Microstructural Characterization and Microhardness of Leucite Glass-Ceramics Synthesized from Sarawak Sand Reserves.

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Abstract. The purpose of this study was to evaluate the effect of varying the sintering temperature and holding time on the crystallization and microhardness of the SiO₂–Al₂O₃–K₂O glass system using SiO₂ from Sarawak sand reserves. A starting glass composition of SiO₂ (from Sarawak sand), Al₂O₃, K₂O, Na₂O, CaO, LiO and TiO₂ was prepared by conventional melt quenching technique followed by ball milling. The glass powder was pressed under pressure into disk-shaped compacts with 2 mm thicknesses and 14 mm diameters. The samples were then subjected to differing heat treatment schedules of 750°C, 800°C and 850°C with 1, 3 and 6 hours holding times. They were characterized by X-ray Diffraction (XRD), Scanning electron microscopy (SEM) and Vickers microhardness. XRD showed the crystallization of tetragonal leucite with minor secondary sanidine phases. SEM showed the formation irregular shaped and non-uniformly dispersed crystals. The hardness values showed an increasing trend with longer holding time at temperatures of 750°C and 800°C. This pattern was inversed for sintering temperature 850°C. In conclusion, sintering temperatures and holding time combinations influenced the crystallization and microhardness values of leucite glass ceramics produced from Sarawak sand silica.

1. Introduction
The demand for aesthetics has driven the development of tooth colored restorative materials. Ceramic materials are the material of choice for aesthetic indirect restoration as it has the advantage of ‘lifelike’ match to the dentition due to its excellent optical properties [1]. In addition, ceramic restorations satisfy other pertinent clinical requirements for example: strength, wear resistance, accuracy of fit, color stability, biocompatibility and chemical inertness [2-5]. Leucite glass-ceramics is one of the earliest developed dental ceramic and is still widely used due to its outstanding aesthetics [6] and clinical
durability [7]. The material is sufficiently strong to withstand occlusal forces when used as various types of indirect dental restorations such as veneers, anterior crowns, inlays and onlays. Furthermore, these restorations have excellent survival rates ranging from 96% to 91% at 4.5 years 7 years for inlays and onlays, 92% to 99% at 3 to 3.5 years for crowns, and 98% after 5 years for veneers [7-9].

In dentistry, there are several possible methods of producing indirect dental restorations. Traditionally, porcelain is fused to metal substructure to produce the restorations. However, this compromises the aesthetics of restoration due to the greyish metal substructure showing-through the translucent overlying porcelain. High strength ceramics were developed to overcome the aforementioned problem. In addition, the conventional method of producing indirect dental restorations is labour extensive requiring the support of dental technicians and is time consuming. In recent years, computer-aided design/computer-aided manufacturing (CAD/CAM) system was introduced to shorten the production time of indirect ceramic restorations and the number of patient visits [10]. The procedure involves digitizing the patient’s dentition and designing a virtual model of the dental restoration. This is immediately followed by direct milling of the ceramic block in the dental clinic and same-day cementation of the dental restoration. CAD/CAM ceramics restorations have been shown to have excellent aesthetics, good fit and clinical longevity [11-13].

At present, the dental industry in Malaysia relies heavily on imported machinable blocks for fabrication of all-ceramic restorations. These restorations are expensive and therefore beyond the means of a larger part of the population. A single leucite crown cost around RM2000-2500. Hence, a cheaper alternative is desired so that more patients can benefit. Malaysia has an estimated resource of 640 million tonnes of high-quality silica sand [14]. Approximately 148 million tonnes exist in natural forms and 492 million tonnes as tailing sand. The states with the highest production of silica by quantity percentage are: Selangor (36%), Sarawak (35%) and Perak (21%) [14]. These sources have the potential to be explored and processed for ‘higher value’ products such as advanced biomaterials. Fully utilised, this huge reserve of sand deposits could help to reduce our country’s present import dependency and add value to our economy.

It is our aim to develop machinable leucite glass ceramics for dental restorations from the high-quality silica sand obtained from Sarawak. The purpose of this study was to explore the nucleation and crystallization kinetics of the glass system SiO$_2$–Al$_2$O$_3$–K$_2$O using raw sand as the source of SiO$_2$. In the present work, we investigated the microstructural characteristics and microhardness of the glass-ceramics which was heat treated at various temperatures and holding times. This knowledge will contribute to our final aim of designing and engineering machinable glass-ceramics for dental applications using local sand reserves.

2. Experimental procedure
Malaysian sand sample from Bintulu, Sarawak was used as the source of SiO$_2$ in this study. All the other chemical components were of analytical grade and purchased from Merck Germany; Unilab, Australia and Hamburg Chemical.

2.1. Glass powder preparation
A starting glass mixture composed of Al$_2$O$_3$, Na$_2$O, K$_2$O, CaO, TiO$_2$, Li$_2$O and sand from Bintulu, Sarawak (as the source of SiO$_2$) was prepared (Figure 1a). The mixture was melted in alumina crucible in an electric furnace at 10°C / min to 1450°C for three hours. The glass melt was quenched by pouring it into deionized water to produce glass frit (Figure 1b). The frit was dried and milled for 1 hour in the planetary ball mill (PM400, Retsch, Germany) using zirconia balls as the crushing media to obtain the glass powder (Figure 1c).

2.2. Glass-ceramic discs fabrication
The fine glass powder samples were pressed into disks (14x2mm) (Figure 1d) in a steel mould using hydraulic hand press (Carver, USA) followed by Cold Isostatic Press (American Isostatic Press, Inc., USA). The green glass compacts underwent heat treatment in an electric furnace (Multimat Touch & Press, Germany) to convert it to glass-ceramics by nucleation and growth of crystals. A heating rate of 10°C / min was used; with temperature of 750°C, 800°C and 850°C and soaking time of 1 hour, 3 hours
and 6 hours. 750°C was selected as the starting point of the sintering temperature in accordance with other studies done on glass ceramics [15, 16].

2.3. Sample characterization

The crystalline phases were determined by a X-ray diffractometer (XRD; Rigaku Ultima IV, Japan) using Ni-filtered Cu Kα radiation at a scan speed of 2°/minute for 2θ from 10° to 80°. The diffraction patterns were compared with tetragonal leucite (ICDD: 01-081-2221) and sanidine. Scanning electron microscope (SU3500, Hitachi) was utilised to determine the morphologies of the leucite phase on the surfaces of the glass-ceramic samples. The indentation hardness of the glass-ceramics was measured by Vickers method at a load of 200 g for 15s. The disc shaped specimens were wet polished to a mirror finish. Five indentations approximately 0.5mm apart were made and the hardness calculated.

![Figure 1](image)

Figure 1. (a) Mixture composed of sand SiO₂, Al₂O₃, Na₂O, K₂O, CaO, TiO₂ and Li₂O (b) Glass frit produced by immediate quenching of the glass melt (c) Glass powder produced by ball milling and (d) Disk-shaped compacts before (upper row) and after (bottom row) sintering.
3. Results and Discussion

XRD revealed that the phases in the glass-ceramics obtained from the SiO$_2$–Al$_2$O$_3$–K$_2$O system using SiO$_2$ from Sarawak sand reserves are tetragonal leucite (major phase) and sanidine (minor phase) (Figure 2). Similar structures have been identified in the leucite glass-ceramic system [16]. In general, phase changes were observed with differing temperature and holding time combination. The minor sanidine phase developed at increased temperature and holding time, with higher temperature showing earlier development of the minor phase. This is in accordance with previous studies which showed that in leucite glass-ceramics, leucite and silica in the residual glass phase transformed to sanidine in the temperature range of 800°C - 950°C at more than 60 min hold [17, 18].
Figure 2. The XRD patterns of samples sintered at 750°C; 800°C and 850°C for (a) 1.0 hour, (b) 3.0 hours and (c) 6.0 hours.

Scanning electron microscopy (SEM) was used to observe the surface microstructure of the samples. Irregular shaped crystals with non-uniform distribution (Figure. 3a) were seen in the glass-ceramics sintered at 750°C and 800°C held for 1, 3 and 6 hrs. Similar microstructure was observed with samples sintered at 850°C were held for 1 and 3 hrs. However, prolonged holding for 6 hours at 850°C led to a decreased crystal quantity and enlarged crystal size (Figure. 3b). This is in accordance with a recent study which showed that the average particle size of synthesized leucite increased with higher sintering temperatures [19]. This could be due to crystal growth via particle coalescence which is facilitated by reduction of glass viscosity at higher crystal growth temperatures [17].

Figure 3. SEM micrographs of (a) sample sintered at 850°C; 1 hour holding time and (b) sample sintered at 850 °C; 6 hours holding time.

Figure 4 shows Vickers microhardness values of glass ceramics sintered at 750°C, 800°C and 850°C with holding times ranging from 1 to 6 hours. The mean hardness values (VHN) of the glass-ceramics ranged from 335.16 ± 20.07HVN at 850°C held for 6 hours to 736.16 ± 77.95HVN at 850°C held for 1 hour. The standard deviation of some of the experimental groups were relatively high showing a high
variance of the data. This may be attributed to the low sample size numbers per group (n=5). The hardness values for leucite glass ceramics showed a clear increasing trend with increased holding time (from 1 hour to 6 hours) at sintering temperatures of 750°C and 800°C. However, the pattern is inversed for sintering temperature of 850°C. Longer holding times at high temperature led to the development of poorly dispersed leucite crystal agglomerations within the glassy matrix (Figure 3b) which may have contributed to the low microhardness values seen in these samples.

![Figure 4](image-url.png)

**Figure 4.** Mean Vickers microhardness of leucite glass-ceramics at 750°C, 800°C, 850°C with 1.0, 3.0 and 6.0 hr holding time.

4. Conclusion
It has been shown that the processing method adopted for producing ceramics greatly influences the composition, microstructure and microhardness of the products. The current study on glass mixture using Sarawak sand silica showed that leucite glass-ceramics could be produced. It was also found that ‘sintering temperature and holding time’ combination is a key factor to control leucite crystallization behaviour, morphology and dispersion with the corresponding hardness within the glass-ceramic material.

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