Effect of P_2O_5 on Crystallization Behavior and Chemical Resistance of Dental Glasses in the Li_2O-SiO_2-ZrO_2 System

G. Maghouli and B. Eftekhari Yekta*

* *beftekhari@iust.ac.ir*

Received: October 2017 Accepted: February 2018

[1] Ceramic Division, School of Materials and Metallurgy Engineering, Iran University of Science and Technology, Tehran, Iran.

DOI: 10.22068/ijmse.15.1.17

Abstract: *Commercial dental lithium disilicate based glass-ceramics containing various amounts of P_2O_5 were synthesized. Regarding the crystallization behavior and physico-chemical properties of the glasses, the optimum percent of P_2O_5 was determined as 8 %wt.*

Crystallization behavior of the glasses was investigated by X-ray diffraction (XRD) and differential thermal analysis (DTA). The micro-hardness and chemical resistance of both glass and glass-ceramic searies were also determined.

According to our results, lithium phosphate was precipitated prior to crystallization of the main phases, i.e lithium meta silicate and lithium disilicate. This early precipitation led to evacuation of residual glass phase from lithium ions, which caused increasing the viscosity of glass and so shifting of crystallization to higher temperatures.

In addition, increasing in P_2O_5 amounts and consequently increasing in Li_3PO_4 , led to significant decrease in the crystallite size and aspect ratio of crystals.

Furthermore, while the chemical resistance of the glasses was decreased with P_2O_5, it was increased with P_2O_5 after heat treatment process. The chemical solubility of the glass-ceramics was between 2080 and 1188 $\mu g/cm^2$.

Keywords: *Glass-ceramic, Lithium-disilicate, P_2O_5, Chemical solubility.*

1. INTRODUCTION

In recent years, ceramics are used extensively in the various field of dentistry due to their biocompatibility and their similarity to tooth in points of light reflection and transmission views. Enough mechanical resistance against forces caused by chewing has been another important point for this tendency. In this regard, glass-ceramics are known as the main candidate. Todays, various kinds of glass-ceramics are used in dental materials field as core, crown, opaque layer, enamels, etc.[1-6]. One of them is a commercial one named as IPSS Empress, has been delivered to global marketing by Ivoclar Vivadent Co. This glass system is based on lithium di-silicate ($Li_2O.\ 2SiO_2$) crystalline phase with commercial name of IPS e.max [7-11].

The aim of this work was to study the effects of P_2O_5 addition on the crystallization behavior, mechanical and chemical properties of a lithium di-silicate based glass, which is used by the Ivoclar Vivadent Co. leaflet as a dental core.

2. EXPERIMENTAL PROCEDURE

The chemical compositions of the three prepared glasses are shown in Table 1. A high

Table 1. Nominal composition of prepared samples (wt.%)

Sample code	SiO_2	Li_2O	ZrO_2	P_2O_5	Al_2O_3	CeO_2	K_2O
P2	60	18	10	2	3	2	2
P5	60	18	10	5	3	2	2
P8	60	18	10	8	3	2	2

[Downloaded from fn.iust.ac.ir on 2025-07-19]

[DOI: 10.22068/ijmse.15.1.17]

purity silica sand (>99.5%), lithium carbonate (Merck, no.1.05670), zirconium oxide(Merck, no.1.00757), aluminum oxide(Fibrona, >99%), P_2O_5 (Merck, no.170540), Potassium nitrate(Merck, no.5063) and commercial cerium oxide(>99%) were used as the raw materials. After the batches were mixed completely, they were melted in alumina crucibles in an electrical furnace at 1450 °C. The heating rate was 10 °C/min, and the soaking time was 2.5 h in each experiment. The melts were then cast into steel mold, and were annealed at 500 °C for 30 minutes. After that, the specimens cooled within the kiln to room temperature, naturally.

Differential thermal analysis (DTA) was used to determine the crystallization temperature for each sample. In this way, 1.5 g of each sample with particle size between 0.3- 0.5 mm was heated up to 1000 °C with a heating rate of 10 °C/min. Heat-treatment of the glasses was performed at the determined peak crystallization temperature for one h.

The crystallinity of the samples, prior and after the heat-treatment process was identified using X-ray diffractometer (Philips PW-1800) with Cu-Kα radiation. XRD patterns were recorded for 2 theta values from 5° to 80° with a step size of 0.1°. Before diffractometry, each sample was pulverized to reach the dimension of < 63 micro meters.

The evaluation of the glass-ceramics microstructure was done by the scanning electron microscope (TESCAN VEGA II). In this way, the samples were mounted, polished and then chemically etched in a 2 wt. % HF solution for 25 s , then coated with a thin layer of gold.

Micro-hardness of the samples was measured using the Vickers micro-hardness tester (MXT-al) with a diamond pyramid indenter. The applied load and the loading time were 300 g and 10 s, respectively. The reported hardness number was the mean of at least ten indentations on each specimen derived by the following equation:

$$VH = \frac{1.854\,F}{d^2}$$

Finally, for chemical solubility measurement of both glasses and glass-ceramics, each sample was pulverized to reach the diameter of approximately 1.895 mm. According to ISO 6872, 3g of each sample was dried at 110 °C for 4 h, and then was soaked in 4vol. % acetic acid and heated at 80 °C for 16 h. The lost weight of the samples was considered as a criterion for their chemical resistance[6].

3. RESULTS AND DISCUSSION

3. 1. Differential Thermal Analysis (DTA)

Fig. 1 shows the DTA trends of the glasses. Based on the results, three exothermic peaks can be seen in each glass. According to X-ray

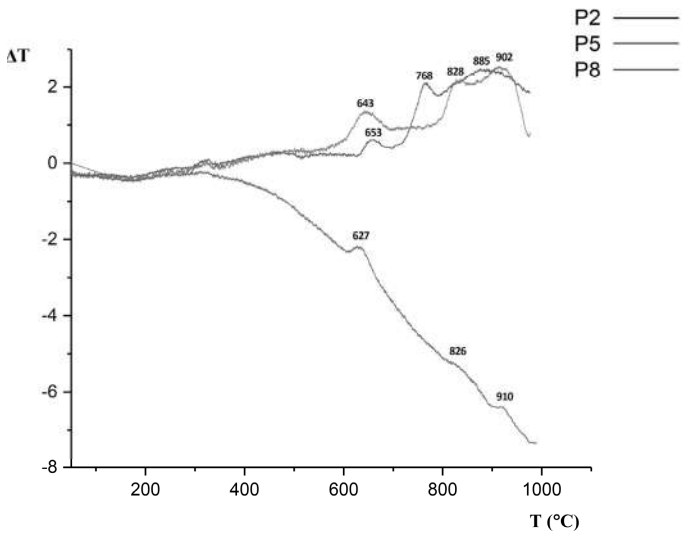

Fig. 1. DTA graph for P_2, P_5 and P8 samples with heating rate 10 °C/min

[Downloaded from fn.iust.ac.ir on 2025-07-19]

[DOI: 10.22068/ijmse.15.1.17]

diffraction results, which are indicated in Figs. 2, 3 and 4, the first exothermic peak is attributed to crystallization of Li_3PO_4. As it can be seen, the first peak reasonably shifts to a lower temperature with increasing of P_2O_5. However, the second and the third peaks that based on the XRD results are attributed respectively to crystallization of lithium meta-silicate and lithium di-silicate, shift inversly to higher temperatures with increasing of P_2O_5. It is clear that crystallization of more lithium phosphate makes the residual glass phase more poor in lithium ion. Therefore, it'll be reasonale that the crystallization temperature of both lithium silicate phases, i.e.meta and di-ones, shift to higher temperatures and their intensities become weaker with more using of P_2O_5. Such an effect of P_2O_5 has already been reported by X. Zheng et al. [7].

3. 1. 1. Phase Evolution and Microstructural Survey

Based on the XRD results, ZrO_2 precipitates also in the glasses with increasing of heat-

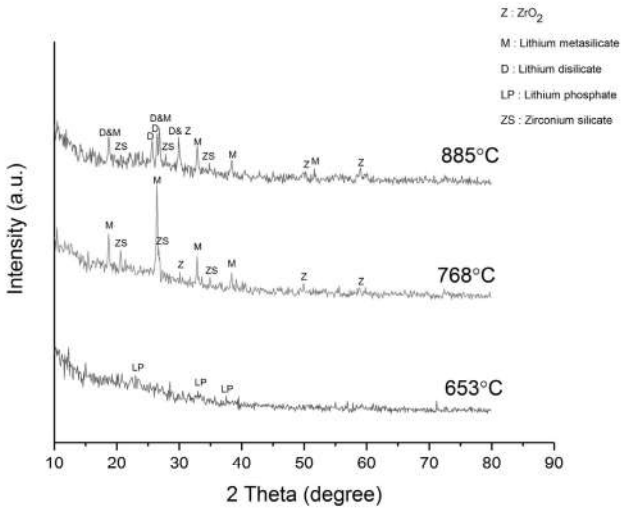

Fig. 2. XRD patterns of glass P_2 after heat-treatment for 1 h at each exothermic peak temperature

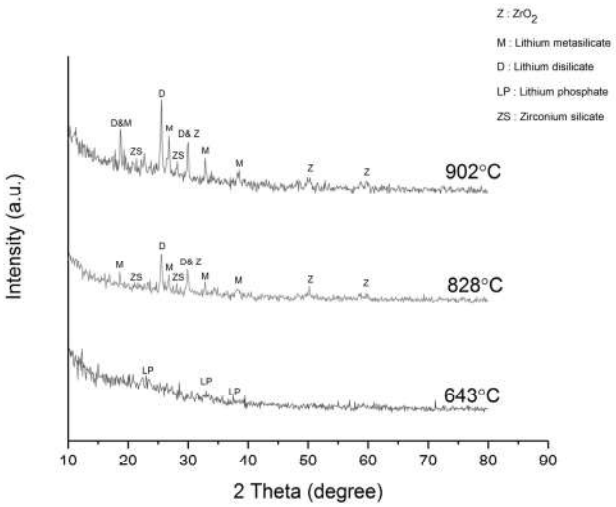

Fig. 3. XRD patterns of glass P_5 after heat-treat-treatment for 1 h at ach exothermic peak temperature

[Downloaded from fn.iust.ac.ir on 2025-07-19]

[DOI: 10.22068/ijmse.15.1.17]

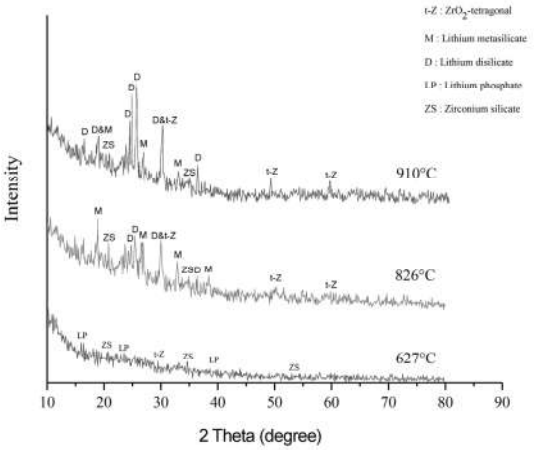

Fig. 4. XRD patterns of glass P_8 after heat-treatment for 1 h at each exothermic peak temperature

treatment temperature. This event is more visible for the sample P_8 in which zirconia shows itself as another main crystalline phase.

Fig. 5 shows the SEM micrographs of the specimens after heat-treatment at different exothermic peaks.

It is said a nucleation and growth type of liquid- liquid phase separation occurs by adding P_2O_5, so that amorphous phosphorous- based drops enriched in Li ions separates into a glassy matrix eventually form nano-size region [12]. During the next heat-treatment process, lithium meta-silicate precipitates which substitutes gradually with temperature by lithium di-silicate. According to our results (Figs. 5a and 5c), the morphology of the silicate phases remains unchanged during this phase alteration. It can be deduced from these results that lithium di-silicate had epitaxic growth on the lithium meta-silicate; means that lithium di-silicate has been deposited layer by layer on the meta lithium silicate substrate with the same microstructure [13-16].

By comparison of XRD patterns and SEM micrographs, it can be concluded that with increasing of P_2O_5 a more but smaller lithium phosphate drops was formed. This will reduce the distance and/or space between the P_2O_5 drops. This inter- drops space will then act as a spatial obstacle for growing of the main crystalline phases, i.e. lithium meta-silicate and/or lithium di-silicate, ultimately leads to finer final morphologies [13,16].

3. 1. 2. Vickers Micro-Hardness

Table 2 shows the average micro-hardness of at least ten indentations on each specimen.

It is known that hardness of glass-ceramics depends on the nature of both the glassy and crystalline phases, the amounts of crystalline phases, their size, their morphology, etc. In these samples, the micro-hardness of the glass-ceramics has been increased with increasing the content of P_2O_5. This improvement can be attributed to precipitation of much more and also finer lithium di-silicate crystals with addition of P_2O_5. It should also be considered that these modifications may improve other mechanical properties of the substance like strength and fracture toughness, which are essential parameters for the dental materials, act via crack deflection, crack pinning, etc. [15-18].

Table 2. Average Vickers Micro-Hardness of prepared samples

Sample code	Vickers Micro-Hardness
P2	779± 3
P5	995± 4
P8	1021± 3

[Downloaded from fn.iust.ac.ir on 2025-07-19]

[DOI: 10.22068/ijmse.15.1.17]

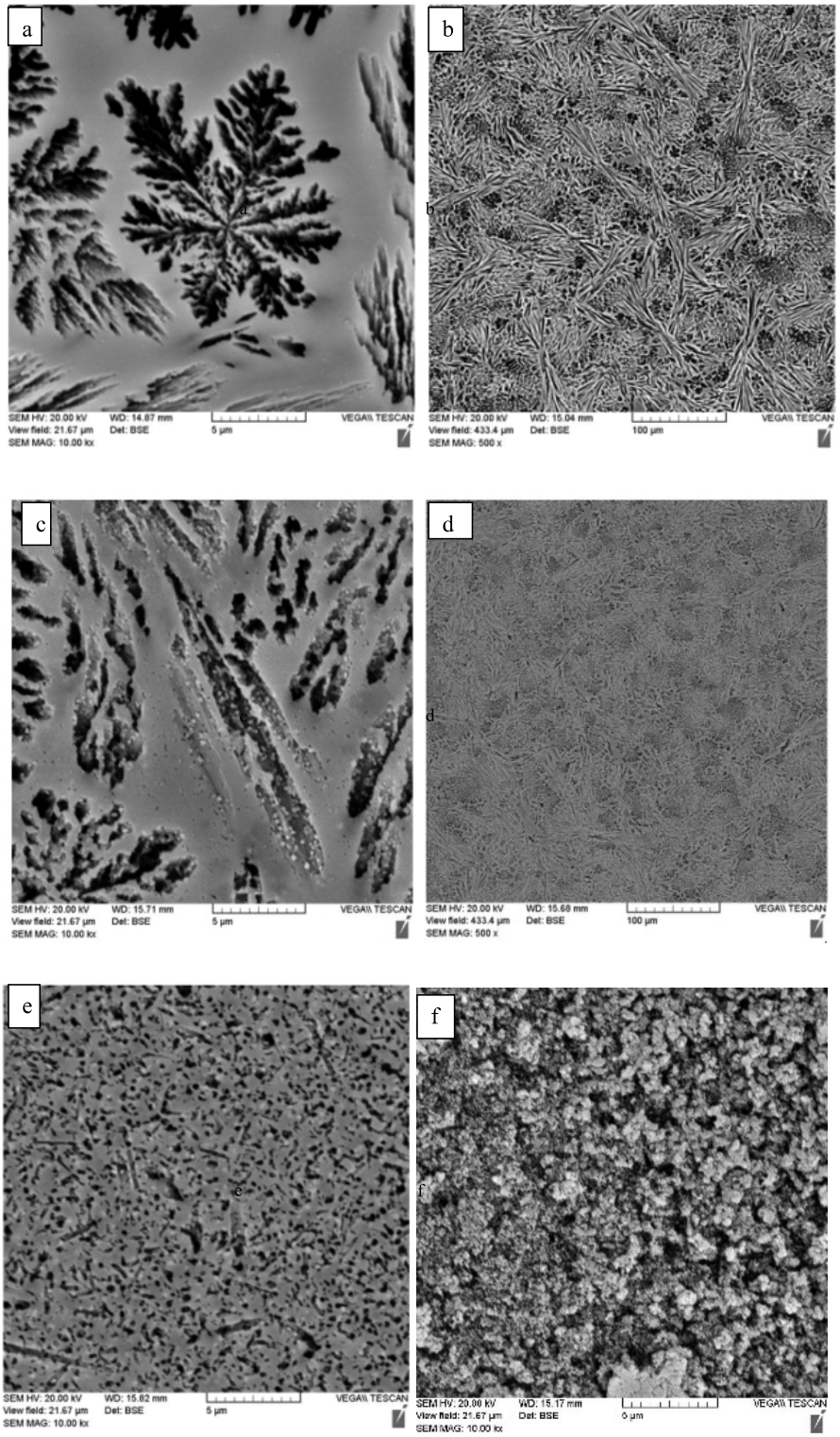

Fig. 5. Microstructures of the specimens: a, b) P_2 afterheat-treatment at its second exo-thermic peak temperature c,d) P_2 after heat-treatment at its third exo-thermic peak temperature e) P_5 after heat-treatment at its third exo-thermic heat-treatment temperature f) P_8 afterheat-treatment at its third heat-treatment temperature

[Downloaded from fn.iust.ac.ir on 2025-07-19]

[DOI: 10.22068/ijmse.15.1.17]

Table 3. Chemical solubility of the prepared samples

Sample code	Initial weight (g)	Secondary weight after acid solubility (g)	Decreased weight (mg)	Chemical solubility ($\mu g/cm^2$)
GC-P2	3	2.986	14	2080.300
GC-P5	3	2.989	11	1634.521
GC-P8	3	2.992	8	1188.743
Glass-P2	2.2	2.130	70	10401.500
Glass-P5	2.2	2.100	100	14859.280
Glass-P8	2.2	1.960	240	35662.280

3. 1. 3. Chemical Solubility

If the particles were supposed to be spherical, its surface area per 3.00 g for each specimen would be approximately 672.98 mm^2. Table 3. shows the results of the chemical solubility measurements of both glasses and glass-ceramics (GC).

According to standard limitations (ISIRI 12396/ISO 6872) for chemical solubility, 2000 is the maximum solubility which can be acceptable for glass-ceramics using as dental cores. Therefore, it can be concluded that except for GC-P_2, the chemical solubility of the other two glass-ceramics are within the standard range. Besides, as it can be seen the chemical resistance of glass-ceramic specimens improve with increasing of P_2O_5. Contrary, a comparison between the three glasses shows that the least chemical resistance belongs to glass P_8, whereas the highest belongs to glass P_2. As it was mentioned previously, P_2O_5 caused liquid- liquid phase separation in these glass systems[19], i.e. a phosphorous- rich and a silica- rich phases. If it happens,the P-rich region will easily dissolve in the corrosive environment leads to decrease of chemical resistance. Apparently, the solubility of Li_3PO_4 is much less than phosphorous ions of glass; therefore, it is expected that the chemical resistance of glasses be improved by removing P^{+5} from the glassy phase in the form of Li_3PO_4. Also, the volumes of residual glass phase decreases considerably with crystallization of the glass. This negligible glass phase being surrounded by the crystalline phases which keeps away it from the access of acid solution [20-23].

4. CONCLUSION

The effect of P_2O_5 on crystallization behaviors, micro-hardness and chemical resistance of three lithium silicate- based glass compositions were investigated. It was found that P_2O_5 encouraged the crystallization of both lithium silicate phases; although it increased the crystallization temperatures of the mentioned phases. Furthermore, P_2O_5 decreased the chemical resistance of the glasses, probably by encouraging the liquid-liquid phase separation in the glasses. On the contrary, the chemical resistance of the glass-ceramics improved by addition of phosphorous. This was attributed to precipitation of insoluble lithium phosphate phase and also protection effect of lithium silicate crystalline phases on phosphorous bearing residual glass phase.

REFERENCES

1. Apel, E., Hoen, C. V., Rheinberger, V. and Höland, W., "Influence of ZrO_2 on the Crystallization and Properties of Lithium Disilicate Glass-Ceramics Derived from a Multi-Component System, ,Journal of the European Ceramic Society, 2007, 27 (2–3), 1571-1577.
2. Malament, K. A., and Socransky, S. S., "Survival of Dicor Glass-Ceramic Dental

[Downloaded from fn.iust.ac.ir on 2025-07-19]

[DOI: 10.22068/ijmse.15.1.17]

Restorations over 16 Years. Part III: Effect of Luting Agent and Tooth or Tooth-Substitute Core Structure", The Journal of Prosthetic Dentistry, 2001, 86 (5), 511-519.

3. Höland, W., Schweiger, M., Frank, M., and Rheinberger, V., "A comparison of the Microstructure and Properties of the IPS Empress®2 and the IPS Empress® Glass-Ceramics", Journal of Biomedical Materials Research, 2000, 53 (4), 297–303.
4. Abolfathi, G. and Eftekhari Yekta, B., "Synthesis of Dental Fluoroapatite Glass - Ceramic Glazes", Ceramics – Silikáty, 2011, 55 (4), 394-400.
5. S. Mollazadeh, S, Eftekhari Yekta, B., Javadpour, J. Yusefi, A., and Jafarzadeh, T. S., "The Role of TiO_2, ZrO_2, BaO and SiO_2 on the Mechanical Properties and Crystallization Behavior of Fluorapatite–Mullite Glass–Ceramics", Journal of Non-Crystalline Solids, 2013, 361, 70–77.
6. B. Eftekhari Yekta, B., and Sh. Honarvar,S., "Effect of TiO_2 Addition on Bonding Strength of CaO-P_2O_5-Na_2O-TiO_2 Bioactive Glass-Ceramic Coating", Iranian Journal of Materials Science & Engineering, 2014, 11 (4), 1-7.
7. McLaren, E. A, and Cao, P. T., Ceramics in Dentistry—Part I: Classes of Materials, inside dentistry, 2009, 94-104.
8. Kelly, J. R., Nishimura, I., and Camp, S. D., "Ceramics in dentistry: Historical roots and current perspectives," Journal of Prosthetic Dentistry, 1996, 75, 18–32.
9. Denry, I., and Holloway, J. A., "Ceramics for Dental Applications: A Review," Materials, 2010, 3, 351-368.
10. M. Montazerian, M., Zanotto, E. D., "Bioactive and inert dental glass-ceramics", Journal of Biomedical Materials Research: Part A, 2017, 105 (2), 619-639.
11. Holand, W., Schweiger, M. , Rheinberger, V., and Kappert, H., "Bioceramics and their application for dental restoration," Adv. Appl. Ceram, 2011,108, 373-380.
12. Jones, H. D. W., "Some properties of dental ceramics," Journal of Oral Rehabilitation, 2007, 2 (4), 379-396.
13. Zheng, X., Wen, G., Song, L., Huang, X. X., "Effects of P_2O_5 and heat treatment on crystallization," Acta Materialia, 2008, 56, 549–558.
14. Holand, G., "Glass Ceramic Technology", American Ceramic Society, 2002,79-81.
15. Borom, M. P., Turkalo, A. M., and Doremus, R. H., "Strength and microstructure in lithium disilicate glass-ceramics," J. Am. Ceram. Soc., 1975, 58, 385-391.
16. Fernandes, H. R., Tulyaganov, D. U., and Ferreira, J. M. F., "The role of P_2O_5, TiO_2 and ZrO_2 as nucleating agents on microstructure and crystallization behaviour of lithium disilicate-based glass," Journal of Material Science,2013, 48, 765–773.
17. Montazerian, M., Alizadeh, B. and Eftekhari Yekta, B., "Pressureless sintering and mechanical properties of mica glass–ceramic/Y-PSZ composite," Journal of the European Ceramic Society, 2008, 28, 2687–2692.
18. Bergmann, C. P. and Stumpf, A., "Dental Ceramics: Microstructure, Properties and Degradation", Brazil: Springer, 2013,15-22.
19. Khalkhali, Z., Eftekhari Yekta, B., Marghussian, V. K. , "Preparation of Lithium Disilicate Glass-Ceramics as Dental Bridge Material", J. Ceram. Sci. Tech., 2014, 1, 39-43.
20. Khalkhali, Z., Eftekhari Yekta, B. , Marghusian, V. K. , "Mechanical and Chemical Properties of Zr and P-Doped Lithium Disilicate Glass Ceramics in Dental Restorations," International Journal of Applied Ceramic Technology, 2012, 9, 497-506.
21. Kelly, J. "Clinically relevant approach to failure testing of all-ceramic restorations," Prosthet., dent., 1999, 81, 652-661.
22. Esquivel-Upshaw, J. F., "Surface Degradation of Dental Ceramics as a Function of Environmental pH," Journal of Dental Research, 2013, 92, 467-471.
23. Sakaguchi R. L. , and Powers, J. M., "Craig's Restorative Dental Materials", Elsevier, ,13 ed., 2012, 83-108.

[Downloaded from fn.iust.ac.ir on 2025-07-19]

[DOI: 10.22068/ijmse.15.1.17]