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RESEARCH PAPER

Investigating the Effect of MgO and CeO_2 on the Crystallization Behavior of ZrO_2 in Li_2O-SiO_2-ZrO_2 Glass to Prepare a Dental Core for the Post Core System

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Abstract: *ZrO_2 is commonly incorporated into glass-ceramic dental post to enhance its radiopacity, mechanical strength, and chemical durability. Experience has shown that the crystallization of tetragonal zirconia in glass will have a more significant effect on the mechanical properties of the resulted sample. Stabilizing oxides are often added to achieve optimal properties in zirconia and enhance its structural and mechanical qualities. In this research, to stabilize the tetragonal phase of zirconia, MgO and CeO_2 were added gradually to the glass-ceramic composition of the Li_2O-SiO_2-ZrO_2 system, and the desired dental core was synthesized through the sintering process. The behavior of sintering and crystallization of basic and optimized glass was investigated using HSM (hot stage microscope) and DTA (differential thermal analyses), respectively. The results showed that the optimal sintering temperature, heat press, and heat treatment were 730°C, 900°C, and 825°C, respectively. To determine the crystallization behavior of the prepared samples, X-ray diffraction, and microstructure images were used. The results also showed that $Li_2ZrSi_6O_{15}$ crystallizes as the main crystalline phase at a temperature of 825°C in the base sample and the sample containing ceria. Also, due to the early formation of $MgSiO_3$ crystals, magnesia prevents sintering and formation of the $Li_2ZrSi_6O_{15}$ and stability of the tetragonal zirconia phase. In the sample containing ceria, during crystallization of ZrO_2 ceria entered into its crystal structure, leading to the stability of the tetragonal zirconia phase up to room temperature.*

Keywords: *Glass-ceramic, Dental glass ceramic, stabilized zirconia, IPS Empress Cosmo.*

1. INTRODUCTION

When the tooth needs nerve extraction, there is a possibility that the crown of the tooth will be lost. In such conditions, according to (Fig. 1-a), the presence of a core is necessary to create a base for the veneer, and the dental core itself needs a post inside the canal, which is the root [1]. Because of their beauty and non-sensitivity, ceramics have replaced metal-based dental restorations [2]. After developing the ZrO_2 post, a blank was required to be placed on the ZrO_2. To fulfill this need, Li_2O-SiO_2-ZrO_2 glass-ceramics with the IPS Empress Cosmo brand were developed by Schweiger et al. [3].

This glass-ceramic is placed on the ZrO_2 post through a heat press, by which a core is made that a leucite glass-ceramic crown will be placed on it [4-5]. Therefore, according to (Fig 1-b), the whole dental blind post system consists of a single product consisting of a stabilized ZrO_2 ceramic (CosmoPost) and a glass ceramic containing ZrO_2 (IPS Empress Cosmo). As a result, two completely different substances are combined and form a product in a specific process.

The composition and microstructure of glass-ceramic containing ZrO_2 after heat pressing at 900°C is characterized by a crystalline phase rich in ZrO_2. This crystalline phase is $Li_2ZrSi_6O_{15}$ [6-9].

Zirconia-based ceramics have attracted special attention in the last two decades due to their unique properties, i.e. high toughness, high mechanical strength, corrosion resistance, etc.). Pure zirconia is a polymorphic substance. This means that during heating and cooling, its crystal lattice changes. Based on this, monoclinic zirconia is stable from zero to 1170°C, tetragonal zirconia is stable from 1170°C to 2170°C, and cubic zirconia is stable from 2170°C up to its melting point (2680°C). Tetragonal to monoclinic transformation occurs at approximately 1170°C, accompanied by a volume expansion of about 3-5% [9]. Also, during heating, the monoclinic phase transforms into tetragonal, accompanied by a decrease in volume of about 9-10% [10]. The stresses caused by these expansions and contractions cause cracks in pure zirconia, which causes the ceramics made of this material to crumble during cooling from the sintering temperature or heating.

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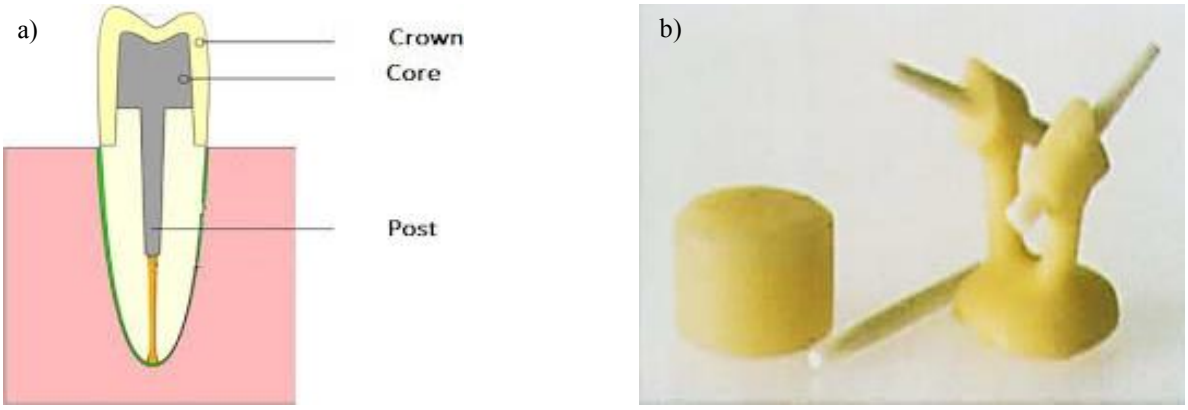

Fig. 1. a) Schematic of a post-core and its crown, b) CosmoPost cylindrical post with a conical tip and IPS Empress Cosmo core, produced using the heat press method

By entering of some metal oxides such as CaO, MgO, In_2O_3, Sc_2O_3, CeO_2, and Y_2O_3 into the zirconia structure, phase transformation will be prevented and the tetragonal zirconia will be stabilized at room temperature [11-12]. In this research, the effect of CeO_2 and MgO addition on the crystallization and sintering behaviors of traditional brand IPS Empress Cosmo glass-ceramic composition has been discussed. We expected that by adding the aforementioned oxides during the crystallization of zirconia, a solid solution of them would be formed in the zirconia network and its stabilization would occur.

2. EXPERIMENTAL PROCEDURES

Glass compositions, G_0, G_1, and G_2, were prepared according to Table 1. G_0 was used as an base composition without any stabilizer, and G_1 and G_2 included ceria and magnesia, respectively, to investigate the role of them in points of sintering and crystallization behaviors and zirconia stabilization ability as well. The raw materials used in this work were a high commercial silica sand (purity >99.5%), Lithium carbonate (Merck No.1.05671), zirconia (Merck No.1.00757), phosphorus pentaoxide (Merck No.1.00540), aluminum oxide (Merck No.1.01095), sodium carbonate (Merck No.1.06392), potassium nitrate (Merck No.1.05061), cryolite (Merck No.1.06457), cerium oxide (Merck No.1.02263), and magnesium oxide (Merck No.1.05865). The completely mixed batches were then poured into a silica crucible and melted for 1 h in an electric furnace at 1450°C. Then, the melt was fritted by quenching into distilled water. Each resulted frit was then ground into a hard mortar until its particles reached to d_{50}= 10 µm.

To investigate the sintering temperature of the glasses a hot stage microscope (HSM), ODHT HSM Misura, with a heating rate of 10°C/min was used. The crystallization behavior of the glass powders was investigated by differential thermal analyzer (DTA, Polymer Laboratories-1640 with the same heating rate of 10°C/min. To study the sintering of the glasses, the ground glass powders were compacted by a hydraulic press into tablets with a diameter of 17 mm, under a pressure of 50 MPa. The X-ray Diffractometry (XRD) of the samples was done by Bruker, Germany D8 advance machine, between 5-90 angles. The microstructural analysis of the fired samples was performed by scanning electron microscope (SEM), Tescan Czech Republic -mira3.

3. RESULTS AND DISCUSSION

Figure 2 indicates the DTA thermographs of the glass powders. Absence of a clear crystallization peak in each DTA trace indicates that if they crystallize during next heat treatment, i.e. during sintering, the crystallization mechanism will definitely be surface type.

Table 1. the chemical analysis of glasses (parts weight)

	SiO_2	Li_2O	ZrO_2	P_2O_5	Al_2O_3	Na_2O	K_2O	F	CeO_2	MgO
G_0	58.7	8	15.2	4.2	5	3.2	4.8	1	-	-
G_1	58.7	8	15.2	4.2	5	3.2	4.8	1	11.8	-
G_2	58.7	8	15.2	4.2	5	3.2	4.8	1	-	11.8

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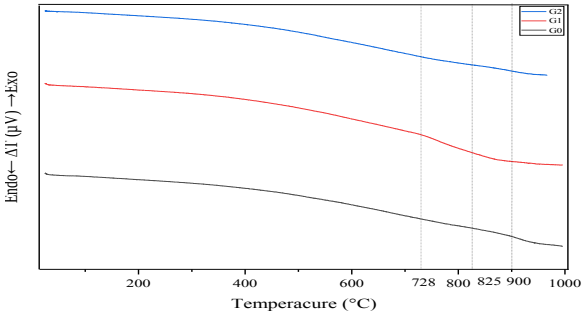

Fig. 2. the DTA curves of glass powders G_0, G_1, and G_2

HSM analysis was used to check the sintering temperature accurately. Instantaneous dimensional changes of glasses with increasing temperature were observed in a thermal microscope, and based on that, the length change curves according to temperature were drawn (Fig. 3). According to this curve, the shrinkage of the sample starts at a temperature of about 650°C. Then, the shrinkage of the sample increases with a steep slope until the shrinkage stops at the temperature interval 800-850°C. After that, contraction continues again. Based on the HSM result, the total decrease in the height of the sample from the ambient temperature to near 1000°C is approximately 55%; and the temperature at which the sample experiences 4-6% shrinkage, i.e. the end of sintering, based on the HSM definition, is about 728°C. Therefore, the samples were heat treated at this temperature for 2 h. Their XRD patterns are shown in (Fig. 4-a).

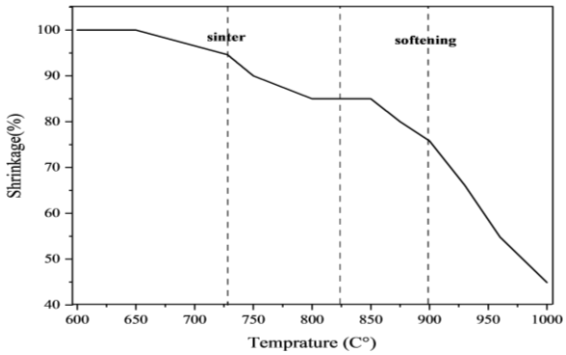

Fig. 3. HSM curve G_0 composition

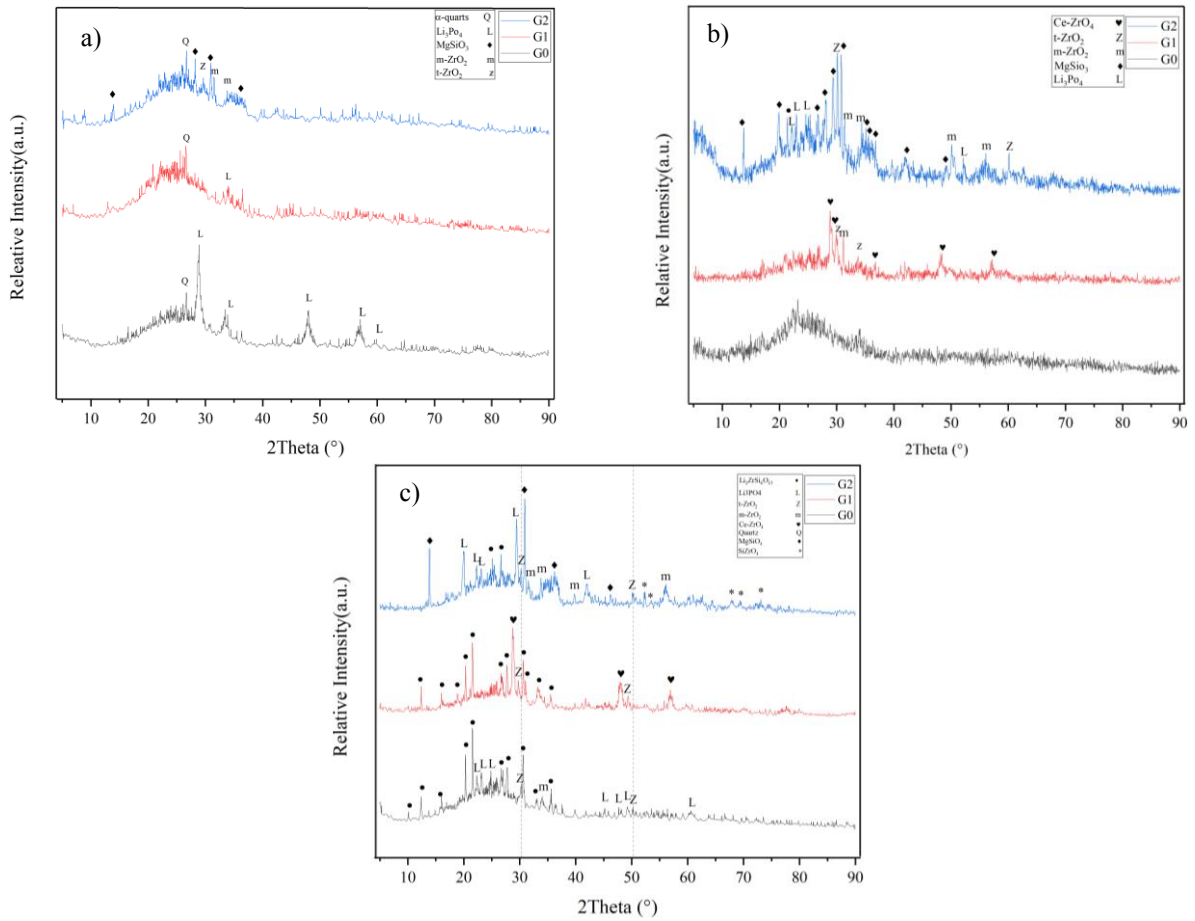

Fig. 4. XRD patterns of the three glasses G_0, G_1, and G_2 a) sintered at 728°C for 2 h. b) heat treatment at 728°C for 2 h, c) sintered at 728°C for 2 h and heat treated at 900°C for 20 min

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Also, the height of the sample remained constant in the temperature range of 800-850°C that was attributed to the occurrence of crystallization in it. Thus, to find the crystalline phase which crystallized at this temperature interval, the samples were heat treated at 825°C with a heating rate of 10°C/min for 2 h. The XRD patterns of these samples can be seen in (Figure 4-c).

After heat treatment at 728°C, the sample containing ceria showed an acceptable sinterability and a high linear contraction as well. Therefore, as can be expected, insignificant crystalline phases have crystallized in it (Fig. 4-a). In the base sample G_0, the main crystalline phase is tiny Li_3PO_4 crystals, which has formed as droplets rich in phosphate. In the magnesia containing sample, $MgSiO_3$ has apparently crystallized faster than other phases. It probably will delay the sinterability of this sample and will shift its sintering temperature to the higher. Also, both monoclinic and tetragonal zirconia and quartz have been precipitated in this glass. Based on the Fig. 4-b and Fig. 5-a, the G_0 which has been sintered at 825°C looks to be amorphous, and it does not show crystalline phase; according to (Fig. 3), this temperature is near to the softening temperature of the glass, i.e. around 900°C. Therefore, crystalline phases that could have crystallized in it before may have dissolved in it during the increase in temperature up to 825°C. It should be noted that at this temperature the sample was deformed. In sample G_1, the primary phase is Ce-ZrO_4 (Fig. 5-b), and the peaks belong to tetragonal zirconia are seen at $2\Theta = 29.85°$ and $2\Theta = 34°$. The peak shift is not comparable enough to check the stability. This sample was also deformed, like the base one. The sample G_2 was not deformed and the main precipitated phases in it were $MgSiO_3$, and Li_3PO_4. Monoclinic zirconia is also seen in it, means that magnesium, as a stabilizer, was unable to enter the zirconia structure during crystallization, and did not act as a stabilizer in this composition as well. It should also be emphasized that despite the expectation [3], the simulated heat press operation in the base sample caused phase dissolution and prevented the formation of the $Li_2ZrSi_6O_{15}$ in all samples. According to (Fig. 4-c) and (Fig. 5-d), $Li_2ZrSi_6O_{15}$ and tetragonal zirconia have precipitated in the G_0. Also, monoclinic zirconia and lithium phosphate can be seen in this sample. The mentioned result is consistent with the results of Schweinger et al. [3], even though in the latter work, they observed those crystalline phases only after heat pressing at 900°C.

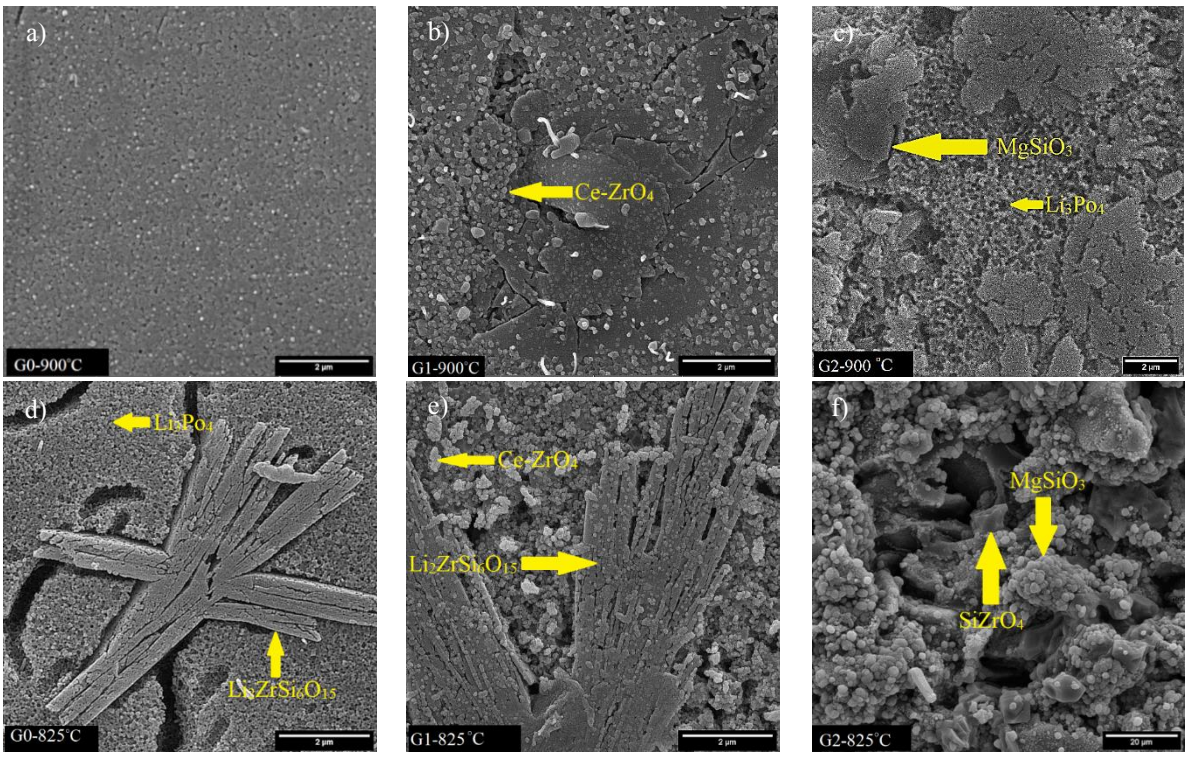

Fig. 5. SEM images of samples heat treated at 900°C for 20 min and chemically etched with 3% HF for 12 s, a) G_0, b) G_1, c) G_2 and heat treated at 825°C for 20 minutes 2 hours, d) G_0, e) G_1, j) G_2

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In sample G_1, the Li_3PO_4 phase is not seen; this sample is deformed and melted after being placed at this temperature. At this condition, the crystalline phase can be dissolved in the residual glass phase, as can be seen for Li_3PO_4 (Fig. 5-e). Due to the faster formation of $Ce.ZrO_4$ compared to ZrO_2, Zr ion consumed, and a small amount of it remains in the residual glassy phase to form tetragonal zirconia. Comparing this sample with the G_0, peak shift to the left, due to the entrance of ceria in the zirconia structure, is observable. Absence of the monoclinic zirconia was also attributed to formation of stabilize tetragonal zirconia in this sample. Sample G_2 indicates monoclinic zirconia, tetragonal zirconia, and $MgSiO_3$. Also, contrary to other temperatures and other samples, zircon (Fig. 5-j) is seen in this sample.

SEM images of the samples heat treated at 825°C show the presence of $Li_2ZrSi_6O_{15}$ phase with snowflake-like morphology in the G_0 and the samples containing ceria (Fig. 5-d and 5-e). The amount of this phase in the sample containing ceria is apparently higher than that of the base composition. Also, in the base sample (Fig. 5-c), Li_3Po_4 is not observed, due to chemical etching. In the G_1, in addition to the $Li_2ZrSi_6O_{15}$, crystals of $Ce\text{-}ZrO_4$ are also seen (Fig. 5-e). In the sample G_2-825°C, which unlike the other two samples, did not show a good sinterability, considerable $MgSiO_3$ and $SiZrO_4$ crystals are visible (Fig. 5-j). Also, monoclinic and tetragonal ZrO_2 crystals were not seen by SEM in all samples due to their small size.

4. CONCLUSIONS

Comparing the sinterability of the samples, while addition of 12 parts by weight of CeO_2 improved the sinterabilty of the base glass, MgO prevented it. Apparently, precipitation of $MgSiO_3$ was responsible for this behavior.

The presence of ceria in the sample heat-treated at 825°C caused that tetragonal zirconia became stabilized up to the room temperature. In the base sample and the sample containing magnesia, we saw the presence of monoclinic zirconia, indicated the instability of the tetragonal isomorph in these two samples.

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