Study of Lithium Disilicate Based Nano Glass Ceramics Containing $P_2O_5$

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Abstract
Multi component lithium disilicate based glasses containing $P_2O_5$ have been synthesized by conventional melt quenching technique. The replacement of $(Li_2O + SiO_2)$ by $P_2O_5$ and its nucleating effect has been discussed. Structural features of glasses were evaluated by differential thermal analysis (DTA), Fourier transform infrared (FTIR) and Raman spectroscopy. The glass samples have been converted into glass ceramics by following three stage heat treatment schedules. X-ray diffraction analysis (XRD), field emission scanning electron microscopy (FESEM), high angle annular dark field imaging (HAADF), energy dispersive X-ray analysis (EDX) and high resolution transmission electron microscopy (HR-TEM) has been carried out for the glass ceramics. Vickers microhardness ($H_v$) and Vickers indentation fracture toughness ($K_{IC}$) of all the glass ceramics have been measured. UV–Visible spectroscopy study has been carried out for glass ceramics to investigate the optical properties. The glass ceramic with 1.5 mol % $P_2O_5$ has the highest transmittance. Glass ceramics with $P_2O_5 \geq 1$ mol % having $Li_2Si_2O_5$ (LS$_2$) as main phase exhibit high $H_v$ about 6.71–6.82 GPa which is suitable for dental and armor applications.

Keywords Lithium disilicate · Crystallinity · Microstructure · Microhardness · Fracture toughness and Translucent glass ceramics

1 Introduction
Lithium disilicate glass–ceramics have been attracting attention of mankind since decades because of their excellent mechanical and translucent properties. Addition of nucleating agents, fluxing agents and colorants has been studied in lithium disilicate system earlier. Fine grain microstructure in these glass ceramics has been reported to improve mechanical properties [1]. Generally surface crystallization dominates in pure lithium disilicate glass ceramics which results in growth of larger crystals hampering the mechanical properties. Hence, it is necessary to add nucleating agents to promote uniform volume crystallization so that the optimized mechanical properties can be achieved [2]. Moreover, suitable heat treatment is essential to induce crystalline part in glassy matrix, as a result the mechanical and optical properties can be further improved [3–5]. Several studies have been carried out related to the lithium disilicate glass ceramics in order to study the crystallization sequence and microstructure with various additives [6, 7]. Earlier, researchers have reported various methods to improve the mechanical properties e.g., traditional ion exchange method, heat treatment effect and residual stress adjustment [8–10]. $P_2O_5$ has been suggested to be a well known nucleating agent for lithium disilicate glass systems. Addition of $P_2O_5$ in lithium disilicate system can induce amorphous phase separation through the precipitation of $Li_3PO_4$ (LP) which leads to the formation of stable $Li_2Si_2O_5$ (LS$_2$) phase [11]. Kun Yuan et al. [12] have reported that the sintering time affects the flexural strength of lithium disilicate based glass ceramics. W. Höland et al. [13] have reported that bulk crystallization can be controlled by addition of $P_2O_5$. Yang Bai et al. [14] have reported that two stage heat treatment is suitable to grow lithium disilicate phase and smaller dimensional crystals can be obtained when the samples are heat treated at temperature lower than the second crystallization peak temperature. $SiO_2-Li_2O-K_2O-ZnO-P_2O_5$ glass ceramic system with $P_2O_5$ content < 0.5 mol % possesses surface crystallization and glass ceramics with $P_2O_5$ content between 1–2.5 mol % have elongated rod shaped crystals [15]. Segre Borone et al. [16] quantitatively reported that precipitation of β-cristobalite at the interface of $Li_2SiO_3$ (LS)/amorphous matrix promotes...
LS₂ phase formation. Along with the mechanical properties, transparency is another important property to be improved for lithium disilicate glass ceramics. Glass ceramics with higher transparency can be used in several applications such as bomb disposal works, bullet proof vests and ceramic cook tops. Transparency can be achieved if the size of crystals is in nano meter range. P₂O₅ is one of the promising nucleating agents for reducing the crystal size and promoting bulk crystallization in lithium disilicate glass ceramic system. Moreover, presence of small crystals improves mechanical properties of glass ceramics. Synthesizing materials containing nano particles is an important aspect because they exhibit subtle properties regarding morphology, distribution and size [17, 18]. Fu wang et al. [19] have studied the flexural strength, microstructure and contrast ratio of lithium disilicate glass ceramics containing P₂O₅ and reported that the glass ceramic with 1 mol % P₂O₅ showed elongated rod like LS₂ crystals and exhibited highest flexural strength. Even though lithium disilicate glass ceramics containing P₂O₅ have been extensively studied the correlation between crystallinity, micro structure, microhardness, fracture toughness and optical properties of these glass ceramics has not been reported earlier.

Thus, the present work is aimed at the study of effect of P₂O₅ addition on the crystallization kinetics, microstructure, Vickers microhardness (Hᵥ), Vickers indentation fracture toughness (Kᵥc) and optical properties of lithium disilicate glass system (SiO₂-Li₂O-ZrO₂-K₂O-Al₂O₃-MgO-CaO-CeO₂) synthesized by melt quenching technique and correlation between the microstructure, physical and optical properties.

2 Materials and Methods

Lithium disilicate glass system (SiO₂-Li₂O-ZrO₂-K₂O-Al₂O₃-MgO-CaO-CeO₂) with addition of 0, 0.5, 1, 1.5 and 2 mol % P₂O₅ has been synthesized by conventional melt quenching technique. P₂O₅ has been added at the cost of SiO₂ and Li₂O by keeping their molar ratio ~ 2.4. Standard laboratory analytic grade SiO₂ (Sigma-aldrich > 99.9%), Li₂CO₃ (Merck > 99%), ZrO₂ (Aldrich > 99%), K₂CO₃ (Merck > 99%), Al₂O₃ (Merck > 98%), MgO (Merck > 97%), CaCO₃ (Merck > 98.5%), CeO₂ (Aldrich > 99.95%) and NH₄H₂PO₄ (Merck > 98.5%) powders were used as the raw materials to synthesize glasses. The compositions and nomenclature of synthesized glasses have been given in Table 1. The batches taken in molar ratio have been melted at 1450°C in platinum crucible for 2 h and quenched into preheated aluminium moulds of 4×5×10 mm, then instantly transferred into annealing furnace in order to remove internal stresses. The glasses have been ground into cuboids of 2×5×10 mm with the help of diamond precision saw.

| Composition | G1 | G2 | G3 | G4 | G5 |
|-------------|----|----|----|----|----|
| SiO₂        | 66.70 | 66.4 | 66 | 65.5 | 65.2 |
| Li₂O        | 27.70 | 27.5 | 27.4 | 27.3 | 27.2 |
| Al₂O₃       | 1.8  | 1.8  | 1.8  | 1.8  | 1.8  |
| ZrO₂        | 1.4  | 1.4  | 1.4  | 1.4  | 1.4  |
| K₂O         | 1.8  | 1.8  | 1.8  | 1.8  | 1.8  |
| P₂O₅        | 0    | 0.5  | 1   | 1.5  | 2   |
| MgO         | 0.2  | 0.2  | 0.2  | 0.2  | 0.2  |
| CaO         | 0.2  | 0.2  | 0.2  | 0.2  | 0.2  |
| CeO₂        | 0.2  | 0.2  | 0.2  | 0.2  | 0.2  |

Crystallization kinetic parameters such as activation energies of crystallization and Avrami parameters have been determined for all the glasses using non isothermal method. The glasses were ground into powder of 100–200 µm granules and the differential thermal analysis (DTA) has been carried out for all the glasses using simultaneous DTA-TG (SHIMADZU). The DTA runs have been carried out from room temperature to 1000 °C under flowing nitrogen atmosphere at different heating rates (α = 5, 10, 15 and 20 K.min⁻¹). All the glasses have been converted into glass ceramics by following three stage heat treatment schedules. The glass transition temperature (Tg), first crystallization onset temperature (Tc₁on) and second crystallization onset temperature (Tc₂on) observed from the DTA curves corresponding to the heating rate of 10 K/min were chosen as holding temperatures for heat treatment of glass samples. The nomenclature and heat treatment schedules are given in Table 2.

Crystalline phases have been identified using XRD (Rigaku, Japan). The analysis has been done using Cu-Kα radiation with a step size of 0.01° and 20 ranging from 10° to 60°. Crystallinity of lithium disilicate glass ceramics has been determined using relation (1) [20].
Crystallinity = \( \frac{A_c}{A_c + A_a} \times 100\% \) \( (1) \)

where, \( A_c \) and \( A_a \) are the area under the peaks representing total crystalline and the amorphous phase respectively.

All the glass ceramics in the shape of cuboids were wet ground with silicon carbide emery papers (grit size ranging from 320 to 2000) and then finally were polished with fine grade alumina suspension (0.3 µm) on velvet cloth. Each sample was indented with ten indentations with the help of Vickers diamond pyramid and knoop indenters (Microhardness tester model: F. AUTO-II, Metatech, India) in order to measure microhardness. A load of 1 kg for 10 s has been used for all the glass ceramics.

The \( H_v \), knoop hardness (Hk), elastic modulus (E) and \( K_{IC} \) were calculated by using the relations (2), (3), (4) and (5) respectively [1, 21, 22].

\[ H_v = 1.8544 \left( \frac{P}{d^2} \right) (Kg mm^{-2}) \] \( (2) \)

\[ H_k = 14.229 \left( \frac{P}{\alpha a} \right) (Kg mm^{-2}) \] \( (3) \)

\[ E = \frac{0.45H_k}{\left( 0.1406 - \frac{b}{a} \right)} (GPa) \] \( (4) \)

\[ K_{IC} = 0.016 \sqrt{\frac{E}{H_v}} \left( \frac{P}{C_{1.5}} \right) (MPa \sqrt{m}) \] \( (5) \)

where, \( P \)-applied load, \( d \)-average diagonal length of Vicker’s indentation mark, ‘b’ and ‘a’ are lengths of minor and major diagonals of knoop indentation mark respectively and \( C \)-length of the crack from indentation center to end of the crack.

The Fourier transform infrared (FTIR) spectroscopy study has been carried out at room temperature for all the glasses using FTIR spectrometer (SHIMADZU IR Affinity-1) in the range of 500–1400 cm\(^{-1}\). For FTIR study the glasses have been ground into fine powder. Raman spectra were recorded on the polished solid glasses with Raman spectrometer (NOST.) using a He–Ne laser (532 nm). The measurements were performed from 300–1400 cm\(^{-1}\) at room temperature with 10 mW incident laser power. 100× objective lens was used to focus on the polished surface of the solid glass samples.

The polished glass ceramics have been etched with 5 vol % hydrofluoric acid for 3 min. Microstructure of all the etched glass ceramics have been observed using FESEM (Zeiss ultra 55). High angle annular dark field imaging (HAADF) analysis has been carried out for the glass ceramics containing 1.5 mol % \( P_2 O_5 \) using scanning tunneling electron microscopy (STEM) technique (TALOS F200S G2). The elements present in the glass ceramic containing 1.5 mol % \( P_2 O_5 \) have been confirmed by energy dispersive X-ray analysis (EDX) and high resolution transmission electron microscopy (HR-TEM) images were recorded to determine the interplanar distance (d-spacing). For this purpose the glass ceramic has been gently ground using white AGATE mortar and pestle. Then the glass ceramic powder has been dispersed in pure ethyl alcohol and kept for ultrasonic bath for few minutes. A carbon coated 200-mesh TEM copper grid was placed in the suspension until the ethyl alcohol gets evaporated leaving the glass ceramic particles on the copper grid before STEM analysis.

UV–Visible transmittance spectroscopy has been carried out for all the glass ceramics by UV–Visible spectrophotometer (AvaSpec-version 2.2) in the range from 300–800 nm. Fine polished 2×5×10 mm samples have been used to perform the UV–Visible spectroscopy.

3 Results and Discussion

3.1 XRD

XRD patterns of all glass ceramics are shown in Fig. 1. It can be observed that glass ceramics with \( P_2 O_5 \leq 0.5 \) mol % has mainly LS phase (JCPDS no. 74–2145) along with minor LS\(_2\) (JCPDS no.82–2396), quartz (JCPDS no. 07–0346) and cristobalite (JCPDS no. 04–0359) phases. In the glass ceramics with \( P_2 O_5 \leq 0.5 \) mol %, LS crystalline phase has been formed due to the reaction between Li\(_2\)O and SiO\(_2\) in the glassy matrix (reaction 6). As discussed in the Sect. 3.4 the formation of cristobalite phase may be due to the increment of \( Q^4 \) units (\( Q^4\)-silica tetrahedra with 4-bridging oxygen) with the addition of \( P_2 O_5 \) which could easily convert into cristobalite phase at second crystallization temperature. The coexistence of cristobalite along with LS and LS\(_2\) phases in GC-2 may be understood as the cristobalite and LS phases act as precursors for LS\(_2\) phase formation as reported earlier [13]. It can be observed from the Fig. 1 that with the addition of \( P_2 O_5 \geq 1 \) mol % LS\(_2\) phase is developed along with minor LP (JCPDS no 25–1030) phase while LS phase is not observed.

The LS\(_2\) phase formation in the glass ceramics containing \( P_2 O_5 \geq 1 \) mol % may occur in following way. The high field strength \( P^{5+} \) ions attract the \( O^{2-} \) ions from the glass matrix leading to the formation of \( PO_4^{3-} \) and the Li\(^{+}\) ions are attracted towards the phosphates in order to balance their negative charge forming the amorphous LP phase (reactions 7 and 8) [23]. Pauline Glatz et al. [24] earlier did the \(^{31}\)P MAS-NMR studies on LS\(_2\) based glasses and reported that the phosphate units are surrounded by Li\(^{+}\) cations which supports our analogy.
These amorphous LP species may serve as nucleation sites for the formation of \( \text{LS}_2 \) phase according to the reaction (9) [23]. Christine Bischoff et al. [25] have previously reported the nuclear magnetic resonance (NMR) and XRD studies of multi component lithium disilicate based glass ceramics which revealed that phosphate species exist in highly disordered state and the heterogeneous nucleation of \( \text{LS}_2 \) phase takes place at the compositional gradient of amorphous LP and the glass matrix. This analogy supports the formation of \( \text{LS}_2 \) phase for the glass ceramics containing \( \text{P}_2\text{O}_5 \geq 1 \text{ mol} \% \) in this study. Thus, the glass ceramics with \( \text{P}_2\text{O}_5 \geq 1 \text{ mol} \% \) exhibit heterogeneous nucleation and crystal growth of \( \text{LS}_2 \) phase.

Moreover, the amorphous LP is expected to be converted into crystalline LP at higher temperature near \( T_{\text{C2on}} \). As expected, the minor content of crystalline LP phase has been observed (reaction 10) in the glass ceramics containing \( \text{P}_2\text{O}_5 \geq 1 \text{ mol} \% \) as the addition of \( \text{P}_2\text{O}_5 \) is small (up to 2 mol %) [26]. This results into \( \text{LS}_2 \) as main phase along with LP as minor phase in the glass ceramics with \( \text{P}_2\text{O}_5 \geq 1 \text{ mol} \% \).

\[
\text{Li}_2\text{O}_{(\text{glass})} + \text{SiO}_2_{(\text{glass})} \rightarrow \text{Li}_2\text{SiO}_3_{(\text{crystal})} \quad (6)
\]

\[
(\text{Si} - \text{O} \cdots \text{Li}^+)_{(\text{glass})} + \text{P}_2\text{O}_5_{(\text{glass})} \rightarrow 3(\text{Si} - \text{O} \cdots \text{Si})_{(\text{glass})} + 2\text{Li}_3\text{PO}_4_{(\text{glass})} \quad (7)
\]

\[
\text{P}_2\text{O}_5_{(\text{glass})} + 3\text{Li}_2\text{O}_{(\text{glass})} \rightarrow 2\text{Li}_3\text{PO}_4_{(\text{glass})} \quad (8)
\]

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\text{Li}_2\text{O}_{(\text{glass})} + 2\text{SiO}_2_{(\text{glass})} \rightarrow \text{Li}_2\text{Si}_2\text{O}_5_{(\text{crystal})} \quad (9)
\]

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\[
\text{P}_2\text{O}_5_{(\text{glass})} + 3\text{Li}_2\text{O}_{(\text{glass})} \rightarrow 2\text{Li}_3\text{PO}_4_{(\text{crystal})} \quad (10)
\]

### 3.2 Differential Thermal Analysis and Non Isothermal Crystallization Kinetics

Figure 2 (a) shows DTA plots for all glasses at 10 K/min. Figure 2(b) shows the DTA plots of glass containing 1 mol % \( \text{P}_2\text{O}_5 \) at 5-20 K/min. All the curves show an endothermic peak corresponding to \( T_g \) and two exothermic peaks \( T_{p1} \) and \( T_{p2} \). The peak \( T_{p1} \) at lower temperature corresponds to \( \text{LS}_2 \) phase and the peak \( T_{p2} \) at higher temperature corresponds to \( \text{LS}_2 \) phase [27]. \( T_g \), \( T_{p1} \) and \( T_{p2} \) for all the glasses have been given in the Table 3. The glasses with \( \text{P}_2\text{O}_5 \leq 1 \text{ mol} \% \) exhibit broad crystallization peaks indicating the larger full width at half maximum. The glasses with \( \text{P}_2\text{O}_5 > 1 \text{ mol} \% \) exhibit sharp crystallization peaks indicating smaller full.
width at half maximum. It has been reported earlier that larger full width at half maximum of DTA peaks results in smaller Avrami parameter ($n$) which indicates surface crystallization while smaller full width at half maximum gives larger Avrami parameter which indicates volume crystallization [28]. Generally the lithium disilicate based glasses without $P_2O_5$ exhibit surface crystallization. With the increase in mol % $P_2O_5$, the $T_g$ has been observed to increase. $T_{P1}$ has been observed to increase with increasing $P_2O_5$ up to 1 mol % while for the glasses containing $P_2O_5>1$ mol % it has been observed to decrease as shown in Fig. 1 (a). $T_{P2}$ has been observed to decrease continuously with the addition of $P_2O_5$.

Kissinger method has been used to calculate the activation energies of crystallization corresponding to the exothermic peaks as given by the relation (11) [27, 29]:

$$\ln\frac{T_p^2}{\alpha} = \frac{E_C}{RT_p} + \ln\frac{E_C}{R\nu}$$

(11)

$T_p$, $\alpha$, $R$ and $\nu$ are the peak temperature observed, heating rate used in DTA, universal gas constant and frequency factor respectively. The expression (11) yields a straight line and the activation energy for crystallization $E_C$ can be determined from the slope of $\ln[T_p^2/\alpha]$ versus $T_p^{-1}$. Once the $E_C$ is known, the Avrami parameter ‘$n$’ can be calculated using the Augis and Bennett relation (12) [28]:

$$n = \frac{2.5 \frac{RT_p^2}{\Delta T}}{E_C}$$

(12)

where ‘$\Delta T$’ is the full width half maximum intensity of the exothermic peak obtained from the DTA.

Table 3 $T_g$, $T_{C1on}$, $T_{P1}$, $T_{C2on}$, $T_{P2}$ values for all glasses at different heating rates

| Heating rate | Heating rate | $T_g$ | $T_{C1on}$ | $T_{P1}$ | $T_{C2on}$ | $T_{P2}$ |
|--------------|--------------|-------|------------|----------|------------|----------|
| G1           | 5 K          | 468   | 613        | 652      | —          | —        |
|              | 10 K         | 474   | 622        | 668      | 859        | 866      |
|              | 15 K         | 477   | 630        | 680      | 865        | 875      |
|              | 20 K         | 480   | 635        | 690      | 869        | 885      |
| G2           | 5 K          | 471   | 618        | 673      | —          | —        |
|              | 10 K         | 476   | 636        | 692      | 838        | 846      |
|              | 15 K         | 477   | 644        | 703      | 840        | 854      |
|              | 20 K         | 483   | 647        | 715      | 842        | 865      |
| G3           | 5 K          | 476   | 623        | 676      | 804        | 837      |
|              | 10 K         | 479   | 632        | 703      | 819        | 839      |
|              | 15 K         | 480   | 636        | 714      | 821        | 846      |
|              | 20 K         | 484   | 643        | 717      | 833        | 852      |
| G4           | 5 K          | —     | 574        | 596      | 775        | 793      |
|              | 10 K         | 482   | 591        | 614      | 780        | 807      |
|              | 15 K         | 489   | 598        | 628      | 791        | 816      |
|              | 20 K         | 491   | 603        | 632      | 794        | 819      |
| G5           | 5 K          | —     | 580        | 597      | 780        | 794      |
|              | 10 K         | 483   | 589        | 614      | 787        | 805      |
|              | 15 K         | 485   | 599        | 625      | 794        | 812      |
|              | 20 K         | 494   | 604        | 635      | 800        | 818      |
The crystallization peak temperature shifts to higher values as the heating rate is increased as observed from Fig. 2 (b). Similar variation has been observed for all the glasses. This may be due to the fact that faster heating rate provides shorter duration of time for nucleation as a result nucleation starts at high temperature at which the melt is at lower viscosity [30]. Using relation (11), the plots have been drawn between $\ln \left( \frac{T_p^2}{\alpha} \right)$ and $10,000/T_p$ as shown in Fig. 3 (a, b). The variation of activation energies with mol % $P_2O_5$ corresponding to the first and second exothermic peaks for all the glasses has been shown in Fig. 3 (c, d) respectively. The decrease in activation energy corresponding to first crystallization temperature $(E_{C1})$ observed from Fig. 3 (c) may be due to the heterogeneous nucleation effect of $P_2O_5$. Addition of $P_2O_5$ causes more number of nucleation sites and thus the crystallization starts at lower temperature which has been predominantly observed for glasses containing $P_2O_5 \geq 1.5$ mol %. The reason for increase in activation energy corresponding to second crystallization temperature $(E_{C2})$ is further to be investigated. The activation energies along with goodness of fit $R^2$ and Avrami parameters for all glasses have been given in Table 4. With the addition of $P_2O_5$ the Avrami parameter corresponding to first crystallization temperature has been observed to increase from 1.15 to 2.48 while for second crystallization temperature it varies between 1.84 to 3.02 as shown in Fig. 4 (a) and 4 (b). From the earlier reports $n \approx 1$ indicates surface nucleation and growth towards inside, $n \approx 2$ volume nucleation and one dimensional growth and $n \approx 3$ indicates volume nucleation and two dimensional growth [27, 31]. This indicates that LS phase forms through surface crystallization and $LS_2$ phase forms through volume crystallization. The surface crystallization has been observed for GC-1 using cross sectional SEM (provided as supplementary file S1). The increment in

![Fig. 3](image-url) (a,b) Plots between $\ln \left( \frac{T_p^2}{\alpha} \right)$ and $10,000/T_p$ and (c,d) Variation of activation energies $E_{C1}$ and $E_{C2}$ with mol % $P_2O_5$ respectively

| Glass | Kissinger method (KJ.mol$^{-1}$) | Augis and Bennet method |
|-------|---------------------------------|-------------------------|
|       | $E_{C1}$ | Goodness of fit $R^2$ | $E_{C2}$ | Goodness of fit $R^2$ | $<n_1> \pm$ S.D. | $<n_1> \pm$ S.D. |
| G1    | 255.40±14.9 | 0.989 | 380±44.49 | 0.984 | 1.15±0.13 | 2.36±0.03 |
| G2    | 240.6±7.8  | 0.996 | 381.1±38.2 | 0.972 | 1.22±0.04 | 1.93±0.37 |
| G3    | 224.4±5.8  | 0.997 | 465±20.7  | 0.993 | 1.47±0.36 | 1.84±0.5  |
| G4    | 223.56±14.1| 0.987 | 487±23.2  | 0.993 | 2.60±0.14 | 2.38±0.36 |
| G5    | 222.86±9.9 | 0.974 | 517±22.4  | 0.994 | 2.48±0.12 | 3.02±0.37 |

$< >$—Average, S.D.—Standard deviation
Avrami parameter for the LS phase indicates that P₂O₅ addition alters the nucleation process and causes heterogeneous volume nucleation.

### 3.3 Microhardness and Fracture Toughness

The variation of Hᵥ, percentage LS₂ phase, total percentage crystallinity and Kᵥ of glass ceramics are given in Fig. 5 (a) and (b) respectively. Mechanical properties of glass ceramics depend upon phases developed, % crystallinity and their microstructure [32]. The phases developed, % crystallinity, Hᵥ, Hᵥ, E, C and Kᵥ of all the glass ceramics are given in Table 5. The glass ceramics containing P₂O₅ ≤ 0.5 mol % possess higher crystallinity and larger crystals [33]. GC-1 (glass ceramic without P₂O₅ content) and GC-2 (glass ceramic with 0.5 mol % P₂O₅) possess mainly LS phase while LS₂ phase could not grow sufficiently, hence these glass ceramics exhibit lower microhardness (5.35–5.83 GPa) compared to the glass ceramics containing P₂O₅ ≥ 1 mol % as the LS phase is less hard.

![Fig. 4](image1)

**Fig. 4** Avrami parameter for all glasses corresponding to (a) first exothermic peak and (b) second exothermic peak respectively

![Fig. 5](image2)

**Fig. 5** (a) Variation of microhardness and % Li₂Si₂O₅ phase with mol % P₂O₅ and (b) Variation of total percentage crystallinity and fracture toughness of glass ceramics with mol % P₂O₅

| Glass ceramic | Phases developed (% Crystallinity) | Total % Crystallinity | Hᵥ ± S.D. | Hᵥ ± S.D. | E ± S.D. | Average crack length (C ± S.D.) (µm) | Kᵥ ± S.D. (MPa√m) |
|---------------|-----------------------------------|-----------------------|-----------|-----------|---------|----------------------------------|-------------------|
| GC-1          | LS (80.65) LiAlSiO₄ (12.34)        | 92.99                 | 5.35 ± 0.23 | 4.53 ± 0.15 | 69.38 ± 11.42 | —                                | —                 |
| GC-2          | LS (46.23), LS₂ (27.82) and SiO₂ (17.32) | 91.37                 | 5.83 ± 0.23 | 5.83 ± 0.25 | 78.55 ± 12.72 | —                                | —                 |
| GC-3          | LP (4.33) and LS₂ (79.91)          | 84.24                 | 6.82 ± 0.09 | 5.93 ± 0.25 | 106.33 ± 11.09 | 60.30 ± 1.45                   | 1.36 ± 0.04      |
| GC-4          | LP (4.77) and LS₂ (76.66)          | 81.436               | 6.75 ± 0.12 | 5.91 ± 0.15 | 98.77 ± 9.10 | 65.984 ± 2.53                  | 1.12 ± 0.05      |
| GC-5          | LP (5) and LS₂ (76.67)             | 81.67                 | 6.71 ± 0.10 | 5.83 ± 0.08 | 91.10 ± 3.406 | 68.57 ± 1.65                   | 1.02 ± 0.06      |
compared to LS₂ phase [1, 34]. The glass ceramics without nucleating agent possess limited number of nuclei. These limited number of nuclei have no restriction on their crystal growth by their neighbor nuclei as a result larger crystals grow in these glass ceramics [35]. These larger crystals possess larger free volume so that these crystals could easily displace when an external load is applied. As a result, the glass ceramics possessing larger crystals (GC-1 and GC-2) exhibit lower microhardness [36]. From FESEM images it can be observed that microscopic structure of glass ceramics containing \( P_2O_5 \geq 1 \text{ mol \%} \) (GC-3, GC-4 and GC-5) has nano size rods and spherical shaped crystals compared to GC-1 and GC-2. Also, the crystallization proceeds from surface to volume of the glass ceramics with an increase in \( P_2O_5 \) content, as observed from FESEM images (as shown in Sect. 3.5) and increase in Avrami parameters. The glass ceramics containing \( P_2O_5 \geq 1 \text{ mol \%} \) possess higher microhardness (6.71–6.82 GPa). Higher \( H_v \) for the glass ceramics with \( P_2O_5 \geq 1 \text{ mol \%} \) can also be attributed to presence of LS₂ nano crystals [1] as observed from FESEM and HAADF images which has been discussed in Sect. 3.5. The improvement in microhardness of glass ceramics GC-3, GC-4 and GC-5 compared to GC-1 and GC-2 can be attributed to the decrease in crystal size from micro to nano meter range. Hall–Petch relation describes an inverse relationship between microhardness and crystal size of glass ceramics [5]. Some recent studies also show that with the decrease in size of the crystals in glass ceramics the microhardness increases [5, 37, 38]. The smaller crystals resist relaxing their internal stress developed when an external load is applied. This leads to prevention of micro cracks which results in higher microhardness for the glass ceramics with \( P_2O_5 \geq 1 \text{ mol \%} \). Therefore, in this study the Hall–Petch relation in Vickers hardness is obeyed. \( K_{IC} \) of glass ceramics with \( P_2O_5 \leq 0.5 \text{ mol \%} \) could not be measured as they do not show proper cracks, while the glass ceramic containing 1 mol \% \( P_2O_5 \) exhibits high fracture toughness (1.36 ± 0.04 Mpa\( \sqrt{m} \)) as observed from Fig. 5 (b). This can be attributed to the presence of rod shaped LS₂ nano crystals which can hinder the crack propagation [4]. To illustrate the improper and proper cracks, the indentation marks corresponding to GC-1 and GC-3 have been shown in supplementary files S2 and S3 respectively. The glass ceramics with 1.5 and 2 mol \% \( P_2O_5 \) exhibit slight lower values of the \( K_{IC} \) (1.12 ± 0.05 and 1.02 ± 0.06 Mpa\( \sqrt{m} \)) respectively compared to the glass ceramic containing 1 mol \% \( P_2O_5 \) which may be due to the decrease in percentage crystallinity and the absence of rod shaped crystals as well. Thus \( P_2O_5 \) addition reduces total crystallinity, crystal growth and increases the \( H_v \) which can be attributed to the development of nano LS₂ crystals.

### 3.4 FTIR and Raman Spectroscopy

Figure 6 (a) shows the IR spectra recorded on the glass powder samples. Due to the amorphous nature and wide range distribution of \( Q^k \) species (where, \( Q^k \) represents silica tetrahedra with \( k \)-bridging oxygens, \( k \) varying from 0,1,2,3 and 4) the IR spectra of glasses have been observed to lack sharp bands and exhibited broad bands. The IR spectra show absorption bands around 540, 789, 932, 1020 and 1160 cm\(^{-1}\)). The bands around 932 and 1020 cm\(^{-1}\)) are the most intense absorption bands. The IR band near 540 cm\(^{-1}\)) can be attributed to the O-Si–O or Si–O-Si deformation vibrations [39]. The band around 789 cm\(^{-1}\) can

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**Table 6** IR peaks of all glasses and their bands assignment

| Wave number (cm\(^{-1}\)) | Assignment                                      | References |
|---------------------------|-------------------------------------------------|------------|
| 540                       | deformation vibrations of O-Si–O or Si–O-Si     | [39]       |
| 789                       | bending mode of Si–O-Si group                    | [40, 41]   |
| 932                       | stretching vibrations of Si–O\(^{-}\)            | [39]       |
| 1020                      | Si–O-Si anti symmetric stretching of bridging oxygens | [42]       |
| 1160                      | asymmetric vibrations of Si–O-Si                | [39, 43]   |
be assigned to the bending mode of Si–O-Si group [40, 41]. The intense band in the range 800–1200 cm\(^{-1}\) corresponds to stretching vibrations of SiO\(_4\) tetrahedron with different number of bridging oxygen atoms. The band at 932 cm\(^{-1}\) can be accredited to stretching vibrations of Si–O\(^-\) [39], the band at 1020 cm\(^{-1}\) corresponds to Si–O–Si anti symmetric stretching of bridging oxygens within tetrahedral [42]. The band around 1160 cm\(^{-1}\) can be attributed to asymmetric vibrations of Si–O-Si [39]. No major changes have been observed in the FTIR spectra of the glasses as the content of P\(_2\)O\(_5\) is small (up to 2 mol %). There is small decrease in intensity of the band at 932 cm\(^{-1}\) which indicates that P\(_2\)O\(_5\) might possibly act as glass former.

From Fig. 6 (b) it can be observed that the Raman spectra for glasses possess two regions one with low frequency from 300 to 800 cm\(^{-1}\) and other with high frequency from 800 to 1200 cm\(^{-1}\) as shown in Fig. 6 (b). The Raman spectra observed for the glasses can be described by Q\(_4\) (SiO\(_4\)), Q\(_3\) (Si\(_2\)O\(_5\)) and Q\(^3\) (SiO\(_4\)) species. The Raman spectra show bands at 470, 592, 787, 947, 1069 cm\(^{-1}\) respectively. The assignments of Raman bands have been given in Table 7. The band at 470 cm\(^{-1}\) can be attributed to the Q\(_4\) unit [44, 45]. The band at 592 cm\(^{-1}\) corresponds to symmetrical valance vibrations due to Q\(^2\) (Si–O–Si) units [44]. The band at 787 cm\(^{-1}\) is due to Si motion in oxygen cage [44]. The band around 947 cm\(^{-1}\) corresponds to Q\(_2\) units as well as the vibrations of P-O bonds and the band centered around 1069 cm\(^{-1}\) corresponds to Q\(^3\) units [24, 44–47]. For the glasses containing P\(_2\)O\(_5\) ≤ 0.5 mol % the band around 1069 cm\(^{-1}\) is dominant which indicates that all the glasses mainly consist of Q\(^3\) structural units. For the glasses containing P\(_2\)O\(_5\) ≥ 1 mol % the intensity of bands around 470 and 947 cm\(^{-1}\) have been observed to increase which indicates the increase in the Q\(^4\) and Q\(^2\) units, while the intensity of the band around 1069 cm\(^{-1}\) decreases which indicates decrease in Q\(^3\) units respectively. The possible mechanism that occurs in the glasses with the addition of P\(_2\)O\(_5\) may be due to the disproportionation reaction as given in reaction (13)[25].

\[
2Q_3^{(glass)} \leftrightarrow Q_2^{(glass)} + Q_4^{(glass)} \quad (13)
\]

The increase in the intensity of the band at 470 cm\(^{-1}\) (corresponding to Q\(^4\) units) and the decrease in intensity of the band at 1069 cm\(^{-1}\) (corresponding to Q\(^3\) units) can be attributed to the polymerization of the glass network. This is also supported by the FTIR results and the increase in T\(_g\) observed from DTA. It has been reported earlier that Q\(^2\) and Q\(^3\) units in the glasses promote crystallization of LS and L\(_S\)\(_2\) phases respectively [28, 44]. Although glasses containing P\(_2\)O\(_5\) ≤ 0.5 mol % mainly possess Q\(^3\) units, the lithium disilicate phase has not been developed rather the LS phase has been developed in their corresponding glass ceramics (GC-1 and GC-2). This can be explained on the basis of reaction (14) [23]. The glasses with P\(_2\)O\(_5\) ≥ 1 mol % show increase in Q\(^2\) and Q\(^4\) units and the L\(_S\)\(_2\) phase could be developed in their corresponding glass ceramics (GC-3, GC-4 and GC-5) which may be due to nucleation effect as explained in Sect. 3.2.

### 3.5 FESEM, HAADF-STEM, EDX and HR-TEM Analysis

Figure 7 (a, b, c, d and e) show the FESEM images of glass ceramics containing 0, 0.5, 1, 1.5 and 2 mol % P\(_2\)O\(_5\) respectively. From the figure it can be observed that with the addition of P\(_2\)O\(_5\) the morphology of glass ceramics has been changed. Glass ceramics with P\(_2\)O\(_5\) ≤ 0.5 mol % (Fig. 7 (a) and 7 (b)) do not exhibit volume nucleation and larger flake like coarse crystals have been formed. It can be observed from the cross sectional SEM image of GC-1 that the crystals have grown from the surface towards interior of the samples as shown in supplementary file S1 which indicates surface crystallization mechanism. The surface crystallization mechanism has been observed to be prominent in GC-1 and GC-2 due to low content of P\(_2\)O\(_5\) (up to 0.5 mol %). The surface crystallization may occur due to solid foreign dust particles acting as nucleation sites upon the surface or the effect of ambient temperatures [48]. With the addition of P\(_2\)O\(_5\) ≥ 1 mol % (Fig. 7 (c), 7 (d) and 7 (e) respectively) nano scale L\(_S\)\(_2\) crystals have been developed which may be due to heterogeneous nucleation at the interface of disordered LP and glassy matrix in the glass ceramics as discussed in XRD results. As the number of nuclei is more the space between each nucleus that leads to crystal growth is less. As a result nano size crystals have been formed.

Among all the glass ceramics, GC-4 with 1.5 mol % P\(_2\)O\(_5\) possesses smallest crystal size as shown in Fig. 7 (d). Thus HAADF-STEM imaging and EDX analysis have been done for GC-4. The HAADF-STEM image has been shown in Fig. 8 (a) and the EDX analysis carried out at the rectangular area represented in Fig. 8 (a) has been shown in Fig. 8 (b). The average particle size has been determined from Fig. 8 (a) by selecting over 50 particles using Image J software.
The particle size distribution is shown in the inset image of Fig. 8 (a). The inset image shows the average particle size is about 16.88 nm.

The EDX analysis of the glass ceramic GC-4 confirms the presence of Si, O, Zr, Al, K, P, Mg, Ca and Ce. The presence of lithium could not be detected from EDX analysis as it has weight below the detection range. The presence of LS2 as main phase and LP as minor phase has been observed in XRD, the other elements must be in the form of residual glassy matrix. The weight percentage of the elements present in the selected region has been given in Table 8. As the distribution of the elements cannot be uniform everywhere in the glass ceramics, EDX analysis could not quantify the exact percentage of the elements present over the selected region. The elemental mapping of GC-4 has been shown in Fig. 9. The individual images of elemental mapping have been given in supplementary files (S4-S12). From the elemental mapping images LS2 crystals could not be distinguished from the residual silica matrix therefore, HR-TEM analysis has been carried out for GC-4 in order to observe LS2 crystals. The HR-TEM image has been shown in Fig. 10 that shows lattice spacing of the crystal to be 0.295 nm which is corresponding to (200) plane of orthorhombic LS2 phase. Therefore, HR-TEM analysis also confirms the presence of LS2 nano crystals.

3.6 UV–Visible Transmittance Spectroscopy

Figure 11 (a) shows UV–visible transmission spectra for all the glass ceramics. The transmission spectra of glass ceramic GC-2 overlaps on transmission spectra of GC-1. Among all the glass ceramics GC-4 shows highest transmittance in visible wavelength range.

Transmittance of visible light in glass ceramics depends mainly on crystal size, crystallinity and refractive index of the phases present. It is well known that if the size of the crystals matches with the wavelength of light incident, greatest scattering takes place [49]. Glass ceramics with P2O5 ≤ 0.5 mol % possess higher crystallinity and larger crystal size as can be observed from XRD and FESEM (Fig. 7(a) and 7(b)) respectively. As a result scattering of visible light takes place on the larger crystals and transparency could not observe. From Fig. 11 (a) it can be observed that the transmittance of glass ceramics with P2O5 ≥ 1 mol % has increased and the glass ceramic GC-4 shows highest transmittance that is 64% at wavelength λ = 550 nm (λ = 550 nm has been taken since human eye is more sensitive at this wavelength). For higher transparency the difference between the refractive index of glass matrix and crystals present should be less. The refractive index of LS2 phase is 1.55 which is closer to that of glass matrix 1.50, as a result transmittance of glass ceramic at visible wavelength increases [50]. The schematic representation of light transmission through glass ceramics has been shown in Fig. 11 (b). The development of LS2 phase in the glass ceramics with P2O5 ≥ 1 mol % has been confirmed from XRD. From HAADF analysis it has been observed that the glass ceramic GC-4 has lowest LS2 crystal size (around 16.88 nm). Thus presence of LS2 crystals with smallest crystal size in the glass ceramic GC-4 causes highest transmittance among all.
the glass ceramics. Hence, the addition of P$_2$O$_5$ to LS$_2$ based glass ceramics increases both the transparency and micro-hardness which are of great importance for several applications such as armors and aesthetics in dentistry.

![Fig. 8](image_url) (a) HAADF-STEM image of glass ceramic containing 1.5 mol % P$_2$O$_5$, the inset image shows the particle size distribution and (b) EDX analysis of glass ceramic containing 1.5 mol % P$_2$O$_5$.

![Table 8](image_url) EDX analysis of glass ceramic containing 1.5 mol % P$_2$O$_5$

| Element | Weight % | Atomic % |
|---------|----------|----------|
| O (K)   | 52.41    | 67.72    |
| Si (K)  | 36.66    | 26.98    |
| Al (K)  | 1.28     | 0.98     |
| Zr (K)  | 3.24     | 0.73     |
| K (K)   | 4.52     | 2.39     |
| P (K)   | 1.38     | 0.92     |
| Mg (K)  | 0.02     | 0.02     |
| Ca (K)  | 0.45     | 0.23     |
| Ce (K)  | 0.04     | 0.03     |
| Totals  | 100      | 100      |

![Fig. 9](image_url) HAADF Elemental mapping of glass ceramic containing 1.5 mol % P$_2$O$_5$.

![Fig. 10](image_url) HR-TEM image of the GC-4, inset image shows the d-spacing of the (200) plane corresponding to orthorhombic LS$_2$ crystal.
4 Conclusions

Addition of P2O5 reduces the overall percentage of crystallinity, crystal size but it facilitates lithium disilicate phase formation and improves Hv. The glass ceramics with P2O5 ≥ 1 mol % have high Hv (6.71–6.82 GPa) and moderate KIC (1.02–1.36 MPa√m) among all the glass ceramics. Glass ceramic containing 1.5 mol % P2O5 exhibits nano crystals of 16.88 nm and shows improved transparency at the wave length 550 nm. A good correlation is obtained between crystallinity, microstructure and microhardness of these glass ceramics. These lithium disilicate glass ceramics with improved mechanical and optical properties have great potential in dental and armor applications.

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Writing – original draft: [Peddy Satyanarayana].
Writing – review & editing: [Anuradha Vilas Deshpande].

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Declarations

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