Fracture toughness of experimental mica-based glass-ceramics and four commercial glass-ceramics restorative dental materials

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INTRODUCTION

Glass-ceramics are widely used as dental restorative materials because of their superior esthetics and excellent biocompatibility. Even they possess low fracture resistance when compared with metal or polycrystalline ceramics but their unique pleasing optical appearance cannot be simply matched by other high strength restorative materials. This is the main reason for their extensive use in dental daily practice. Many glass-ceramic systems are developed or modified to resolve their inferior fracture toughness and brittleness. An increase in the crystallinity by a controlled crystallization process or adding some crystalline particles are frequently utilized to improve their mechanical properties1-3.

There are several types of glass-ceramic restorative dental materials such as mica-based, leucite-based, lithium disilicate-based and zirconia reinforced lithium silicate (ZLS) ceramics2-5. The leucite-based ceramic is commonly used to fabricate partial coverage dental restorations such as inlay, onlay, and veneers. Because of its low fracture toughness (approximately 1.3 MPa·m1/2)5, the leucite-based ceramic is not recommended for use as a full coverage crown and bridges in the area with high chewing loads. For a lithium disilicate-based ceramic, this material consists of rod-like lithium disilicate crystals (approximately 70% as claimed by the manufacturer), the fracture toughness is approximately 2.3–2.9 MPa·m1/2 and its use is expanded to a full coverage crown and bridges for the anterior teeth5. ZLS is a newly developed dental glass-ceramic. This material consists of fine lithium silicate crystals and 10 wt.% zirconia, and its mechanical properties are expected to be comparable to those of a lithium disilicate-based ceramic5. The major advantage of leucite-based, ZLS and lithium disilicate-based ceramics is that they have varieties of color and translucency to match those of the natural teeth. The ability to bond to the tooth structure using silane coupling agents also enhances their clinical application by increasing the fracture resistance of the bonded restoration5-9.

The mica-based glass-ceramic had been used in dentistry since the late 1980’s. Dicor was the first commercially available dental glass-ceramic based on the tetrasilicic fluororna (KMg2.5Si4O22F2) phase10. By using a lost-wax technique, a full anatomical restoration could be cast from the melting glass and heat-treated afterward to get a glass-ceramic restoration. It was also used as a machinable glass-ceramic block when there was an introduction of a computer-aided design and computer-aided manufacturing process (CAD/CAM) for use in dentistry. However, its use was discontinued shortly after an introduction into the dental applications because of its high fracture rate when compared with other dental restorative materials11,12. Because mica-based glass-ceramics possess excellent machinability and biocompatibility, some alterations in composition and processing techniques have been explored by many researchers. Various compositions of mica-based materials were developed such as fluorophlogopite (KMg(AlSi3O10)F2), calcium-mica (Ca4(AlSi3O10)(F2)), potassium fluorrichterite (KNaCaMg2Si14O40F8) and calcium-mica (Ca4(AlSi3O10)(F2)). The

The mica-based glass-ceramics were prepared in the SiO2-Al2O3-MgO-MgF2-SrCO3-CaCO3-CaF2-P2O5 glass system. There were four mica-based glass-ceramics produced in this study according to the pigment added (CeO2 or Fe-ZrSiO4/Fe-ZrSiO4) and crystallization time (5–35 min). Four dental glass-ceramics, which were leucite-based, lithium disilicate-based and two zirconia reinforced lithium silicate ceramics, were also tested. The phase identification of mica-based glass-ceramics was performed using an X-ray diffractometer. The fracture toughness (KIC) was determined using the fractographic analysis approach. The one-way ANOVA was used to analyze the significant differences among the obtained KIC values at α=0.05. The results from the phase analysis showed that the mica glass-ceramics consisted of calcium-mica, fluorapatite and strontiumapatate. The KIC of mica-based glass-ceramics ranged between 1.36 to 1.53 MPa·m1/2 which were superior to only that of a leucite-based glass-ceramic. The shade and translucency of mica-based glass-ceramics appeared to be acceptable for dental application when compared with other dental glass-ceramics.

Keywords: Glass-ceramic, Mica, Fracture toughness, Dental
addition of Ca²⁺ to replace K⁺ or Na⁺ at the interlayers was devised to strengthen the bulk material^{16}. The mica-based material containing some fluorapatite crystals (Ca₅(PO₄)₃F) were also formulated to promote the bioactivity and toughen the glass-ceramic^{16}. In addition, an increase in the fracture toughness of a mica-based material was reported from few studies when the glass-ceramic was fabricated using a hot pressing technique^{16,17}. An increase in the fracture toughness was a result of the realignment of the mica crystals perpendicular to or along the hot pressing direction.

In a previous study, the calcium-mica containing fluorapatite was developed for a potential use as a dental restorative material^{16}. Introduction of Sr²⁺ to the interlayer ions of the mica structure could modify the hardness of this material to match that of human enamel while growing some fluorapatite (Ca₅(PO₄)₃F) within the calcium-mica, therefore, it could increase its flexural strength and fracture toughness^{19}. The high fracture toughness (2.04 MPa·m¹/²) was reported due to its high crystallinity caused by prolonged crystallization time (3 h). This result was in agreement with that obtained from a study by Taruta et al.^{20} who reported that higher content of fluorapatite crystals combined with a fine calcium-mica microstructure gave higher bending strengths and hardness than those with a lower amount of fluorapatite crystals. However, its high opacity and white color were not suitable for a dental use. Therefore, the nucleation and crystallization times were modified to obtain a more translucent material in this study. The objective of this study was to investigate the effect of crystallization times on the fracture toughness of glass-ceramics containing calcium-mica and fluorapatite crystals. The effect of oxide pigments on the microstructure and property of this glass-ceramic was also examined.

MATERIALS AND METHODS

Preparation of mica-based glass-ceramic specimens

The composition of the experimental base glass in weight percent was SiO₂ 37%, Al₂O₃ 11.9%, MgO 15.9%, MgF₂ 11.5%, SrCO₃ 13.6%, CaCO₃ 6.5%, CaF₂ 0.6%, and P₂O₅ 3%. All compositions were mixed in a ceramic bottle and rotated in a rolling machine for 2 h to assure the thorough mixing. The mixed chemicals were melted for 1 h at 1,450°C in a high temperature furnace (HT 16/18, Nabertherm, Lilienthal, Germany) and quenched in water at room temperature to obtain the glass frit. The frit was dried, crushed and sieved through a 325 mesh (45 µm). The oxide ceramic pigment was added to the glass frit and mixed using a rolling machine for 2 h.

The pigments chosen for this study are CeO₂ and zircon-based pigments (ZrSiO₄). ZrSiO₄ consisted of Pr-ZrSiO₄ and Fe-ZrSiO₄ and they were mixed with a ratio of 10:3. Pr-ZrSiO₄ and Fe-ZrSiO₄ are yellow and deep brownish red shades respectively. CeO₂ is a yellow substance. These coloring substances were added to the experimental glass-ceramics in order to make them suitable for dental applications^{21}. CeO₂ can also be used as a flux and a nucleating agent^{22,23}. Zircon-based pigments are widely used in the ceramic industry because of their high color intensity and excellent color stability. They are stable at temperatures up to 1,300°C^{21,24,25}. They could be used to adjust the color level in substances, such as yellow praseodymium zircon (Pr-ZrSiO₄), red ferrite red zircon (Fe-ZrSiO₄), red bricks and blue vanadium zircon (V-ZrSiO₄), respectively, as well as an opacifier in a glass-ceramic^{26}. The ratio of oxide pigments used in this study is shown in Table 1.

Fig. 1 The nucleation and crystallization heat treatment process of mica-based glass-ceramics.

The obtained glass frit (mica frit+pigment) was re-melted and poured into a cylindrical carbon mold. After annealing at 582°C for 1.5 h, a glass rod specimen was cooled down to a room temperature and cut into a rectangular block with a height of 18 mm and heated to the nucleation and crystallization temperature at 16/18, Nabertherm, Lilienthal, Germany) and quenched in water at room temperature to obtain the glass frit. The frit was dried, crushed and sieved through a 325 mesh (45 µm). The oxide ceramic pigment was added to the glass frit and mixed using a rolling machine for 2 h.

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| Mica frit (wt%) | Pigment (wt%) | Nucleation (min) | Crystallization (min) | Group       |
|----------------|--------------|------------------|-----------------------|-------------|
| 99             | 1            | —                | 10                    | MicaCe35    |
| 99             | 1            | —                | 10                    | MicaCe5     |
| 96             | —            | 4                | 10                    | MicaZr30    |
| 96             | —            | 4                | 10                    | MicaZr12.5  |
642 and 897°C respectively in order to transform into a glass-ceramic block, as shown in Fig. 1.

**Microstructural analysis: X-ray diffraction (XRD) for phase analysis.**

After the nucleation and crystallization processes, the crystalline phases of glass-ceramics were analyzed using an X-ray diffractometer with Cu-Kα, X-ray (PW3040/00, Philips, Eindhoven, the Netherlands). The specimens in each group were scanned from 5° to 85° with a step size of 0.01° and account the time of 0.5 s at 30 kV and 40 mA.

**Microstructural analysis: Percent crystallization**

Bar-shape specimens (1.5×4×18 mm) were prepared for the percent crystallization analysis of mica-based glass-ceramics. The surfaces of these specimens were ground through 2000-grit silicon carbide abrasive and polished through 1 µm-alumina paste suspension. The etched surface was coated with gold using a sputtering technique (Polaron SC7620 sputter coater, Quorum Technologies, Lewes, UK). Five micrographs were taken randomly from each group were scanned from 5° to 85° with a step size of 0.01° and account the time of 0.5 s at 30 kV and 40 mA.

**Fracture toughness determination: The quantitative fractographic analysis approach**

The fractographic analysis is well established for analyzing the fracture surface of ceramics, glasses and other brittle materials. The estimation of fracture toughness (KIC) can be obtained via the fractographic analysis of strength test specimens. By identifying the location, size and geometry of the failure-initiating flaw and the stress at failure are known, KIC can be calculated using the Griffith-Irwin Equation. The significant advantage of this approach is that a small specimen can be used without any complicated surface crack or notch preparation. The calculation using the Griffith-Irwin Equation is also simple and straight forward. In this study, fifteen bar-shape specimens of each mica-based glass-ceramic were cut from crystallized rectangular blocks using a low-speed cutting machine and diamond-coated disk (Isomet®, BUEHLER, Lake Bluff, IL, USA) with water lubrication. Then, they were wet polished on the grinding machine through 2000-grit silicon carbide (SiC) abrasive papers respectively. The four sharp edges of each specimen were rounded with a 600-grit SiC paper. Final dimensions of all bar specimens were 1.5×4×18 mm.

Four commercial dental glass-ceramics which were leucite-based, lithium disilicate-based and ZLS ceramics were also prepared and used as control groups. The details of these materials are summarized in Table 2. Fifteen bar specimens of each dental glass-ceramic were cut from rectangular blocks and finished using similar protocols as previously described for mica-based glass-ceramics.

In order to produce a semi-circular controlled flaw, a Vickers indentation was made on the mirror-like surface of each specimen (FM-700, Future-Tech, Tokyo, Japan). The criteria for selecting an optimal Vickers indentation load were (1) only four radial cracks originated from the corner of indentation were presented with the length more than 2.5 times of Vickers pyramidal impression, (2) the indentations were symmetry without crack chipping or branching. From these criteria, the Vickers loads used were 2.94 N for MicaZr12.5 and MicaZr30, 9.8 N for CELTRA, VITA SUPRINITY and IPS Empress CAD. For IPS e.max CAD, a Vickers indentation load was 49 N. For MicaCe5 and MicaCe35, an indentation-controlled flaw could not be made because of chipping of material at all loads selected. The hardness values of all experimental were also determined using the Vickers indentation at 2.94 N load and 15 s dwell time for use as reference information.

After indentation, all specimens were loaded to fracture at the cross speed of 0.5 mm/min using a three-point bending fixture mounted on a universal testing machine (LF Plus Lloyd instruments, Ametek, Largo, FL, USA) with an indentation on the tensile surface. Failure loads of the bar specimens were used to calculate the flexural failure stress (σ) using the following equation.

\[
\sigma = \frac{3PL}{2wb^2}
\]

**Table 2 Details of four commercial dental glass-ceramics used in this study**

| Product          | Type/Composition                                         | Manufacture                        |
|------------------|----------------------------------------------------------|------------------------------------|
| IPS Empress CAD  | Leucite-based glass ceramic/60-65% SiO₂, 16–20% Al₂O₃, 10–14% K₂O, 3.5–6.5% Na₂O and others | Ivoclar-Vivadent, Schaan, Liechtenstein |
| IPS e.max CAD    | Lithium-disilicate-based glass ceramic/57–80% SiO₂, 11–19% Li₂O, 0–8% ZrO₂ and others   | Ivoclar-Vivadent                   |
| Celtra® Duo      | Zirconia reinforced lithium silicate glass ceramic/ ~10% ZrO₂ but not specified for SiO₂, Li₂O and others | Dentsply, Hanau-Wolfgang, Germany    |
| VITA SUPRINITY®  | Zirconia reinforced lithium silicate glass ceramic/ 56–64% SiO₂, 15–21% Li₂O, 8–10% ZrO₂ and others | VITA Zahnfabrik H. Rauter, Bad Säckingen, Germany |
Fig. 2 XRD patterns of as-received glass and a glass-ceramic crystallized at 897°C.

Where $P$ is the load at failure (N); $l$ is the distance between center of outer support rollers or test span, which is 16 mm; $w$ is the width of specimen, and $b$ is the thickness of the specimen.

The fracture specimens obtained from the 3-point bending test were used for the fracture surface analysis. These specimens were cleaned with ethanol in an ultrasonic cleanser for 10 min and blown dried before mounted on a metal stub with a conductive carbon adhesive tape. They were sputter-coated with gold using a sputter/carbon coater (SPI Module®, SPI Supplies, Structure Probe, Ontario, Canada). The critical flaw size was measured on the fracture surface using an optical stereomicroscope at 120 magnifications (Nikon SMZ1000, Tokyo, Japan) with an optical fiber illuminator (Photonic PL2000, Vienna, Austria). The critical flaw size ($c$) was determined according to the following relation:

$$c = (ab)^{1/2}$$  \hspace{1cm} (2)

Where $a$ is the depth of the crack and $b$ is the half-width.

Then, the fracture toughness was calculated by Equation

$$K_{IC} = Y \sigma_f (c)^{1/2}$$  \hspace{1cm} (3)

Where $Y$ is a constant dependent on the crack geometry and loading conditions ($Y=1.65$ for indented specimen, $Y=1.24$ for specimens without indentation), $\sigma_f$ is the flexural failure stress (MPa) and $c$ is the critical crack size (m).

The fracture surfaces of specimens in each experimental group were also examined using a scanning electron microscope (SEM, Phillips XL 30) and the SEM images were recorded from the representative fracture surfaces to identify the failure pattern.

The optical characteristics of mica-based glass-ceramics were compared with those of four dental glass-ceramics to confirm the suitability for dental applications of these glass-ceramics. The rectangular-shape specimens with the dimension of 14×12×1 mm were cut from the mica-based and four dental glass-ceramic blocks and polished through 600-grit silicon carbide abrasive papers on both sides. These glass-ceramic slices were positioned on the printed transparent plastic sheet and an X-ray film illuminator box and a photograph was taken using a digital camera (Canon EOS 60D DSLR with Macro Lens EF-S 60 mm f2.8 USM and Macro Ring Lite MR-14EX, Canon, Tokyo, Japan).

Statistical analysis of the fracture toughness values

The Shapiro-Wilk test and Levene’s test were used for testing the normality of data and the homogeneity of variance. The one-way analysis of variance was performed to determine the statistically significant differences of the mean fracture toughness values among materials tested, followed by Tukey’s HSD post-hoc test for comparisons of the mean values at $\alpha=0.05$.

RESULTS

Phase analysis and percent crystallization

The XRD results of all mica-based glass-ceramics are shown in Fig. 2. The XRD pattern of a base glass showed hump peaks indicated that it was amorphous material. After crystallization, the glass-ceramics contained calcium magnesium aluminum fluoride silicate ($CaMg_6Al_2Si_6O_{20}F_4$), fluorapatite ($Ca_5(PO_4)_3F$), strontiumapatite ($Sr_6Ca_4(PO_4)_6F_2$), strontium aluminum silicate ($SrAl_2Si_2O_8$) and cordierite ($Mg_2Al_4Si_5O_{18}$) ceramic phases. The pigments added did not affect the type of crystals because of no obvious differences among the crystals grown in the four ceramics. The percent crystallization of mica-based glass-ceramics is summarized in Table 3. The representative SEM pictures of mica crystals are shown in Fig. 3.

In this study, the nucleation and crystallization times were modified to obtain a more translucent material. Two levels of translucency were produced for...
Table 3  The mean fracture toughness values and their standard deviation of dental ceramics used in this study

| Materials            | Mean $K_{IC}$ (MPa•m$^{1/2}$) | Hardness (GPa) | Percent crystallization (%) |
|----------------------|---------------------------------|----------------|-----------------------------|
| MicaCe35             | 1.36 (0.11)$^A$                 | 3.5            | 71.8                        |
| MicaCe5              | 1.38 (0.13)$^A$                 | 3.7            | 69.5                        |
| MicaZr30             | 1.41 (0.19)$^{A,B}$             | 3.5            | 72.2                        |
| MicaZr12.5           | 1.53 (0.10)$^B$                 | 6.6            | 65.9                        |
| IPS Empress CAD      | 1.09 (0.10)$^C$                 | 5.5            | 35–45$^*$                   |
| IPS e.max CAD        | 2.64 (0.19)$^C$                 | 5.5            | =70$^*$                     |
| CELTRA               | 1.75 (0.21)$^D$                 | 6.8            | N/A                         |
| VITA SUPRINITY       | 1.86 (0.11)$^D$                 | 6.8            | N/A                         |

Values with different superscript letters are statistically different ($p<0.05$).

*Data obtained from the manufacturers.

Fig. 3  The microstructure of the chemically etched surface of mica-based glass-ceramics (a) MicaCe35 (b) MicaCe5 (c) MicaZr30 (d) MicaZr12.5.

Fig. 4  The optical characteristics of glass-ceramic specimens tested in this study. (a) MicaCe35, (b) MicaCe5, (c) MicaZr30, (d) MicaZr12.5, (e) IPS Empress CAD, (f) IPS e.max CAD, (g) CELTRA, (h) Vita SUPRINITY and (i) Mica.
each CeO₂ and Pr-ZrSiO₄/FeZrSiO₄-added mica-based glass-ceramic by controlling the crystallization time. However, because of different chemical and thermal properties of the pigments added, the crystallization times were slightly different for each pigment. The effect of crystallization time on the optical characteristics of mica-based glass-ceramics are illustrated in Fig. 4. The amount of crystal phases for the mica-based materials developed in this study was approximately 68–72% and they were more translucent (Fig. 4a–d) than the prototype materials (Fig. 4i) but comparable to other dental glass-ceramics (Fig. 4e–h).

The fracture toughness determination

The mean fracture toughness values of mica-based and dental glass-ceramics obtained from the fractographic analysis method are shown in Table 3. The results from the Shapiro-Wilk test showed that the fracture toughness values of mica-based glass-ceramics, leucite-based glass-ceramic, lithium-disilicate-based glass-ceramic and ZLS glass-ceramics were normally distributed (p>0.05). The homogeneity of variances was confirmed using Levene’s test. The results from the one-way analysis of variance and Tukey’s HSD test showed that the fracture toughness of IPS e.max CAD was significantly higher than those of the other groups while the fracture toughness of IPS Empress CAD was the lowest. The fracture toughness of mica-based glass-ceramics was inferior to those of lithium-disilicate-based glass-ceramic and ZLS glass-ceramics but they were superior to that of a leucite-based glass-ceramic. These mica-based glass-ceramics could be classified as dental ceramics type II class 1 and 2 according to their fracture toughness values as recommended by ISO 6872:2015-Dentistry-Ceramic materials. These types of ceramic can be used as monolithic or substructure of adhesively cemented single-unit anterior or posterior prostheses, veneer, inlays, onlays. The fracture toughness of mica-based glass-ceramic containing Pr-ZrSiO₄: Fe-ZrSiO₄ tended to be higher than those with CeO₂ color pigment which might be the results from the slight differences in their microstructure.

The representative pictures of the critical flaw of indented and un-indented specimens taken under an optical stereomicroscope at 120 magnifications are shown in Fig. 5. The black arrows outlined the critical flaw of each specimen on the fracture surface. The representative SEM pictures of fracture surfaces of all glass-ceramics used in this study are shown in Figs. 6 and 7. For mica-based glass-ceramics (Figs. 6a–d), the plate-like structures were clearly observed and they were surrounded by the glass matrix. Because of randomly oriented mica crystals, the fracture surface appeared to be tortuous from transcrystalline fracture. Crack paths could be along the cleavage planes or tilted across the layered structure of mica crystals. For MicaZr12.5, the glass matrix surrounded the crystals was more discernable because of its lower crystallinity.

For a leucite-based dental ceramic (Fig. 7a), the microstructure of IPS Empress CAD consists of a glassy matrix and leucite crystals with the diameter of 1–5 µm. Its fracture surface appeared to be tortuous with the clearly seen glass matrix. For a lithium-disilicate-based glass-ceramic, it consisted of fine rod-like crystals embedded in a glass matrix (white arrows in Fig. 7b). For ZLS dental ceramics (Figs. 7c–d), they consisted of

![Fig. 5](image)

The critical flaw on a fracture surface of (a) MicaCe5 (without indent), (b) MicaZr12.5 (with indent) and (c) IPS Empress CAD (with indent) under an optical stereomicroscope of specimen at 120×.
very small lithium silicate crystals which resulted in a homogeneous microstructure.

DISCUSSION

In this study, the mica-based glass-ceramics have been developed in an attempt for use as a dental glass-ceramic. For dental applications, a glass-ceramic should have acceptable mechanical properties to resist...
fracture during repeated chewing loading. The color and translucency are also an important factor as this ceramic should imitate the color and translucency of natural teeth for an esthetic reason. Few glass-ceramics have been developed for dental applications with an acceptable outcome such as a lithium-disilicate-based, a leucite-based glass-ceramic. Recently, ZLS glass-ceramics have been manufactured but there is limited information regarding their clinical performance. As previously emphasized, these dental glass-ceramics play a major role in restorative dentistry because of their esthetically pleasing optical appearance irrespective of their low-to-moderate fracture resistance. Because of their successful use in dentistry, they were chosen as control materials in this study with a wide range of dental application.

The mica-based glass-ceramic had been used in dentistry since 1980’s. Dicor was the first commercially available dental glass-ceramic based on the tetrasilicic fluormica (KMg$_2$Si$_4$O$_{10}$F$_2$) phase. However, its use was discontinued because of its high fracture rate when compared with other dental restorative materials. Afterward, various compositions of mica-based glass-ceramics were developed in order to improve their mechanical properties and expand their use into the dental community.

The composition of a mica-based glass-ceramic consisted mainly of calcium-mica and fluorapatite was developed in a previous study by Chaysuwan et al. The higher fracture toughness (2.04 MPa-m$^{1/2}$) of this mica-based glass-ceramic was due to its high crystallinity caused by prolonged crystallization time (3 h). However, its chalk-like appearance was not suitable for a dental use. Therefore, the nucleation and crystallization times were modified to obtain a more translucent material in this study. Not only the translucency of a mica-based glass-ceramic was modified, the pigments were also added to regulate the color of a glass-ceramic. CeO$_2$ was basically used to improve the crystallization of a glass-ceramic by decreasing the viscosity of the melted glass and crystallization time and temperature. Pr-ZrSiO$_4$ and FeZrSiO$_4$ were yellow and coral red color pigments. These zircon-based pigments including blue vanadium-ZrSiO$_4$ pigment are widely used in ceramic glazes because of their excellent thermal and chemical stability at high temperature production process. This triaxial color system is useful because a wide range of color could be produced by mixing these blue, red and yellow pigments at a different proportion to obtain the desired color. The tooth color is in the range of yellow and red, therefore, Pr-ZrSiO$_4$ and FeZrSiO$_4$ have been chosen to color the mica-based glass-ceramics. These zircon-based pigments were able to produce tooth-like colors without significant effects on physical or mechanical properties when they were mixed with lithium disilicate glass-ceramic. As shown in Fig. 4, the color of MicaCe5, MicaCe35, MicaZr12.5, and MicaZr30 were not as strong as those of the four dental glass-ceramics (Fig. 4e–h). However, it is encouraging that CeO$_2$ and Pr-ZrSiO$_4$/FeZrSiO$_4$ could be used for shading of the mica-based glass-ceramics. Modification of the amount and ratio of pigments added should be further investigated to obtain a wide variety of yellow-red color and translucency suitable for the dental application.

As presented in Fig. 3, the microstructures of MicaZr30 and MicaZr12.5 consisted of plate-like elongated crystals while the mica crystals within MicaCe35 and MicaCe5 appeared to be irregular in shape with lower aspect ratio. The crystal sizes of MicaZr30 and MicaCe35 also appeared to be slightly larger than those of MicaZr12.5 and MicaCe5, respectively. For mica-based glass-ceramics, crack deflection was reported to be the main toughening mechanism which caused an increase in the fracture toughness for materials in this group. When cracks propagate within a glass-ceramic, they are not only influenced by the mechanical properties of the glass matrix and the crystal phases, but it is also affected by the residual stresses generated from the thermal expansion and elastic constant mismatch between these two phases. In this study, the thermal expansion coefficients of the parent glass and mica-based glass-ceramics were determined in a laboratory and reported to be 7.5×10$^{-6}$/°C and 9.3–10.8×10$^{-6}$/°C, respectively. When the thermal expansion coefficients of the glass matrix ($\alpha_{\text{glass}}$) is lower than the thermal expansion coefficients of a crystal phase ($\alpha_{\text{crystal}}$), the residual compressive stress caused from the thermal expansion mismatch is generated in the glass matrix and parallel to the glass/crystal interface which should divert the crack to go around the crystal. In this situation, there is also a tensile residual stress developed within a crystal. However, the observation from the fracture surfaces of mica-based glass-ceramics showed that transcryalline fracture was the typical fracture mode for these materials (Figs. 6a–d). The fracture along or tilted to the cleavage plane was observed which was the result of a crack deflection within a crystal. This incident might indicate that the extent of residual compressive stresses near the interface was not sufficient to deflect the crack because of the slight thermal expansion difference. Another reason might be the complex structure of mica-based glass-ceramics. For a group of mica glass-ceramics, their crystal structure is monoclinic. The repeated arrangement of these monoclinic units produces a mica layer which consists of two tetrahedral sheets and one octahedral sheet and these mica layers bond to each other by the large alkali ions located within the so-called interlayer sites. The weak bonds between mica layers allow an uncomplicated machining process through these interlayer or cleavage planes and this property is a unique characteristic of mica-based glass-ceramics. However, because of asymmetric noncubic crystal structure, the thermal expansion coefficients of mica glass-ceramics were different along the different crystallographic directions. The internal residual stresses arose from these thermal expansion coefficient differences and could promote cracking along or tilted to the cleavage plane depending upon the type and amount of the residual stresses. Additionally, when the crystal...
size was large and anisotropic, the fracture path tended to be transcrystalline because of the excessive deflection angle. For MicaZr12.5, the crystals were smaller than the other groups and they were not connected to each other. Therefore, the crack deflection around the crystals could be noticed in addition to the deflection within the crystals as the wake hackle was observed in Fig. 6d (black arrow). Wake hackle is a fracture marking occurred when the crack fronts sweep past a particle or a pore on both sides with slightly different planes and leave a step toward the direction of crack propagation. This additional fracture pattern might be a reason for a slight increase in the fracture toughness of MicaZr12.5.

The effect of residual stresses caused from the thermal expansion mismatch on the fracture process was also reported for other glass-ceramics. For a leucite-based glass-ceramic (\(\alpha_{\text{glass}}<\alpha_{\text{crystal}}\)), cracks propagated near or through the crystals as a result of residual stress fields was reported. For a lithium disilicate-based material (\(\alpha_{\text{crystal}}<\alpha_{\text{glass}}\)), the crack deflection was more pronounced even the residual stresses should attract the crack to go through the crystal. However, the lithium disilicate crystals also had different thermal expansion coefficients along the different crystallographic directions and this resulted in a complex toughening mechanism and an increase in the fracture toughness. From these findings in the previous studies, it appeared that several factors affected the residual stress fields in the glass-ceramics such as the thermal expansion and elastic constant anisotropy, crystal structure, crystal size and shape, crystal volume fraction. These residual stresses could modify the mechanical properties of the glass-ceramics.

The hardness of mica-based glass-ceramics developed in this study ranged between 3.5–3.7 GPa which was lower than the hardness of leucite-based, lithium disilicate-based and ZLS glass-ceramics. The hardness of human dentin is 0.13–0.51 GPa and 3–6 GPa for enamel. For dental ceramics with higher hardness, excessive wear of opposing natural teeth is a major concern because these ceramics would come into contact with dentin and enamel inevitably during function or parafunction. Materials with low hardness would be more preferable in this case. The hardness of mica-based glass-ceramics was comparable to that of enamel and appeared to be more desirable in terms of the prevention of progressive damage of restoration and tooth structure. For MicaZr12.5, the hardness was comparable to that of the parent glass because it had lowest percent crystallinity and consisted of more glass phase than other mica-based glass-ceramics.

By controlling the nucleation and crystallization times, the translucency of CeO\(_2\) and Pr-ZrSiO\(_4\)/FeZrSiO\(_4\)-added mica-based glass-ceramic could be modified to a satisfactory level which was appropriate for dental application. However, the decrease in the fracture toughness was observed as a consequence of decreasing the crystal phases. According to the fracture toughness values of these mica-based glass-ceramics, they could be used to fabricate some dental restorations according to the recommendation claimed by ISO 6872:2015-Dentistry-Ceramic materials. However, higher fracture toughness values would be more preferable to assure a better clinical performance of these materials. The size of mica crystals developed in this study was large (≈5–10 µm in width and 10–20 µm in length) compared with those of other dental glass-ceramics. In order to obtain finer Ca-mica crystals with higher crystal volume fraction, adding some nucleating agents or adjusting the nucleation times would be the possible solution for the modification of the microstructure of these mica-based glass-ceramics without the sacrifice of a desired optical property.

**CONCLUSIONS**

From the results obtained in this study, the following conclusions could be drawn:

1. The fracture toughness of mica-based glass-ceramics was within the range of fracture toughness obtained from other dental glass-ceramics and they could be suitable for use as restorative dental materials.

2. CeO\(_2\) and zircon-based ceramic pigments could be used for shading of mica-based glass-ceramics without any significant effect on their microstructure.

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