

# Ultra-Low Thermal Expansion Co-efficient of Lithium Aluminosilicate Glass–ceramics

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**Abstract.** Aluminosilicate (LAS) glass-ceramics (GC) finds use in many high-tech applications, e.g., motor pistons and telescope mirrors etc. due to its ultra-low thermal expansion coefficient (ULTEC). The crystallization of lithium aluminosilicate glass ceramics was investigated by different techniques including differential thermal analysis and X-ray diffraction.  $\beta$ -quartz solid solution phase in the  $\text{Li}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2\text{-P}_2\text{O}_5$  glass system has been precipitated by controlled heat-treatment of the parent glass prepared by melt-quench technique which has been confirmed by XRD analysis of heat-treated material.

**Keywords:** Lithium Aluminosilicate glasses, DTA, XRD.

## INTRODUCTION

Aluminosilicate Lithium (LAS) glass-ceramics (GCs) have gained considerable commercial attention because of their unique combination of properties, such as, very low thermal expansion, transparency, high chemical durability, and strength<sup>1</sup>. Few widespread applications are telescope mirror blanks, ring-laser gyroscopes, optically stable platforms, and cooktop panels<sup>2</sup>. The most important commercial transparent glass-ceramics capitalize on their superior thermal properties, particularly ultra-low thermal expansion coupled with high thermal stability and thermal shock resistance<sup>3</sup>. The LAS-type glass-ceramics, the “ $\beta$ -quartz” (or “ $\beta$ -eucryptite”) and “ $\beta$ -spodumene” glass-ceramics, are characterized by very low thermal expansion. These glass-ceramics are so called because the main crystalline phase developed is “ $\beta$ -quartz” and “ $\beta$ -spodumene”. LAS-type glass-ceramics are  $\beta$ -eucryptite ( $\text{Li}_2\text{O-Al}_2\text{O}_3\text{-2SiO}_2$ ) /  $\beta$ -quartz ( $\text{SiO}_2$ ) solid solutions and  $\beta$ -spodumene ( $\text{Li}_2\text{O-Al}_2\text{O}_3\text{-4SiO}_2$ ) / keatite ( $\text{SiO}_2$ ) respectively. The peculiar ultra-low thermal expansion property is due to good matching of the volume fraction of the negative-expansion  $\beta$ -quartz solid solution (ss) crystals (~70 vol%) and the positive-expansion residual glass<sup>4-5</sup>. The properties of multiphase systems depend on the properties of the individual phases, the amount of each phase present, and the microstructure. Temperature and time of heat-treatment largely control crystal volume fraction, morphologies of crystals etc. that in turn determine thermal expansion, mechanical and other properties of the material<sup>6</sup>. Crystallization kinetics of the LAS system has been studied extensively by the researchers<sup>7,8</sup>. Researchers suggested that a three-dimensional (3D) diffusion-controlled reaction mechanism governs the crystallization process. Researchers illustrated how and why the properties of a glass-ceramic are determined by both the microstructure and the compositions of the phases present<sup>9,10</sup>. The ability to control both of these parameters through controlled heat treatments has made glass-ceramic technology an important commercial process<sup>11</sup>. Hu<sup>12,13</sup> and co-workers studied the expansion behavior of LAS glass-ceramics with different quantity of various additives.

## EXPERIMENTAL

The glass was prepared from high-purity chemicals of Quartz ( $\text{SiO}_2$ ) (99.8%, Sipur Al Bremtheler Quartzitwerk, Uisingen, Germany), Aluminum oxide hydrate [ $\text{Al}(\text{OH})_3$ ] (CHP-340S, Sumito Chemical Company, Japan), Aluminum orthophosphate ( $\text{AlPO}_4$ ) (Chemische Fabrik Budenheim KG, Budenheim, Germany), Lithium carbonate ( $\text{Li}_2\text{CO}_3$ ) (Merck KGaA, Darmstadt, Germany), Sodium nitrate ( $\text{NaNO}_3$ ) (Riedel-de Haen, Germany), Magnesium hydroxide carbonate [ $\text{MgCO}_3\cdot\text{Mg}(\text{OH})_2$ ] (Merck KGaA, Darmstadt, Germany), Titanium oxide ( $\text{TiO}_2$ ) (99.3%, Merck KGaA, Darmstadt, Germany), Zirconia ( $\text{ZrO}_2$ ) (Grade TZ – 0, TOSOH, Tokyo, Japan), Zinc oxide ( $\text{ZnO}$ ) (Merck KGaA, Darmstadt, Germany), Arsenic tri-oxide ( $\text{As}_2\text{O}_3$ ) (Fluka production GmbH, Buchs, Switzerland), Potassium nitrate ( $\text{KNO}_3$ ) (Merck KGaA, Darmstadt, Germany) and Aluminum nitrate 9-hydrate [ $\text{Al}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ ] (Riedel-de Haen, Seelze, Germany) by the conventional melt-quench technique. The glass batch was mixed thoroughly by a mixer (EIRICH R08, Hardheim, Germany) and was melted in an oxide dispersed strengthened (ODS) platinum crucible in an electric furnace at 1600 °C for 4-6 h in air with intermittent stirring, employing a platinum stirrer. The glass melt was poured onto a preheated iron mold (heated to 1000 °C), followed by annealing at 675 °C for 2 h. The as-prepared glass block was shaped into desired dimensions by cutting and optically polished to carry out heat-treatment as well as various characterization experiments. The glass block was heat-treated at 695 °C for 1.5 h for nucleation and crystallized at 820 °C for 1.5 h.

DTA of the precursor glass powder was carried out at temperatures up to 1100 °C at the rate of 10 °C/min with a NETZSCH instrument (Model STA 449 C, NETZSCH-Gerätebau GmbH, Germany). Co-efficient of thermal expansion (CTE) of the glass-ceramic was evaluated using a horizontal dilatometer (Model DIL 402 C, NETZSCH-Gerätebau GmbH, Selb, Germany) with temperature range of -100 to 400 °C and accuracy  $\pm 0.01 \times 10^{-6} / \text{K}$ .

XRD data were recorded using an Xpert-Pro MPD diffractometer (PANalytical, Almelo, The Netherlands) with the Anchor Scan Parameters wavelength  $\text{CuK}\alpha = 1.5406 \text{ \AA}$  at 25 °C, having a source power of 40 kV and 30 mA, in order to identify the developed crystalline phases of the glass-ceramics.

## RESULTS AND DISCUSSION

In order to obtain information on crystallization behavior, DTA analysis of base glass powder was carried out. From the DTA scan of the precursor glass (Fig. 1), it can be seen that the first crystal phase forms at nearly above 730 °C, which is apparent from the large exothermic peak. The glass transition ( $T_g$ ) temperature is found to be around 570 °C, which is evident from the first exothermic peak and subsequent slope change of the curve in the DTA scan. In the DTA diagram, two distinct exothermic peaks are identified at temperatures 730 °C and 890 °C. These exothermic peaks in the DTA trace are characteristics of nucleation (730 °C) and evolution of  $\beta$ -quartz (ss) (890 °C).

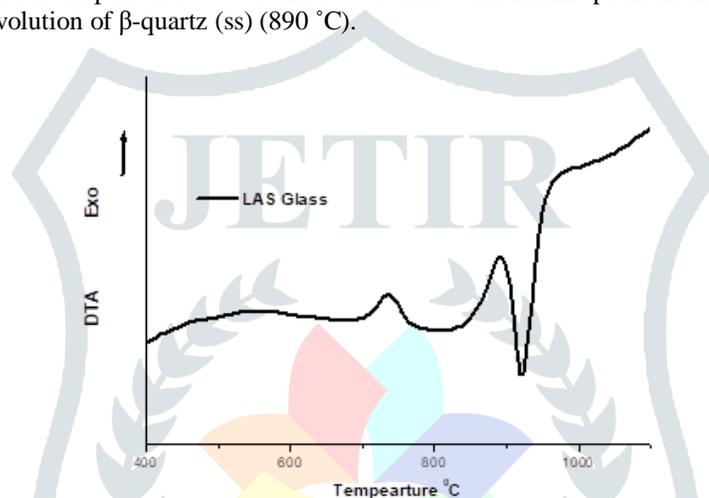


Figure 1. DTA thermogram of lithium aluminosilicate glass powder

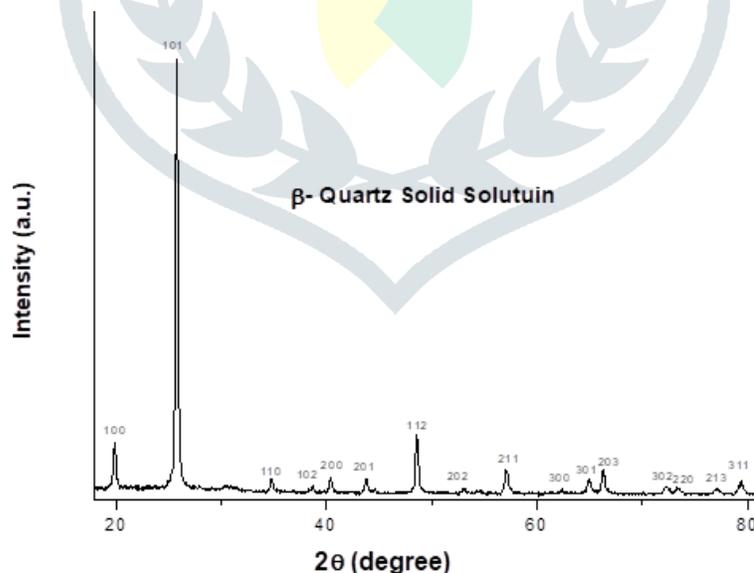


Figure 2. XRD pattern of lithium aluminosilicate glass-ceramics

X-Ray diffractions study was carried out to determine phase assemblage in the heat-treated samples of LAS GCs. XRD analysis of the heat-treated GCs revealed presence of only virgilite phase (Fig.2). The term virgilite is not used in the literature, instead  $\beta$ -quartz solid solution (ss) is used. Diffraction pattern was matched with the JCPDS card file no. 31-0707 which is due to the  $\beta$ -quartz (ss) i.e. Virgilite,  $\text{Li}^+$  and  $\text{Al}^{3+}$  stuffed disordered  $\beta$ -quartz hexagonal structure of stoichiometry close to  $\text{Li}_x\text{Al}_x\text{Si}_{3-x}\text{O}_6$ . This finding is in good agreement with the observations of the previous researchers<sup>6,7</sup>. Closer observation of Fig. 2 suggests that the highest intensity peak as noticed in the  $2\theta$  of 25.79° is due to the diffraction from the (101) plane of  $\beta$ -quartz (ss).

Other intense peaks observed are due to the diffraction from other planes of  $\beta$ -quartz (ss) crystal that are indicated in Fig. 2. Interestingly, no other crystalline phase is observed in the heat-treated GCs. Hence, it becomes easy to establish that the property of the GC is solely governed by the  $\beta$ -quartz (ss) crystal and the residual glass. From the full width at half maximum (FWHM) of the intense diffraction peak of  $\beta$ -quartz (ss), the average crystallite size (diameter,  $t$ ) is calculated by using Scherrer's formula<sup>14</sup>.

$$t = \frac{0.9\lambda}{\beta \cos\theta}$$

where  $\lambda$  is the wavelength of X-ray radiation ( $\text{CuK}\alpha = 1.5406 \text{ \AA}$ ) and  $\beta$  is the full-width at half-maximum (FWHM) of the peak at  $2\theta$ . The average crystallite size was estimated as  $\sim 35 \text{ nm}$ . These small sizes of the crystallites are responsible for its very high transparency and mechanical properties.

## CONCLUSIONS

The lithium aluminosilicate glass-ceramics and various properties of the material are investigated. Two exothermic peaks in the DTA trace are observed which are characteristics of nucleation at  $730 \text{ }^\circ\text{C}$  and evolution of  $\beta$ -quartz (ss) at  $890 \text{ }^\circ\text{C}$ , whereas, glass transition temperature was detected as  $570 \text{ }^\circ\text{C}$ . XRD analysis of the glass-ceramics confirmed the presence of  $\beta$ -quartz (ss) crystals in large quantity. Presence of other phases was not observed in the heat-treated glass-ceramics.

## REFERENCES

1. G. H. Beall, "Design and Properties of Glass-Ceramics," *Annu. Rev. Mater. Sci.*, 22, 91–119 (1992).
2. A. Jacobsen and T. Marx, "Applications of the Glass-Ceramic Zerodur", pp. 198–211 in *Low Thermal Expansion Glass-Ceramics*. Edited by H. Bach. Springer-Verlag, Berlin, Germany, 1995.
3. G. H. Beall and L. R. Pinckney, "Nanophase Glass-Ceramics," *J. Am. Ceram. Soc.*, 82 [1] 5–16 (1999).
4. L. Arnault, M. Gerland, and A. Rivi'ere, "Microstructural Study of Two LAS-type Glass-ceramics and Their Parent Glass", *J. MAT. SC.*, 35, 2331 – 45 (2000).
5. U. Schiffner and W. Pannhorst, "Nucleation in a Precursor for a  $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$  Glass-Ceramic, Part I: Nucleation Kinetics", *Glastech. Ber.*, 60 [6], 211–21 (1987).
6. J. M. Jewell, M. S. Spress, R. L. Ortolano, and J. E. Shelby, "Effect of Heat-Treatment Temperature on the Properties of a Lithium Aluminosilicate Glass", *J. Am. Ceram. Soc.*, 74 [1], 92–7 (1991).
7. L. Barbieri, C. Leonelli, T. Manfredini, C. Siligardi, A. B. Corradi, P. Mustarelli, and C. Tomasi, "Nucleation and Crystallization of a Lithium Aluminosilicate Glass", *J. Am. Ceram. Soc.*, 80 [12] 3077–83 (1997).
8. B. Karmakar, P. Kundu, S. Jana, and R. N. Dwivedi, "Crystallization Kinetics and Mechanism of Low-Expansion Lithium Aluminosilicate Glass-Ceramics by Dilatometry", *J. Am. Ceram. Soc.*, 85 [10] 2572–4 (2002).
9. P.W. McMillian, *Glass-Ceramics*, 2d ed. Academic Press, New York, 1978. Holland Press, New York, 1984.
10. G. H. Beall and D. A. Duke, "Glass-Ceramic Technology", pp. 404-44 in *Glass Science and Technology*, Vol. I, Glass Forming Systems. Edited by D. R. Uhlmann and N. J. Kreidl, Academic Press, New York, 1983.
11. G. H. Beall and R. C. Damon, "Glass-Ceramics", pp. 21-35 in *Encyclopedia of Physical Sciences and Technology*, Vol. 6. Academic Press, New York, 1987.
12. A.-M. Hu, M. Li and D.-L. Mao, "Crystallization of Spodumene-Diopside in the LAS Glass ceramics with CaO and MgO Addition", *J. Therm. Anal. Calorimetry*, 90[1], 185–9 (2007).
13. A. M. Hu, M. Li, and D. L. Mao, "Growth Behavior, Morphology and Properties of Lithium Aluminosilicate Glass Ceramics with Different Amount of CaO, MgO and TiO<sub>2</sub> Additive", *Ceram. Inter.*, 34, 1393–7 (2008).
14. B. D. Cullity, *Elements of X-Ray Diffraction*, 2nd edition, pp. 101–2. Addison-Wesley Publishing Co., London, 1978.