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Crystallization of leucite in potassium-alumino-silicate glasses

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Leucite crystals were successfully precipitated in a glass matrix which had the precise stoichiometric composition of leucite ($KAlSi_2O_6$). Potassium silicate compound was first produced. Then, alumina was added to obtain the potassium alumino-silicate glass. Crystallization took place at 1550°C for 24 h in air with a heating rate of 3°C/min. The resultant material comprised a glass matrix where dense round polycrystalline clusters (200-300μm) of leucite were homogenously dispersed, seemingly acting as crack arresters. The leucite crystals (~2-4μm thick and ~10μm long) were well-interlocked one to the other. The produced glass-ceramics exhibited good aesthetics with regards to their potential in dental applications.

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1. Introduction

From the ancient Egyptian times of tooth replacement prostheses made of gold-wire, ox bone, or wood, through the renaissance of the air-fired porcelains and the cast-gold dental restorations about two hundred years ago [1], nowadays restorative and implant dentistry addresses its interest to biocompatible porcelains and glass-ceramics [2]. The significant progress of the processing of ceramic materials, namely porcelains [3] and glass-ceramics [4], and the consequent improvement of ceramics properties directly resulted in developing better materials for dental applications [5, 6, 7]. In this general aspect, some gleaned landmarks are those made by Duchateau and de Chement (1774), Fonzi (1808), Land [Jacket (1886)], Stookey [Corning Glass Ceramic (1952)], Vines (1962), Weinstein (1962), Mc Lean and Hughes [Alumina ceramic (1952)], Mc Culloch [Porcelain tooth on removable prosthesis (1968)], and Hobo's Hydroxyapatite Crown Cérapearl® (1977) [6]. In the particular case of glass-ceramics, the phenomena of nucleation and crystallization in glasses are of great importance for the development of specialized glass-ceramics. With regards to biomedical and dental applications, the following types of materials have attracted specific interest and their nucleation and crystallization have been studied in details: mica glass-ceramics, mica-apatite glass-ceramics, leucite glass-ceramics, leucite-apatite glass-ceramics, ZrO_2-containing glass-ceramics, lithium disilicate glass-ceramics, and apatite containing glass-ceramics [7].

Porcelain dental crowns and bridges featuring high aesthetics and good mechanical properties have been in dental practice since the 1980s [8, 9]. For single restorations, Dicor (1984), Empress, Cerec, Optec (1987), Celay (1992), Cerec 2 (1993), OPC System, Finesse All Ceram, Golden Gate, Cera Quickpress (1993) outline the recent history of the high technological improvements of dental ceramics without metallic substructure. In-Ceram had begun the era for porcelain bridges without metallic substructure (1990), followed by Empress 2 (1993) that achieved 3-segmented bridges, Procera (1995), Wol Ceram, Fit Cicero (1998), Girrbach Digident (2000), Cerec 3 (2002), Cynovad Pro (2002), and the zirconia ceramic Cercon (2002) [6].

Leucite ($KAlSi_2O_6$), naturally occurring in volcanic deposits, is an attractive feldspathoid crystalline ceramic phase with high thermal expansion that is suitable for incorporation in materials used to veneer metal frameworks of crowns, bridges or inlays [5, 10, 11, 12]. Leucite was initially introduced into dental porcelains to increase the thermal expansion coefficient in order to match that of casting alloys (that is important during cooling). Moreover, due to martensitic tetragonal-cubic transition, leucite can improve fracture toughness in a structure of a composite material. Accordingly, leucite ceramics are indicated for producing ceramic-fused-to metal restorations. In general, most dental porcelains consist of a leucite crystal-containing frit and at least one other frit to control various physical and mechanical properties. The leucite-component forms a refractory skeleton and the glass fills the spaces in between, adding special properties required for dental porcelains [5].

Höland has demonstrated the development of a leucite-based glass-ceramic via controlled surface crystallization of a glass with a batch composition (in wt%) of 63% SiO_2, 17.7% Al_2O_3, 11.2% K_2O, 4.6% Na_2O, 0.6% B_2O_3, 0.4% CeO_2, 1.6% CaO, 0.7% BaO, and 0.2% TiO_2 at 800°C-1200°C [2]. Leucite containing ceramics were also produced via hot-pressing at 1120°C-1180°C [11]. Nevertheless, due to the brittleness of the conventionally made leucite-based dental porcelains, these materials have not demonstrated a sufficiently high clinical success rate to be used for all ceramic posterior crowns. Some improvements were made with the addition of Cs_2O which seems to affect the transformation toughening mechanism [13].

Höland *et al.* reported the controlled development (in a two step process for heterogeneous nucleation and crystal growth) of leucite-based, lithium disilicate and leucite-apatite glass-ceramics, whose fine microstructure results in a very high flexural strength of ~400MPa [14]. The controlled processing also results in excellent aesthetics and translucence of the resultant glass-ceramic. Veneered with an apatite containing glass-ceramic, the material can be used as 3-unit dental bridge.

In this work, the process of the formation of leucite crystals in a glass matrix, which has the precise composition of leucite ($KAlSi_2O_6$), is presented. Earlier studies report no success at obtaining leucite crystals from glasses whose composition was precisely adjusted to stoichiometric leucite. Only Scharrier and Bowen [15] have reported that heat treatment at high temperatures overcomes the barrier of high activation energy of crystallization resulting in some crystallization of leucite.

2. Experimental

Powders of quartz (SiO_2), alumina (Al_2O_3), and potassium carbonate (K_2CO_3) of reagent grade were used. Table 1 presents the purity and Table 2 the particle size analysis of the powders, given by the manufacturer (Sisecam Glass Inc. - Turkey).

Table 1. Purity of the powders (wt.%).

	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O
Quartz	99.42	0.34	0.01	0.01	0.01	-	0.13	0.08
Alumina	-	99.58	-	-	-	-	-	-
Potassium carbonate	-	-	-	-	-	-	-	67.91

Table 2. Particle size analysis of the powders (wt.%).

	500µ	106µ	75µ	<75µ
Quartz	0.4	84	8.1	7.5
Alumina	-	13.9	-	86.1
Potassium carbonate	30.6	69.3	-	0.1

We first produced a homogeneous potassium silicate precursor compound as follows. Quartz and potassium carbonate powders, with a Si/K ratio fixed at the precise stoichiometry of leucite, were well mixed. To facilitate decarbonization, the powder mixture was heated up at 600°C in air in a platinum crucible, with a heating rate of 10C/min. After 24h dwell at 600°C, the crucible was quenched in air. The same process was repeated three times at increasing temperatures, specifically 700°C, 800°C, and 900°C. In the last heat treatment at 900°C, cooling was gradually occurred in the furnace. The resultant material was melt in Pt-crucible at 1300°C in air for 10min and then naturally cooled down inside the furnace. The obtained potassium silicate compound was grounded down to fine powder.

In the second step of the process, alumina was added in the potassium silicate powder. The mixture (where the raw materials incorporated had the precise composition of leucite) was heated up at 1600°C (in a SFL electrical furnace, UK) in air in a Pt-crucible with a slow heating rate of 3°C/min. After 15min dwell at 1600°C, the glass was quenched in cold water. To increase the homogeneity of glass, the quenched glass was ground into fine power and then re-melted following the same schedule, but the crucible with the powder was entered directly to the hot chamber of the furnace at 1600°C. This procedure was repeated for 10 consecutive times. In the final (10th) cycle, the glass, in a form of a block, cooled slowly (~2°C/min) inside the furnace

The development of leucite crystals in the glass matrix was done via heat treatment of the glass block at 1550°C for 24h in air (the heating rate was 3°C/min). The crystallographic analysis of the product was carried out with X-ray diffraction (XRD, Philips-PW3710 brand equipment, Cu-K_α, 20kV). The samples of the crystallized glasses were sectioned with a precise diamond cutter and the sections were observed with a stereo-optical microscope (Leica MZ 9.5 brand). The microstructure of the obtained material was observed with a scanning electron microscope (SEM, Jeol JCXA733), equipped with energy dispersive spectroscopy (EDS) analyzer.

3. Results and discussions

The crystallization of the produced glass (at 1550°C for 24h) resulted in developing big, round and highly-dense clusters of crystals with a size of 200-300µm, homogenously distributed in the glass matrix, as observed with the stereo-optical microscope in the sections made in the samples (Fig. 1). Figure 1b suggests that the clusters are polycrystalline. Closer observation with SEM showed that the clusters are well embedded in the glass matrix and the interfaces between the crystallized and the glassy areas are well defined (Figure 2a). Observations at higher magnifications in the core of the crystallized area (Figure 2b) showed that the big round clusters consist of prismatic crystals with a size of ~2-4µm thick and ~10µm long, well interlocked one to the other. This fine microstructure plausibly suggests good mechanical properties. Elemental analysis of the crystals shown in Figure 2b (by EDS spot analysis) showed that these crystals consists of Al, Si and K (table in Fig. 2c). Since the content of leucite (in wt%) are K 32%, Al 22% and Si 46%, the experimental results of the EDS elemental analysis suggest that the observed crystals are likely attributed to leucite. Indeed, the crystallographic analysis of the devitrified glass by XRD

(Fig. 3) confirms that leucite crystals were developed in the glass matrix.

In Fig. 2a, several micro-cracks can be observed, either in the core of the crystallized cluster or in the glass matrix, directed towards the outer surface of the cluster. These micro-cracks likely occur due to the cubic-tetragonal phase transformation of leucite at ~625°C [16]. According to Griffith's crack theory [17], in micro-cracks subjected to stress, the energy accumulated at the ends of the cracks tend to increase the surface area in such a way as the crack will develop towards material's border resulting in total breaking of the structure. In the particular case of glasses, if there is not any preventing structure in the glass matrix, then the cracks initiate and propagate very fast. Accordingly, the leucite crystals distributed in the glass matrix (Figure 1) should function as crack-arresters, i.e. they prevent crack propagation in the glass matrix (Figure 2a) by absorbing the fracture energy along the cracks. Hence, the development of the leucite-crystals is expected to improve the toughness of the produced glass-ceramic [18, 19, 20].

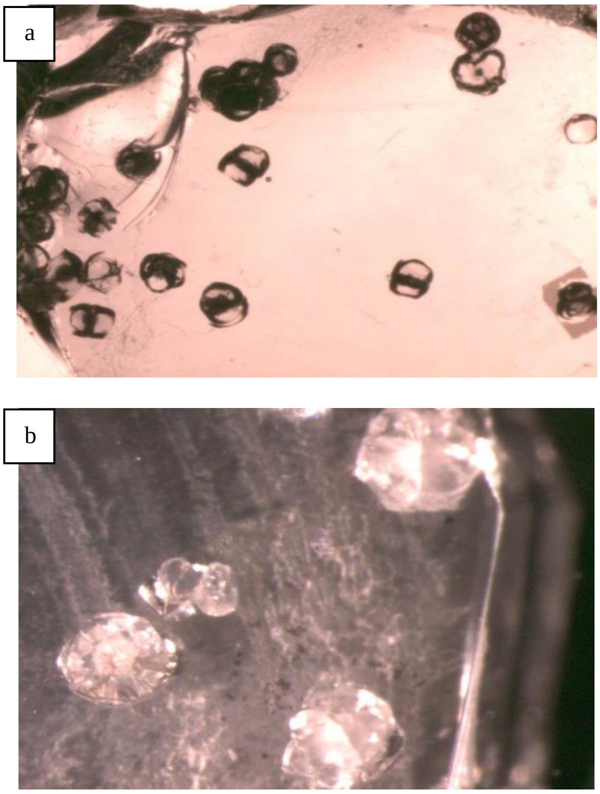
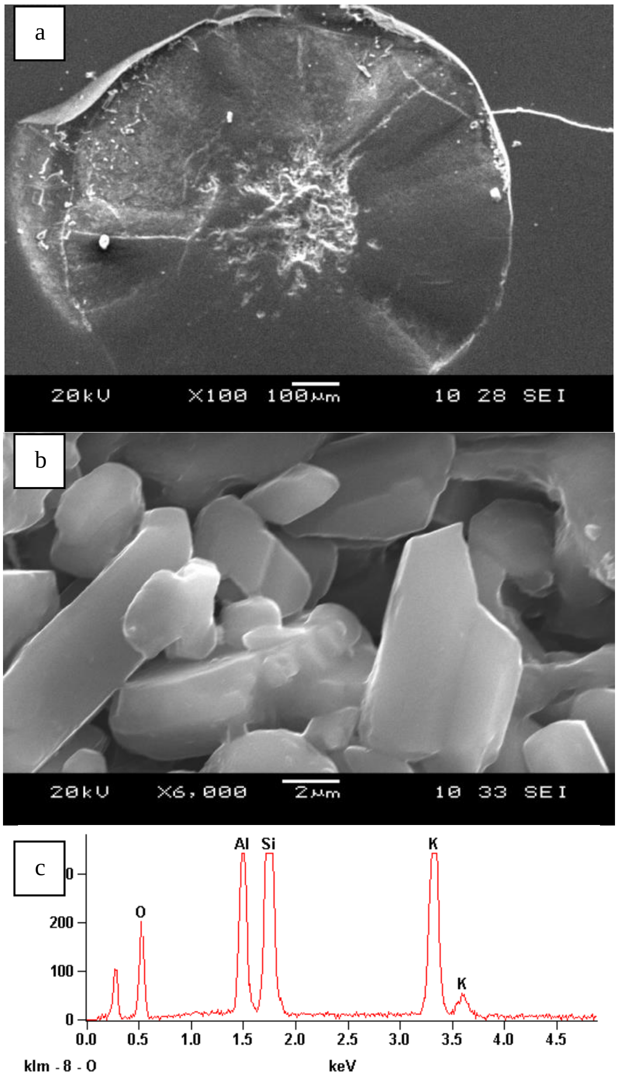


Fig. 1. Images of sections of the glass, containing leucite crystals, at lower (a) and higher (b) magnifications, obtained with stereo-optical microscope (for scale estimation, the bigger crystals are about 250 - 300 µm)

Beyond mechanical properties, in dental implants, aesthetics is a crucially important issue, as well. Accordingly, the produced glass-ceramic can combine the transparency of glass with the opacity on the homogeneously dispersed white leucite crystals (Figure 1) resulting in a translucent dense white material with high aesthetics, potentially suitable for dental applications.

Consequently, the careful thermal treatment, applied in the similarly carefully prepared homogeneous potassium-alumino-silicate glass, resulted in homogenous precipitation of leucite crystals from glass reservoir. The prolonged (24h) heat treatment at a relatively high temperature (1550°C) with a slow heating rate (3°C/min) suggests high activation energy of crystallization [15]. The formation of leucite crystals in the entire bulk of glassy phase (Fig. 1) suggests that the process followed favors crystallization of leucite via bulk crystallization mechanism. Comparing to surface crystallization, bulk crystallization is usually the demanded crystallization mechanism because it results in glass-ceramics with fine microstructures of small crystals, such as those shown in Figure 2b, which imply good mechanical properties (strength and toughness).



Element	K	Al	Si
(wt%)	24.96	20.55	54.49

Fig. 2. SEM images at lower (a) and higher (b) magnifications and EDS elemental analysis (c) of the crystals shown in the image (b)

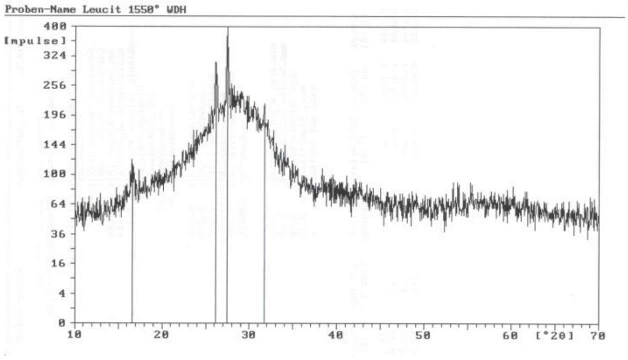


Fig. 3. The X-ray diffractogram confirms that leucite crystals have been crystallized in the glass matrix. (Leucite PDF card 38-1423)

In the frame of this work, many glasses were also produced with a smaller number of thermal cycles. However, all these glasses had not reproducible properties, mainly with regard to their crystallization behavior. As mentioned in the introduction, leucite glass-ceramics are very attractive materials in dentistry but also very difficult to be produced. Thus, many reports are specifically dedicated at developing novel production methods which result in leucite-base materials with highly reproducible properties. The results of this study emerged two key factors for the production processing: the repetition of the thermal cycles as well as the production of the glass in 2 steps.

4. Conclusions

Leucite crystals were successfully precipitated in a glass matrix which had the precise stoichiometric composition of leucite ($KAlSi_2O_6$). For the production of the glass, the raw materials had only the precursors of the basic components of leucite; no additives were incorporated to facilitate nucleation. The process of glass production comprised two stages. First, potassium silicate compound was produced. Then, alumina was added in the potassium silicate compound to produce the potassium alumino-silicate glass. Crystallization took place at 1550^{o}C for 24h in air with a slow heating rate of 3^{o}C/min.

The resultant material comprised a glass matrix where dense round polycrystalline clusters (200-300μm) of leucite were homogenously dispersed. Micro-cracks, likely developed due to the cubic-tetragonal phase transformation of leucite, were seemingly arrested by the crystallized clusters of leucite. Accordingly, the crystallized clusters of leucite should enhance the toughness of the resultant glass-ceramic since they prevent crack propagation in the glass matrix by absorbing the fracture energy along the cracks. The fine microstructure of the clusters, which comprise small prismatic leucite crystals (~2 - 4μm thick and ~10μm long), well-interlocked one to the other, as well as the mono-mineral nature of the crystallization products (i.e. only leucite), are factors which should further enhance the toughening effect of the resultant glass-ceramic.

The formation of leucite crystals in the entire bulk of the glass matrix suggests that the investigated glass is prone to bulk-crystallization. The prolonged (24h) heat treatment at relatively high temperature (1550^{o}C) with a slow heating rate (3^{o}C/min) suggests high activation energy of crystallization.

The distribution of leucite crystals in the glass matrix can be considered as an advantage with regard to the aesthetics (translucence and whiteness) of the produced glass-ceramic as a potential dental material.

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