped samples.

<sup>6</sup>**Guo et al**, studied the effects of fluorine and found that as  $F^-$  ion have similar radius as of  $O^{2-}$  ion; so it substitutes  $O^{2-}$  of silicate structure. So, some of Si-O-Si, becomes Si-F-Si and the structure become relax thereby helping the diffusion of ions in the glass improving the nucleation and crystallisation.

<sup>7</sup>**Riello et al**, have reported that for transparency of LAS GC critical size of crystals should be  $\sim 50$ nm. They have also reported that glass heated at 1003K for 10h and 12h, showed good transparency having high crystallinity of around 77 and 78 wt% of  $\beta$ -eucryptite (ss). Nucleation was done at 953K for 20h. They deliberately crystallised  $\beta$ -eucryptite (ss) as it imparts high wear resistance to the article.

<sup>8</sup>**Guo et al**, reported that fluorine addition in LAS GC decreases the crystallization temperature with the formation of small crystal size as homogeneous nucleation is promoted. There is a direct formation of  $\beta$ -Spodumene (ss) without the transformation of  $\beta$ -Quartz to  $\beta$ -Spodumene (ss). Thermal shock resistance and water resistance (i.e. durability) also increased on  $F^-$  addition.

<sup>9</sup>**Zheng et al**, have reported a decrease in viscosity and melting temperature of LAS glass on increasing the content of yttria. Yttria was used in the presence of titania and zirconia. Decrease in viscosity accompanied the deviation from volume to surface

crystallisation with direct formation of  $\beta$ -Spodumene (ss). This is the reason for increase in activation energy of crystallisation with addition of yttria.

<sup>10</sup>**Sung et al**, have reported that LAS glass doped with boria or titania or both simultaneously, when glass have lower range between  $T_o$  (onset) and  $T_g$ , will have poor sintering due to more tendency of formation of crystal which would inhibit viscous flow aiding sintering. They have also reported same degree of sintering for all the composition of LAS glass with boria or titania or together.

<sup>11</sup>**Rapp** has reported that 0.10wt %  $Nd_2O_3$  drastically decreased the TEC of LAS GC for laser material. In the temperature range of 0-300<sup>0</sup>C, TEC was observed to get reduced from  $+39.5 \times 10^{-7}/^0C$  (pure LAS glass) to  $-5 \times 10^{-7}/^0C$  (doped GC) which is possible due to decrease of non-bridging oxygen and construction of  $\beta$ -quartz (ss) crystal.  $Nd_2O_3$  addition led to increase of laser threshold from glass to GC almost 2 times.

So, from literature survey it has been observed that there is little information available on the sole effects of yttria addition, in the presence of only titania or zirconia at a time, on the crystallisation kinetics and activation energy of the crystal. This has led to the present investigation to find out the relation between the increase in the content of nucleating agent and yttria and the corresponding changes in the Bulk density, TEC and Vickers Hardness of the LAS GC along with the phase evolution.

## 3. OBJECTIVE

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Objectives of this project work have been subcategorized as follows:

1. Development of  $\text{LiO}_2\text{-Al}_2\text{O}_3\text{-SiO}_2$  (LAS) based glass ceramic system
2. Study of the effects of nucleating agent,  $\text{ZrO}_2$  and  $\text{TiO}_2$  combined with  $\text{Y}_2\text{O}_3$  in the LAS glass system.
3. Optimization of concentration of nucleating agents
4. Study of the phase evolution of LAS GC on variation of nucleating agents and heat treatment schedule.
5. Study of effect of glass ceramic crystalline phases on TEC variation.
6. Study of the variation in Vickers hardness of the LAS GC obtained following various schedule and compositional changes.



## 4. EXPERIMENTAL PROCEDURE

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### 4.1: Preparation of batch

In the present investigation glass has been prepared from high purity chemicals of SiO<sub>2</sub> (Loba Chemie PVT., LTD.), Potassium carbonate anhydrous- K<sub>2</sub>CO<sub>3</sub> (Loba Chemie PVT., LTD., Min. Assay: 99.9%), titanium (IV) oxide TiO<sub>2</sub>, sodium carbonate Anhydrous Na<sub>2</sub>CO<sub>3</sub> (SISCO RESEARCH LABORATORIES PVT., LTD., Min. Assay: 99.9%), aluminium oxide active (neutral) Al<sub>2</sub>O<sub>3</sub> (Loba Chemie PVT., LTD., Min assay: 99.9%), zirconia ZrO<sub>2</sub>, Yttrium (III) oxide Y<sub>2</sub>O<sub>3</sub> (Alfa Aesar, Min assay: 99.9%) and Orthoboric acid H<sub>3</sub>BO<sub>3</sub> (Loba Chemie PVT., LTD., Min assay: 99.5%).

Batch of the composition in wt % as shown in Table 2 and Table 3 were initially mixed and stored in polybags for subsequent melting. Various glass batches and their corresponding glasses were designated as Y1T4, Y2T3, Y3T2, Y1Z4, Y2Z3 and Y3Z2.

Sample ID	Li <sub>2</sub> O	Al <sub>2</sub> O <sub>3</sub>	Si <sub>2</sub> O	Na <sub>2</sub> O	K <sub>2</sub> O	Y <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>
Y1T4	4.5	21.5	65	2	2	1	4
Y2T3	4.5	21.5	65	2	2	2	3
Y3T2	4.5	21.5	65	2	2	3	2

**Table No 2:** Composition of glasses containing TiO<sub>2</sub> as nucleating agent.

Sample ID	Li <sub>2</sub> O	Al <sub>2</sub> O <sub>3</sub>	Si <sub>2</sub> O	Na <sub>2</sub> O	K <sub>2</sub> O	Y <sub>2</sub> O <sub>3</sub>	ZrO <sub>2</sub>
Y1Z4	4.5	21.5	65	2	2	1	4
Y2Z3	4.5	21.5	65	2	2	2	3
Y3Z2	4.5	21.5	65	2	2	3	2

**Table No 3:** Composition of glasses containing ZrO<sub>2</sub> as nucleating agent.

Another batch having composition where SiO<sub>2</sub> has been replaced by B<sub>2</sub>O<sub>3</sub>, as presented in Table 4 and Table 5, were prepared after blending the components and stored in polybags for subsequent melting. Glasses obtained were designated as BY1T4, BY2T3, BY3T2, BY1Z4, BY2Z3 and BY3Z2 in their tabulated order.

Sample ID	Li <sub>2</sub> O	Al <sub>2</sub> O <sub>3</sub>	Si <sub>2</sub> O	B <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	Y <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>
BY1T4	4.5	21.5	60	5	2	2	1	4
BY2T3	4.5	21.5	60	5	2	2	2	3
BY3T2	4.5	21.5	60	5	2	2	3	2

**Table no 4:** Composition of glasses containing TiO<sub>2</sub> as nucleating agent.

Sample ID	Li <sub>2</sub> O	Al <sub>2</sub> O <sub>3</sub>	Si <sub>2</sub> O	B <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	Y <sub>2</sub> O <sub>3</sub>	ZrO <sub>2</sub>
BY1Z4	4.5	21.5	60	5	2	2	1	4
BY2Z3	4.5	21.5	60	5	2	2	2	3
BY3Z2	4.5	21.5	60	5	2	2	3	2

**Table No 5:** Composition of glasses containing ZrO<sub>2</sub> as nucleating agent.

#### ***4.2: Batch melting, casting and annealing***

Batch glasses composition as in table 2, table 3, table 4 and table 5 were melted in Sillimanite crucible, in the temperature range of 1600-1650°C for removal of bubbles for 2h followed by temperature lowering down in the range of 1500-1550°C to enable casting on a preheated graphite mould at 250-300°C. Annealing of the casted glass was carried out in the range of 500-550°C with a soaking duration of 4h to remove internal thermal stress generated earlier while fast cooling of the melt. This was followed by cooling annealed glass in the furnace to prevent further build-up of thermal stresses.

#### ***4.3: Thermal analysis***

The base glasses were subjected to thermal analysis using Differential Scanning Calorimetry (DSC) (NETZSCH STA 449 C- JUPITER®) at different heating rates of 5, 10, 15 and 20°C/min up to the 1000-1100°C.

#### ***4.4: Ceramization of glass***

Glasses containing B<sub>2</sub>O<sub>3</sub> were ceramized to generate appropriate crystalline phases in the glass matrix. The samples were heat treated at different temperatures such as 820°C, 850°C, 880°C and 920°C at a heating rate of 3°C/min with variation in soaking duration such as 2h, 4h, 6h and 10h.

#### ***4.5: Density measurement***

Density of the glass and GC sample was measured by Archimedes' principle, wherein, the sample is weighed both in air and suspended in a liquid of known density. Due to buoyancy effect, sample displaces water which will be equal to the weight of the

sample. The difference in weight equals the weight of the displaced liquid. Since we know the density of the liquid,  $\rho_L$ , we can calculate the displaced volume using the product of mass and density of liquid. Dividing the weight of the sample in air,  $W$ , by the volume of liquid displaced then yields the density of the sample.

$$\text{Density} = \frac{\text{Weight in air} * \rho_L}{\text{weight in air} - \text{suspended weight}}$$

**4.6: Phase Identification** X-ray Diffraction data were recorded using X'pert Diffractometer (PAN Analytical- PW3040X00) with parameters as 15-70°, 3°/min) to recognize the developed phases in the glass-ceramic sample.

#### **4.7: Thermal Expansion Coefficient Measurement**

Measurement of thermal expansion co-efficient was done using NETZSCH- DIL 402C Dilatometer working on the conventional double push-rod method, as shown in Figure No 1, in the temperature range of 25-750°C with a heating rate of 3°C/min. Data is plotted between  $\Delta L/L_0$  versus temperature and slope at any point on the curve gives the value of linear thermal expansion coefficient.

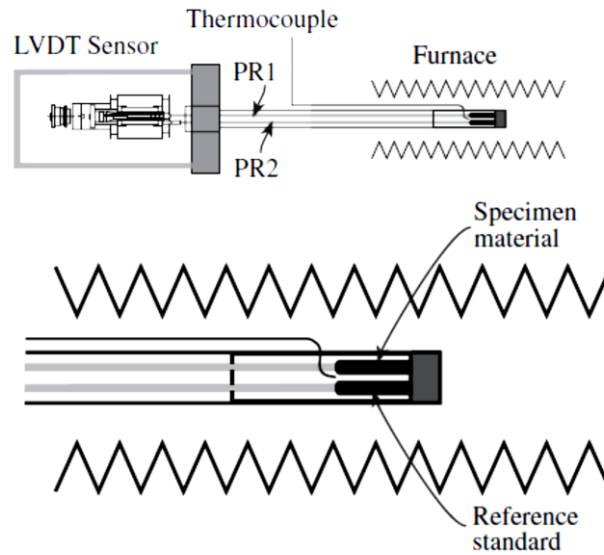
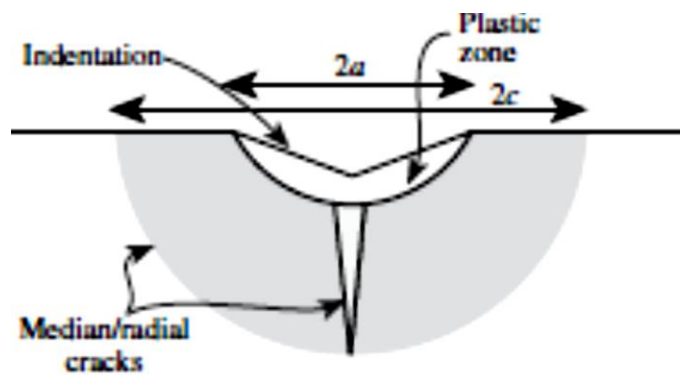


Figure No. 1: Schematic of double push-rod dilatometer. (from *C. Barry Carter & M. Grant Norton, Ceramic Material Science & Engineering, pp. 631, 2007*)

#### 4.8: Hardness testing

Figure No 2 shows the schematic of indentation on the ceramic sample. Vickers indentation tester **LEO Vickers Hardness Tester LV 700 (Model: LV-700, SER. NO.: FV7471 AND DATE: 11-2007)** was used for measuring the hardness of the ceramized sample. Indenter has square pyramidal shape. The diagonals of the Vickers indents were carefully measured using optical microscope and subsequently, the hardness was calculated using the standard equation for the Vickers geometry  $Hv = 1.8544 \frac{P}{d^2}$  .

Where  $H_v$  is the Vickers hardness number (VHN) in  $\text{Kg/mm}^2$ ,  $P$  is the normal load in Kg, and  $d$  is the average diagonal length of the indentation in mm.



**Figure No.2 : Indentation made on a ceramic sample. Observe the diagonals. (C. Barry Carter & M. Grant Norton, Ceramic Material Science & Engineering, pp. 300., 2007)**

## 5. RESULTS & DISCUSSION

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### **5.1: Physical Observation of base glass**

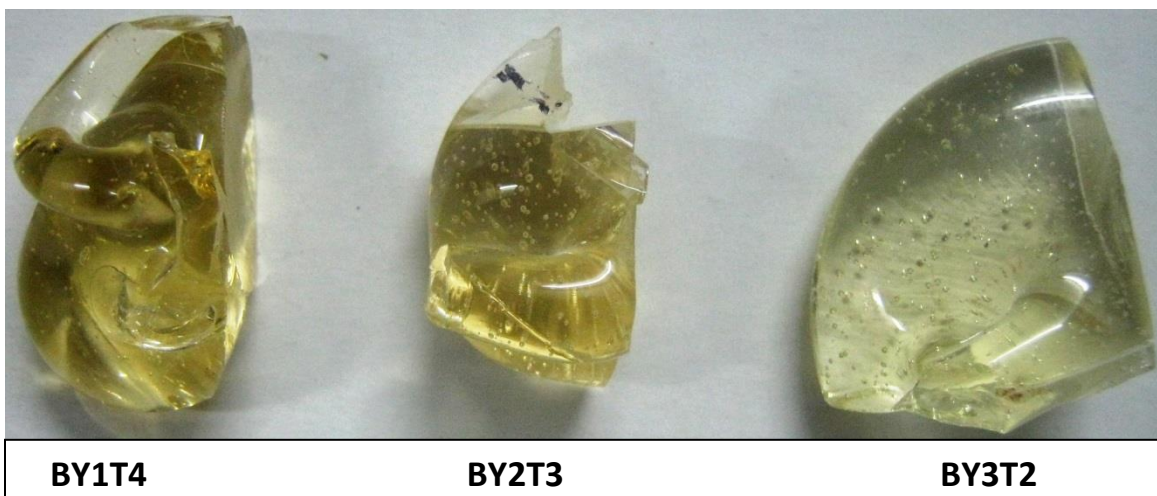
High viscosity has been observed on melting batch glass composition from table 2 and table 3. This has occurred due to high content of Silica ( $\text{SiO}_2$ ), i.e. 65 wt%, and Alumina ( $\text{Al}_2\text{O}_3$ ) i.e 21.5 wt%.

Now, it is known that viscosity of glass melt can be easily decreased by incorporating flux such as  $\text{Na}_2\text{O}$  (soda) and  $\text{PbO}$ . But, in this investigation  $\text{PbO}$  cannot be used due to its toxicity, whereas excessive use of alkali oxide shall lead to serious degradation in many properties specially TEC. Chemical durability of high alkali oxide containing glasses is very low, so, they can no longer be used for containers or GC cooktop panels. Another demerit is a high value of CTE of the glass matrix due to the increase in number of non-bridging oxygen in the glass network, which leads to degradation of TEC of the GC article. This is undesirable in the temperature range of application of cooktop panels.

Hence,  $\text{SiO}_2$  content was decreased by replacing 5wt % of silica with  $\text{B}_2\text{O}_3$ . High thermal shock resistant property of borosilicate glass is known, so it is expected that  $\text{B}_2\text{O}_3$  addition will lower the viscosity of the melt along with keeping the CTE of the glass matrix lower.

Figure No 3, shows the BY1T4, BY2T3 and BY3T2 glass, from left to right. Figure No 4, shows the BY2Z3 and BY3Z2 glass. Presence of titania in  $\text{Ti}^{+4}$  state in the base glass is responsible for the characteristic amber (yellowish-brown) color, as in Figure No. Fine bubbles have been observed, although  $\text{As}_2\text{O}_3$  was added as refining agent, in the base

glass due to the absence of intermittent stirring step during melting and higher melting temperature.



**Figure No 3:** Base glasses containing  $\text{TiO}_2$  as nucleating agent.

Bubbles were not observed for zirconia containing base glasses, however, there were unmelted  $\text{ZrO}_2$  present as cord, as is evident in Figure No 4.

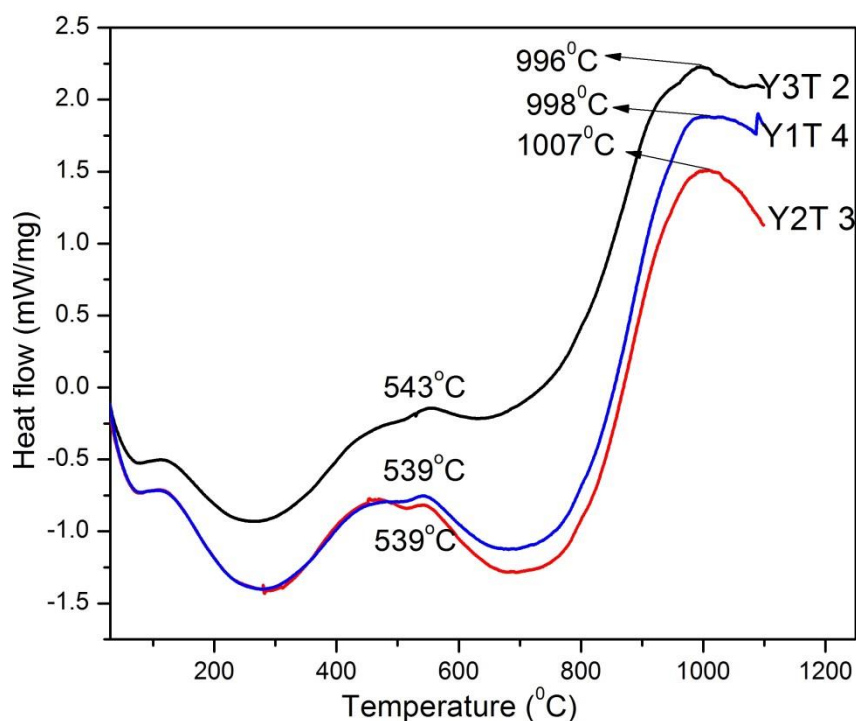


**Figure No 4:** Base glasses containing  $\text{ZrO}_2$  as nucleating agent



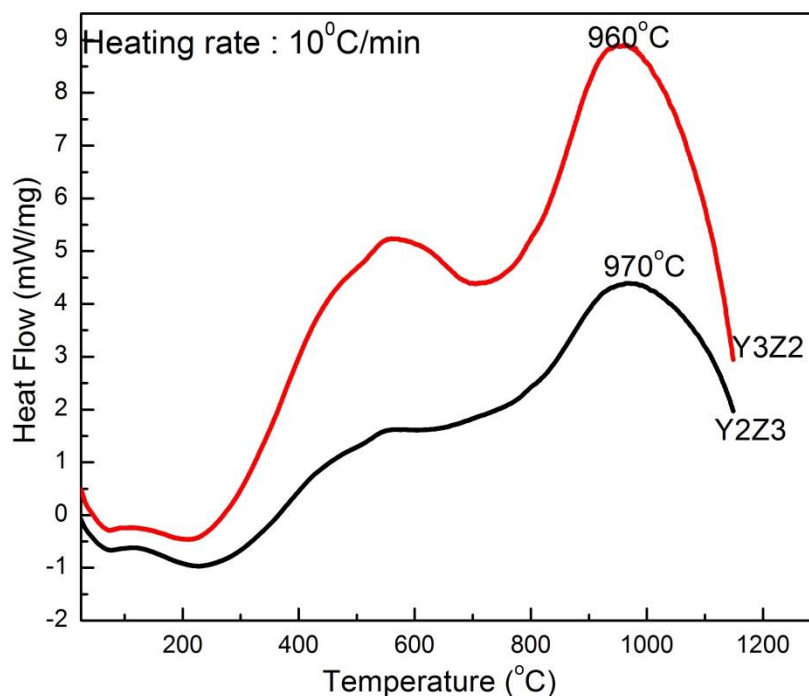
## 5.2: Differential Scanning Calorimetry analysis

From the DSC curve shown in Figure No 10, exothermic peaks are observed at 998°C, 1007°C and 996°C for Y1T4, Y2T3 and Y3T2 respectively at a heating rate of 10°C/min. These peaks roughly correspond to one of the phases in LAS GC such as  $\beta$ -quartz,  $\beta$ -Spodumene and  $\beta$ -eucryptite which shall be analyzed in Phase analysis section. Glass transition temperature ( $T_g$ ) have been observed at 539°C, 539°C and 543°C for Y1T4, Y2T3 and Y3T2 respectively. This increase in  $T_g$  is due to the  $Y_2O_3$  content increase in the composition of the base glass. However, effects of variation of  $Y_2O_3$  and  $TiO_2$  content on crystallization peak temperature ( $T_P$ ) have been mostly negligible most probably due to highly viscous nature of base glass.



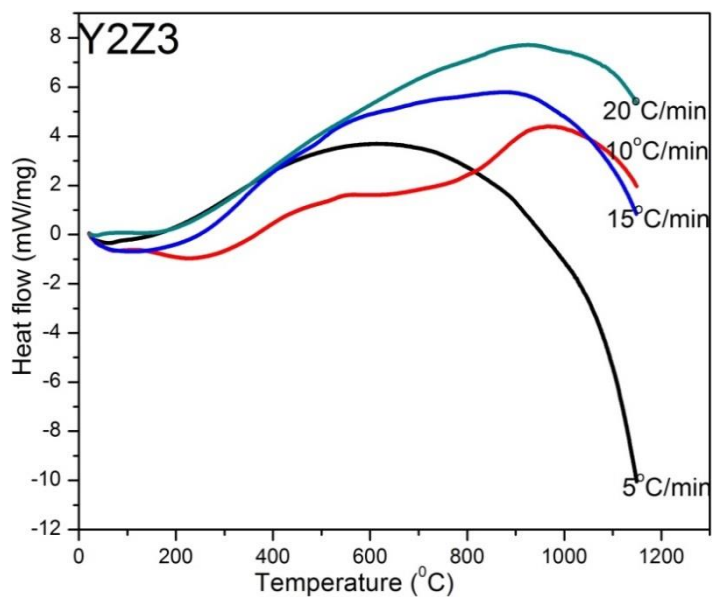
**Figure No.5:** DSC curve at heating rate of 10°C/min for a glass containing titania as nucleating agent.

DSC curve of yttria and zirconia containing glass at heating rate of  $10^{\circ}\text{C}/\text{min}$  has been depicted in Figure No 6. Exothermic peaks are evident at  $970^{\circ}\text{C}$  and  $960^{\circ}\text{C}$  for Y2Z3 and Y3Z2 glasses respectively.

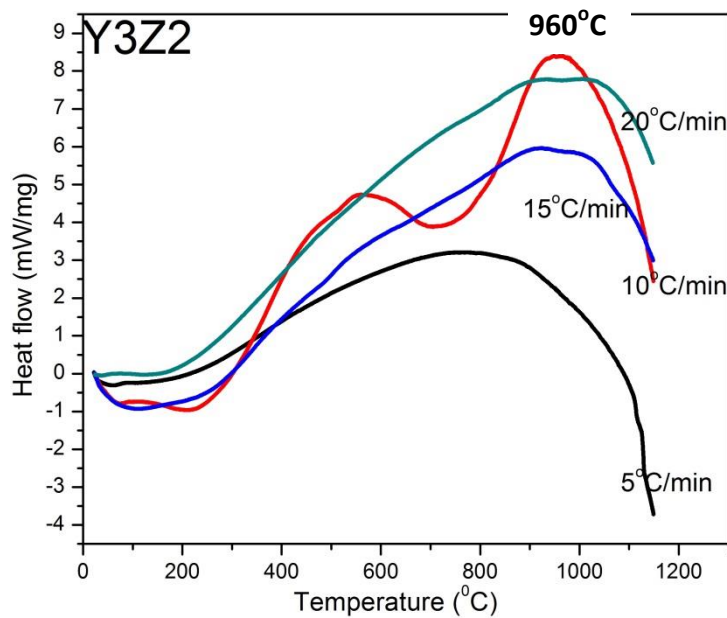


**Figure No.6:** DSC curve at heating rate of  $10^{\circ}\text{C}/\text{min}$  for a glass containing zirconia as nucleating agent.

Calculation of activation energy of a crystal phase and other kinetic parameters requires the value of peak temperature of crystallization at four different heating rates. Figure No 7 and Figure No 8, shows the DSC curve of Y2Z3 and Y3Z2 glasses carried out at different heating rate viz 5, 10, 15 and  $20^{\circ}\text{C}/\text{min}$ .  $T_p$ , however, could not be obtained from the curve owing to its irregular pattern.



**Figure No. 7:** DSC curve at different heating rates for Y2Z3 base glass.



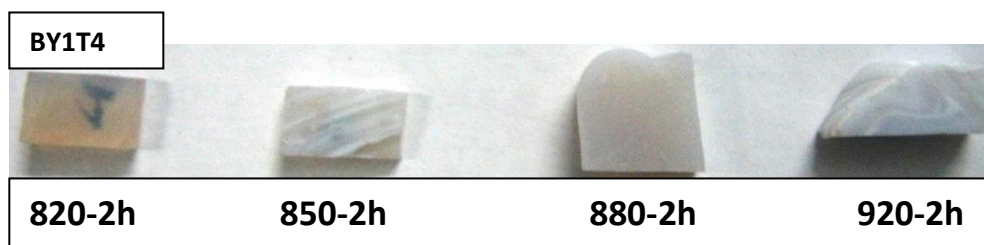
**Figure No. 8:** DSC curve at different heating rates for Y3Z2 base glass.

So, base glasses- Y1T4, Y2T3, Y3T2, Y2Z3 and Y3Z2, have been discarded due to their inhomogeneity. To facilitate homogeneity of melt glass by decreasing viscosity, SiO<sub>2</sub> has been replaced by B<sub>2</sub>O<sub>3</sub> in the base glass composition.

### 5.3: Ceramization of LAS glass

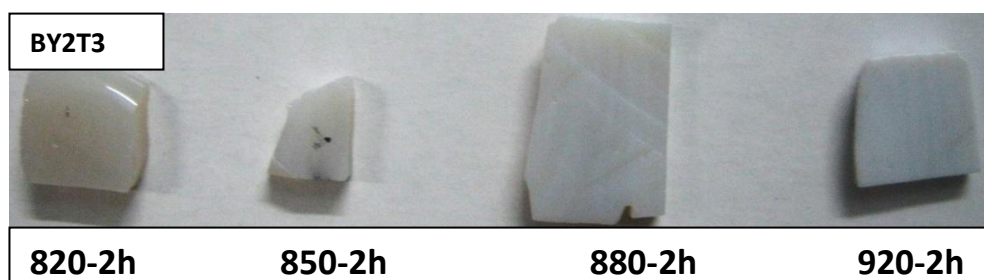
Ceramized glass sample are shown in figure no 9, figure no 10, figure no 11, figure no 12, and figure no 13.

It has been clearly observed that with the increase in ceramization temperature, base glass BY1T4 has lost its translucency after 880°C-2h, due to the increased crystal size which should have been larger than the wavelength of the visible light.



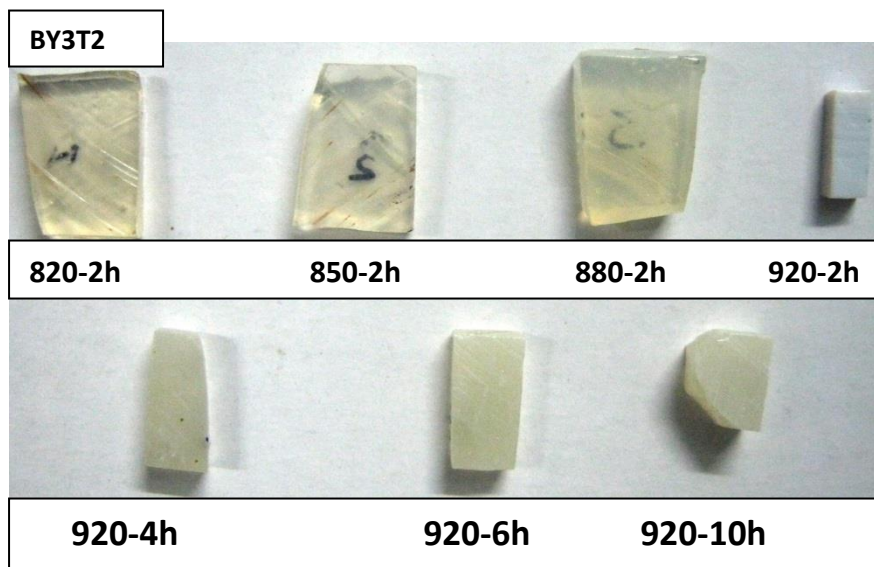
**Figure No 9: Glass ceramic samples of BY1T4 heat treated at different temperature.**

BY2T3 showed no translucency right from the start at 820-2h and has been opaque thereafter, as in Figure no 10.



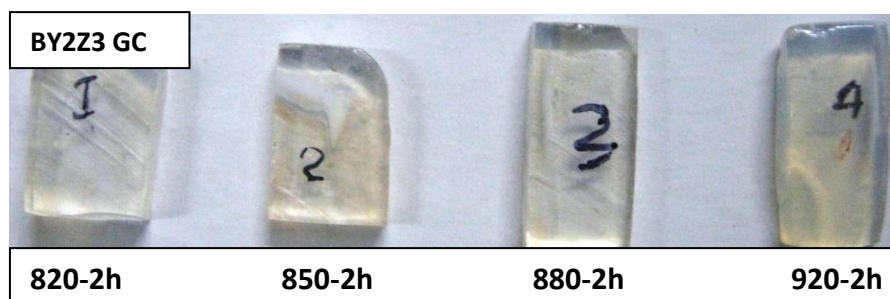
**Figure No 10: Glass ceramic samples of BY2T3 heat treated at different temperature.**

Highest content of yttria in BY3T2, which has a property to increase the rigidity of the glass network leading to increase in viscosity, has resulted in GC at 820-2h having translucency similar to the parent base glass. As in figure no 11, till 880-2h translucency has deteriorated; finally at 920-2h complete opaque GC is obtained and the same has been observed for GC ceramized for longer time.



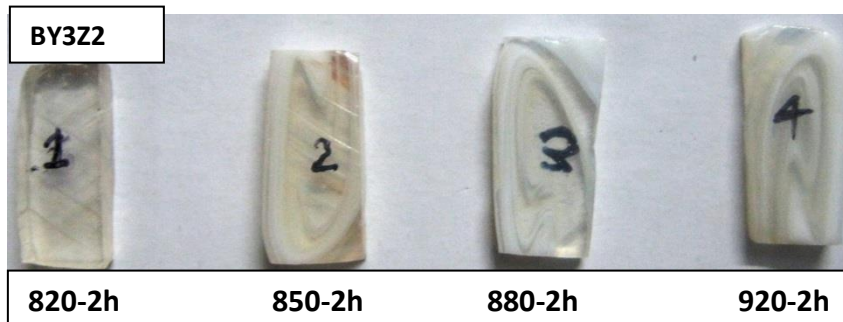
**Figure No 11:** Glass ceramic samples of BY3T2 heat treated at different temperature and time.

As shown in Figure No 12, BY2Z3 GCs were visibly transparent in patches. This is again due to inhomogeneity of the parent glass which had cords. So, only that region rich in  $ZrO_2$  content has undergone nucleation. This GC cannot be further investigated.



**Figure No 12:** Glass ceramic samples of BY2Z3 heat treated at different temperature.

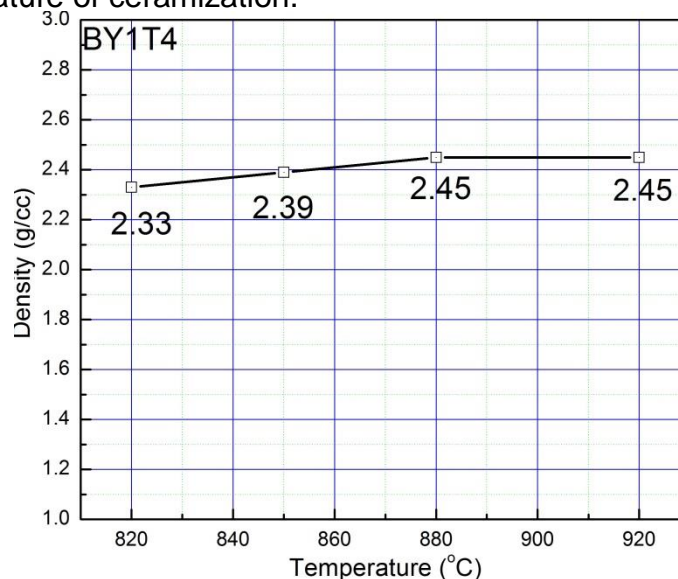
Similar to BY2Z3 GCs, BY3Z2 GCs also has patchy appearance in translucency along with gradient in the extent of crystallization, as in Figure No 13.



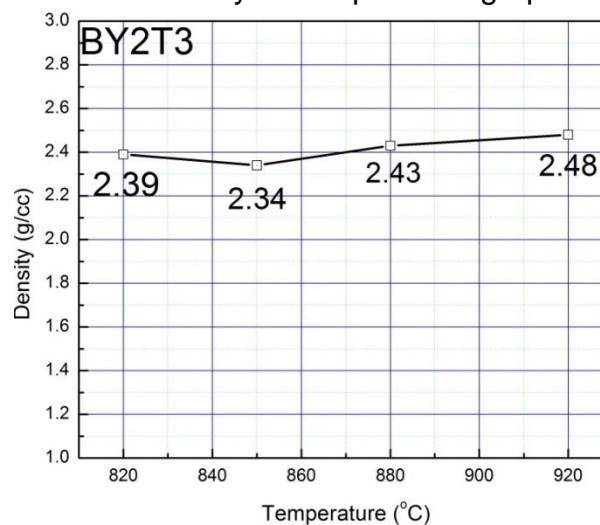
**Figure No 13:** Glass ceramic samples of BY3Z2 heat treated at different temperature.

#### 5.4: Bulk density

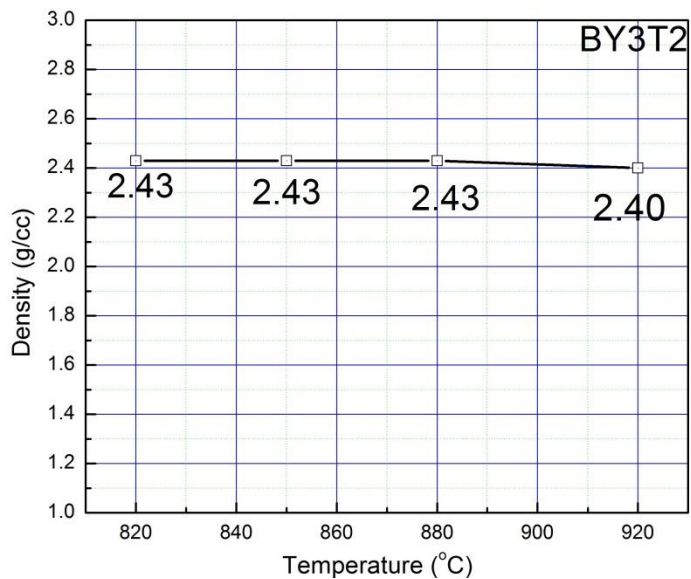
Figure No 14-17, shows the variation of bulk density of a glass ceramic sample with increase in temperature of ceramization.



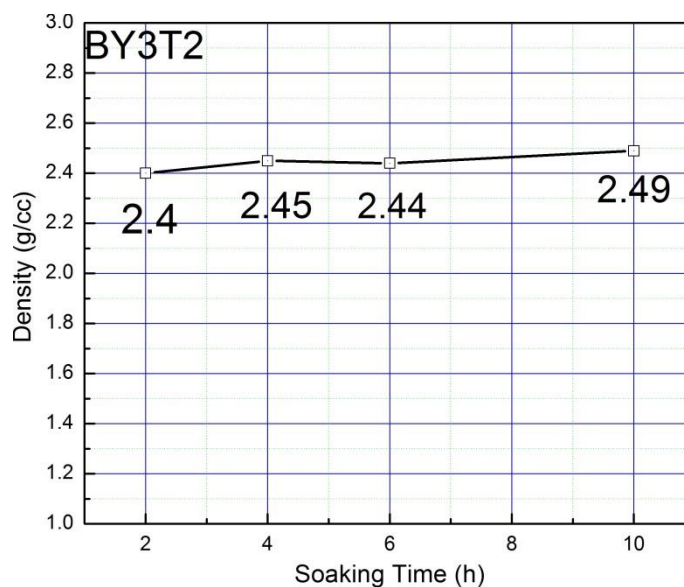
**Figure No. 14:** Bulk Density vs temperature graph of BY1T4 gc.



**Figure No 15:** Bulk Density vs temperature graph of BY2T3 gc.



**Figure No 16:** Bulk Density vs temperature graph of BY3T2 gc.



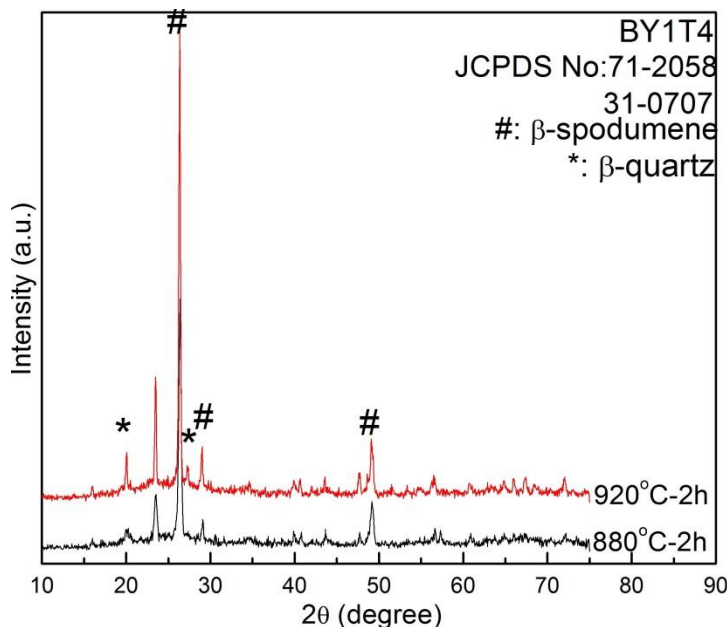
**Figure No 17:** Bulk Density vs time graph of BY3T2 gc.

It should be mentioned, here, that soaking time of ceramization has been 2h. For glass ceramic sample BY1T4, as in figure no , it can be seen that bulk density has increased from 2.33g/cc at 820°C to 2.45g/cc at 880°C.

This must be due to temperature activated diffusion induced transfer of material for the crystallisation and growth alongwith filling up of bubbles left in the base glass. Further increase in temperature did not lead to any variation in density. Similar result has been observed for BY2T3 glass ceramic, as shown in figure no 15. Bulk density at 820° has been found to be 2.39g/cc, which has increased with temperature of ceramization to 2.48g/cc at 920°C. Figure no 16, depicts that at 880°C, bulk density of BY3T2 is 2.43g/cc which hasn't changed till 880°C. Increasing the soaking time of crystallisation at 920° has also increased the density from 2.4g/cc (2h) to 2.49g/cc (10h), as shown in figure no 17.

### 5.5 : Phase analysis

Phases developed in BY1T4 GC when heat treated at 920°C and 880°C for 2h, has been identified as  $\beta$ - Spodumene (major phase) and  $\beta$ -quartz (minor phase) according to JCPDS file number 71-2058 and 31-0707 respectively, as the same is shown in figure no 18.  $\beta$ -Spodumene peaks have become more prominent as the ceramization

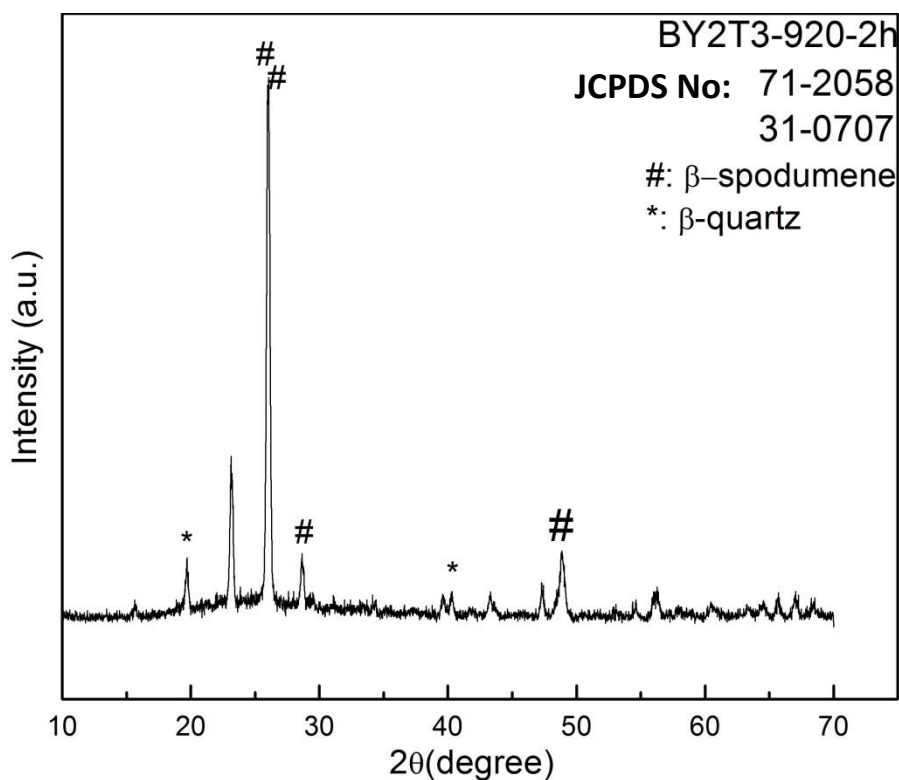


**Figure No 18:** XRD plot of BY1T4 GC heat treated at 920 and 880°C 2h



temperature has been increased. However, some peak could not be identified.

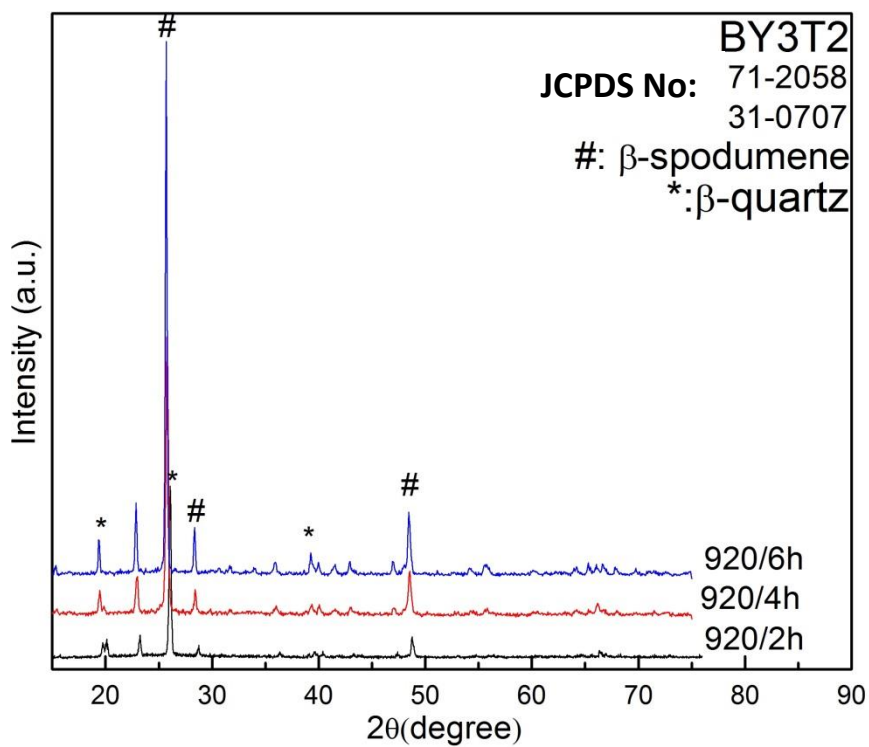
Similar results has been observed for BY2T3-920-2h GC as shown in figure no 19 but, peak at  $26.9^\circ$  is less intense than in BY1T4 GC at  $920^\circ\text{C}$  due to difficulty in nucleation crystallisation of  $\beta$ -spodumene owing to lower titania content and higher yittria content.



**Figure No 19:** XRD plot of BY2T3 GC heat treated at 920-2h .

BY3T2 GCs showed an increase in the crystalline phase i.e.  $\beta$ -Spodumene content as can be observed from figure No 20, by noting the increase in intensity of the peak at  $\sim 26.9^\circ$ . Other peaks near  $30^\circ$  and  $50^\circ$  have also become prominent with the increase in the ceramization time from 2h to 6h at  $920^\circ\text{C}$ . As the ceramization time has increased

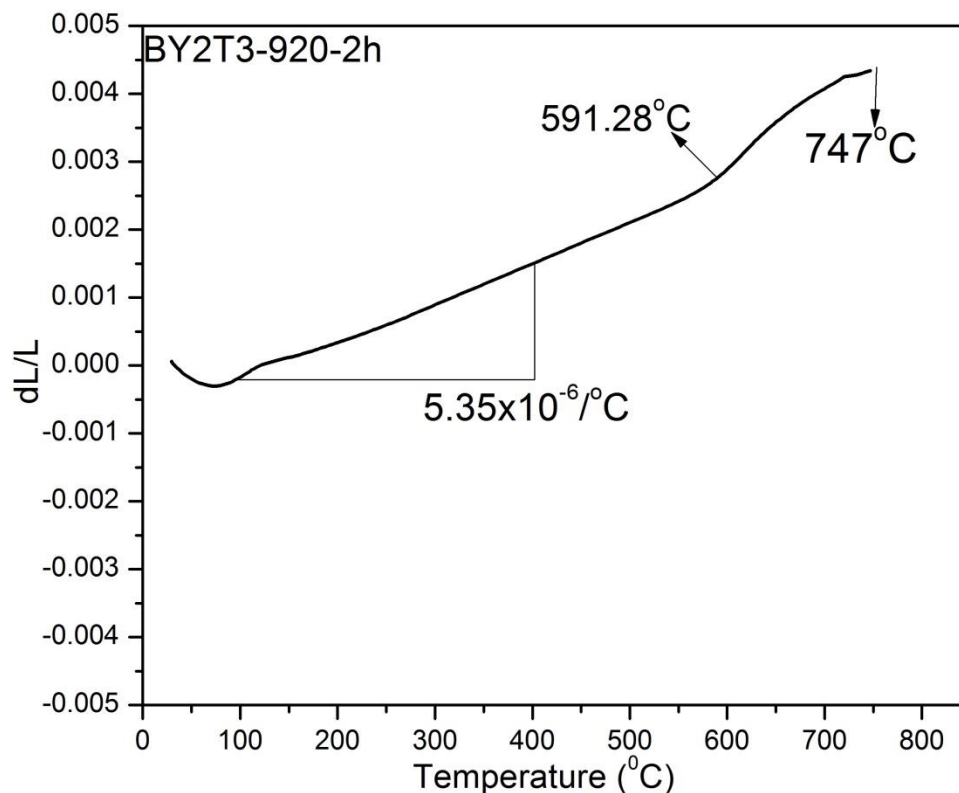
mass transfer from glassy matrix to the crystalline phase has also increased, which would result in larger crystallite size and higher crystalline phase in the GC.



**Figure No 20:** XRD plot of BY3T2 GC heat treated at 920 for 2, 4 and 6h.

### 5.6: Dilatometry analysis

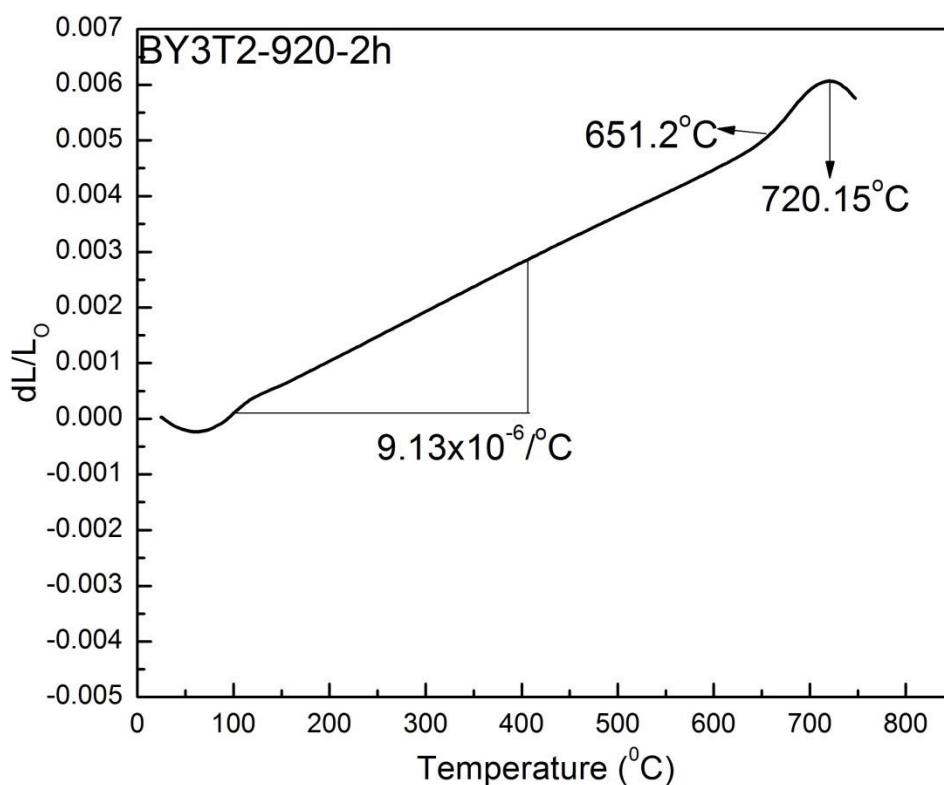
From the Figure No 21, for BY2T3-920-2h GC (dilatometric softening temperature)  $T_s$  and  $T_g$  has occurred at  $747^\circ\text{C}$  and  $\sim 591^\circ\text{C}$  respectively. In the temperature range 100-400 $^\circ\text{C}$ , TEC has been calculated to be  $5.35 \times 10^{-6}/^\circ\text{C}$ .



**Figure No 21:**  $dL/L_0$  versus Temperature curve of BY2T3 GC ceramized at  $920^\circ\text{C}$ -2h.

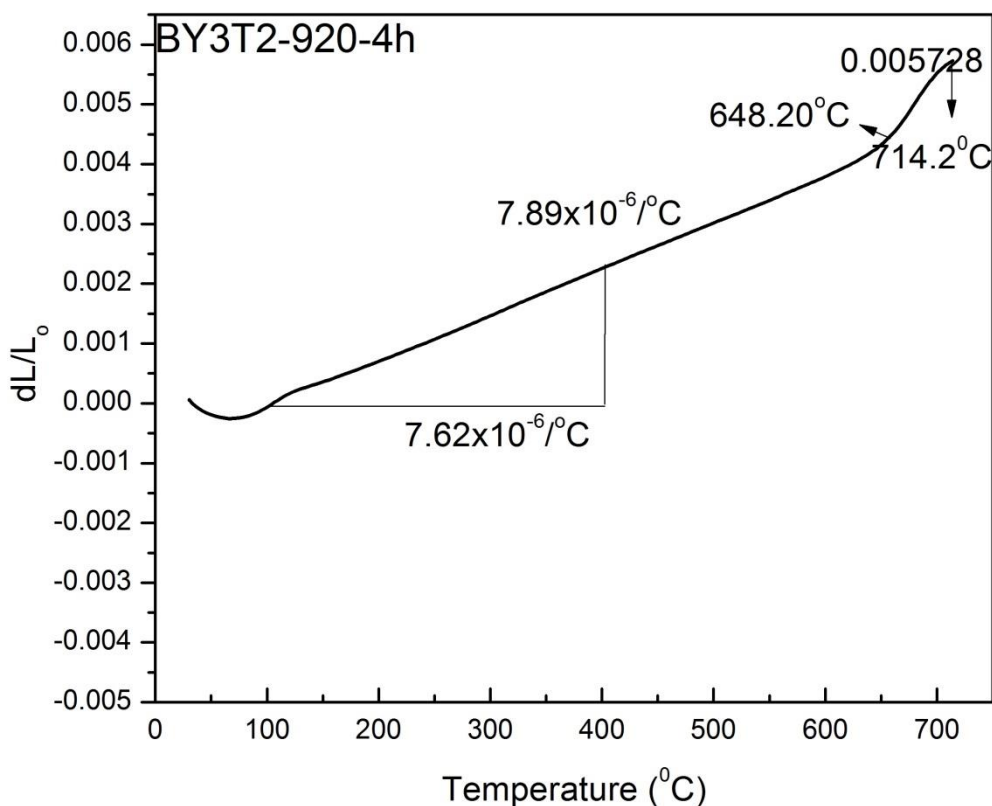
$\beta$ -spodumene developed in the glass matrix at 920-2h is responsible for the low CTE of the LAS GC, as shown in figure no 22.  $^{12}\beta$ -spodumene i.e.  $\text{LiAlSi}_2\text{O}_6$  is a derivative of  $\beta$ -quartz in which Si and Al atoms are distributed randomly in the tetrahedra. Here, Li ions has four coordination and stuffed into interstitial positions. These are randomly distributed among three equivalent sites. The Li tetrahedra is irregular and shares two edges with two Si, Al tetrahedra. As Si,Al-Li distance is short, so a strong cation

repulsion is produced which leads to expansion in a- and b- axes. On the other hand, c-axis which depends on Li-O distance contracts, because increasing Si,Al-Li distance decreases the shared edges which decreases the Li-O bond. This results into overall reduction in TEC of the  $\beta$ -spodumene containing GC. BY3T2-920-2h GC has comparatively lower value of TEC i.e.  $9.13 \times 10^{-6} / ^\circ\text{C}$  than BY2T3-920-2h GC, as shown in Figure no 21, which is due to relatively higher content of  $\text{Y}_2\text{O}_3$  which increases the viscosity of the glass matrix thereby obstructing the mass transport required for crystallisation of  $\beta$ -spodumene.



**Figure No 22:**  $dL/L_0$  versus Temperature curve of BY3T2 GC ceramized at  $920^\circ\text{C}$ -2h.

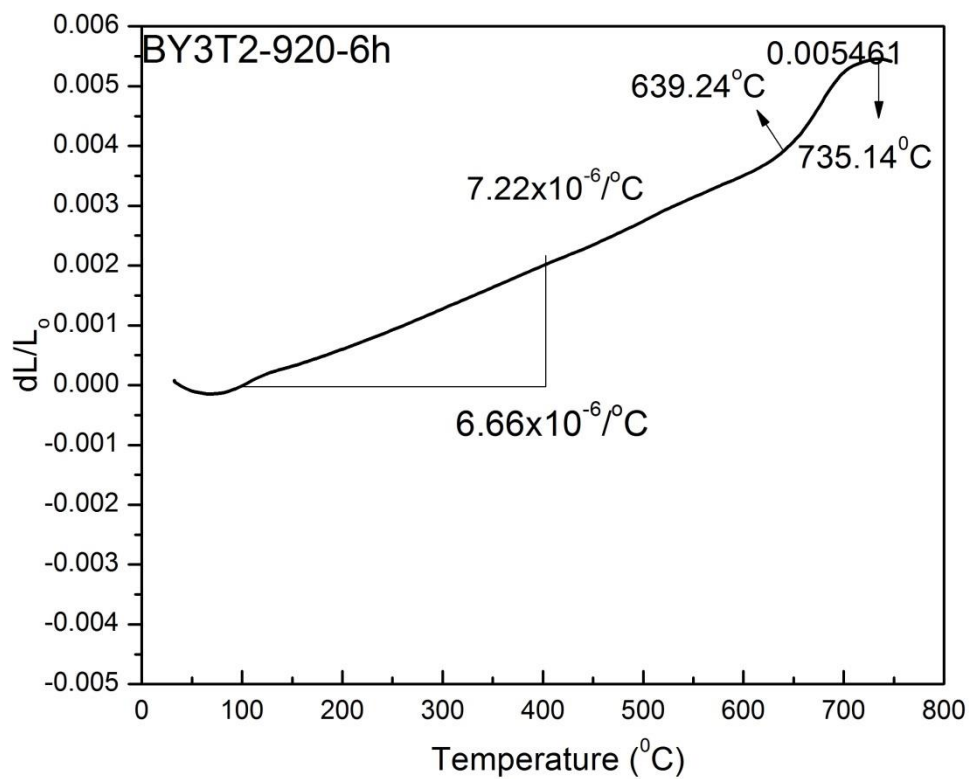
To achieve lower TEC value of BY3T2 GC soaking time during crystallization has been prolonged to 4h and 6h. As a result, Figure No 23, shows that the TEC value of BY3T2-920°C-4h GC in temperature range of 100-400°C has decreased to  $7.62 \times 10^{-6} / ^\circ\text{C}$  due to higher content of  $\beta$ -Spodumene phase evident from increased peak intensity.



**Figure No 23:**  $dL/L_0$  versus Temperature curve of BY3T2 GC ceramized at 920°C-4h.

As expected TEC of BY3T2-920-6h GC has further, although slightly, dipped to  $6.66 \times 10^{-6} / ^\circ\text{C}$  in the temperature range of 100-400°C, as shown in figure no 24. Further prolongation of soking time of ceramization is not required. So, the minimum value of

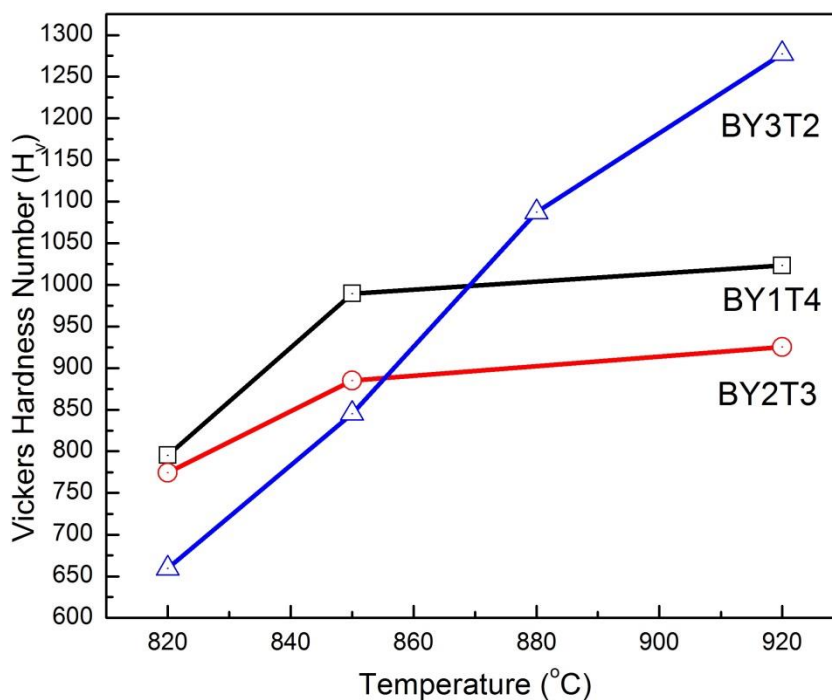
TEC achieved for BY3T2 GC is  $6.66 \times 10^{-6} / ^\circ\text{C}$  which is near to that observed for BY2T3-920-2h GC ( $5.35 \times 10^{-6} / ^\circ\text{C}$ ).



**Figure No 24:**  $dL/L_0$  versus Temperature curve of BY3T2 GC ceramized at 920°C-6h.

### 5.7: Vickers Hardness Analysis

Figure no 25 shows the graph obtained after plotting Vickers hardness of the GC surface versus different temperature of ceramization. It has been observed that as the temperature of



**Figure No 25:** Vickers Hardness of GC surface vs temperature of ceramization

ceramization has increased, Vickers hardness of the GC surface has also increased. This is due to the corresponding increase in the  $\beta$ -Spodumene phase in the glassy matrix of the GC.

Observed Vickers Hardness values at 0.5Kgf with 2s dwelling time has been tabulated in table no 6. Highest hardness has been observed for BY3T2 GC heat treated at 920 for 2h.

<b>Sample ID</b>	<b>TEMPERATURE (°C) &amp; Time</b>	<b>Vickers's Hardness Number (H<sub>v</sub>) at 0.5Kgf for 2s</b>
<b>BY1T4</b>	820-2h	795.4
	850-2h	989.5
	920-2h	1023.2
<b>BY2T3</b>	820-2h	774.5
	850-2h	885
	920-2h	925.5
<b>BY3T2</b>	820-2h	659.3
	850-2h	845.9
	880-2h	1087.3
	920-2h	1277.3

**Table No 6:** Vickers Hardness of GC measured at 0.5Kgf with a dwelling time of 2s.



## 6. CONCLUSION

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LAS GCs containing nucleating agent as titania in the range of 2-4 wt% in combination with 1-3 wt%  $Y_2O_3$  has been successfully developed.  $ZrO_2$  containing LAS GC could not be developed due to the inhomogeneity of base glass. It can be concluded that addition of 4 wt%  $TiO_2$  combined with 1%  $Y_2O_3$  in glass composition leads to effective crystallization of  $\beta$ -Spodumene phase in the glassy matrix at  $920^\circ C$ -2h. However, when  $Y_2O_3$  content was increased to 3 wt% combined with 2 wt%  $TiO_2$ , crystallization of  $\beta$ -Spodumene has been observed to get suppressed as authenticated from the phase analysis of BY3T2 GC. Bulk density of the LAS GC has been observed to increase with temperature and time of ceramization of base glass. It has been observed to be highest of 2.49g/cc for BY3T2 GC, containing 3 wt%  $Y_2O_3$  combined with 2 wt%  $TiO_2$ , ceramized at  $920^\circ C$  for 10h. BY2T3 GC, containing 2 wt%  $Y_2O_3$  combined with 3 wt%  $TiO_2$ , obtained after ceramization of base glass at  $920^\circ C$ -2h has been found to have  $\beta$ -Spodumene as the major crystalline phase and has lowest TEC of  $5.35 \times 10^{-6}/^\circ C$ . TEC of BY3T2 GC can be lowered by prolonging the ceramization time of base glass at  $920^\circ C$  to 6h and TEC has been observed to  $6.66 \times 10^{-6}/^\circ C$ . Vickers Hardness of the LAS GC samples has been observed to monotonically increase with an increase in temperature of ceramization of the base glass from  $820^\circ C$  to  $920^\circ C$ . Highest Vickers Hardness of 1277.3 VHN has been observed for BY3T2 GC ceramized at  $920^\circ C$  for 2h, whereas at the same temperature BY1T4 and BY2T3 have hardness value of 1023.2 VHN and 925.5 VHN respectively.

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