

LEUCITE PORCELAIN FUSED TO METALS FOR DENTAL RESTORATION

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Submitted January 12, 2009; accepted May 14, 2009

Keywords: Dental restoration, Leucite, Ceramics, Crystallization

The aim of this work is to provide an overview of dental porcelains fused to metal used for dental restorations. The paper shortly adverts to a historical development of leucite ceramics as well as to a description of leucite itself. A ternary-phase equilibrium diagram of the $K_2O-Al_2O_3-SiO_2$ system with its area of the primary crystallisation of leucite is briefly discussed. The methods of preparing industrially produced leucite powder as well as new, 'low temperature' methods are presented. The fusing temperature of leucite porcelain with regards to its resultant properties is also discussed.

INTRODUCTION

Porcelains are widely used in dentistry these days as natural-looking tooth restorations thanks to their numerous advantages such as colour, strength, aesthetic, opacity, translucency, durability etc. On the other hand the biggest disadvantage of dental porcelains is its brittleness. Another major drawback is the potential to cause abrasive wear on the opposing dentition. Today, there are two principal types of ceramic restorations – all-ceramic and metal-ceramic. Newer, all-ceramic systems generally comprise a ceramic body instead of the traditional metal, with at least one additional porcelain layer. All-ceramic systems are made from a ceramic with substantial crystal content (> 50 vol.%) from which their higher strength and toughness are derived. These systems, which have generated greater and greater interest in the past two decades, can provide more natural translucency and therefore improve the aesthetics. Nevertheless, metal-based restoration is still common; there, several layers of porcelain powder in aqueous slurry are sequentially fused to a metal framework to simulate natural teeth [1, 2], see Figure 1. These layers have three different levels of translucency. The first, opaque layer is used to mask the dark metal substrate. The intermediate layer, the so-called dentine, is the principal bulk construction of the artificial tooth structure and is also used to provide translucency of the porcelain. The upper, most translucent layer is called the enamel or incisal porcelain. Each layer must subsequently be fused in an electric or vacuum furnace at about 1000°C to obtain the optimal properties. It is evident that these dental porcelains must blend many frits or components, which are variously combined to achieve the desired properties, such as colour, strength, translucency, shock resistance and the coefficient of thermal expansion α .

Metal ceramics

First attempts of firing ceramics on metal alloys are dating back to the eighteenth century. In 1886 Land firstly introduce the fused feldspathic porcelain crowns on platinum foil. Though, because of many problems, the attempts remained unsuccessful for many decades [3]. Before the 1960s, the only materials available for metal-ceramic restorations were conventional dental porcelains with a maturing temperature of 1000-1300°C which were fused to platinum alloys of iridium or ruthenium [2]. Their use involved serious procurement problems and difficult fabrication techniques, finally yielding a product which was liable to a high degree of failure. As a consequence, the role of dental ceramic materials was limited mainly to an aesthetic one in the anterior teeth. Another significant limitation of these dental porcelains

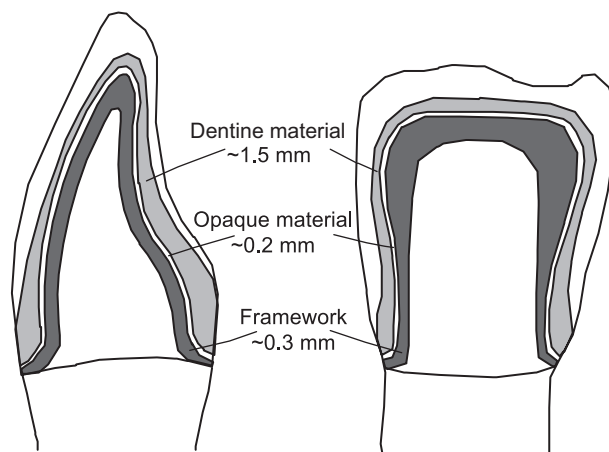


Figure 1. Metal framework and ceramic layers on an anterior crown.

was their low coefficient of thermal expansion, which was only about $8 \times 10^{-6} \text{ K}^{-1}$, and therefore bonding it to a metal framework was extremely difficult.

In 1962, Weinstein obtained porcelain by mixing glass and glass-ceramic frits of different compositions and different coefficients of thermal expansion. Using this method, Weinstein prepared dental porcelain with α of up to $17 \times 10^{-6} \text{ K}^{-1}$, which was a significantly higher value than had been hitherto presented. Due to this invention it was possible to fuse such prepared porcelain to a metal frame without bigger difficulties. Weinstein successfully demonstrated how to bond porcelain to a metal during the firing and therefore he may be considered as an inventor of metalceramic. Later, it was ascertained that Weinstein's porcelain consisted of a glassy matrix and tetragonal leucite particles. In 1964 O'Briand et al. firstly mentioned leucite as a component of dental porcelain. Sixteen years later, in 1980 Hahn and Teuchert satisfactorily examined the problem of reliable weldability between ceramics and metals [4]. They deeply studied recrystallization mechanism of leucite mineral in the glass ceramic system $\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ and showed its importance for metal ceramic restorations. Tetragonal leucite was recognised as a critical component in glass-

ceramics for obtaining the correct thermal expansion matching. Additionally, its presence in dental porcelain was acknowledged as advantageous, because it could impart higher strength, greater durability as well as the desired translucency to the final porcelain.

At present, dental ceramics exhibit a wide range of coefficients of thermal expansion, from as low as about $\alpha = 8 \times 10^{-6} \text{ K}^{-1}$ (e.g. alumina) to as high as approximately $\alpha = 18 \times 10^{-6} \text{ K}^{-1}$ (e.g. some leucite-reinforced ceramics). It is very important for metal ceramic systems that the coefficient of thermal expansion of the porcelain either matches or is slightly lower than that of the metal base (commonly $13.5-14.5 \times 10^{-6} \text{ K}^{-1}$, range 20-500°C), as a result of which no cracks are produced in the porcelain layers due to the thermal expansion mismatch stress occurring during cooling. In this way, the ceramic is placed in compression, when it is strongest, rather than in tension, when it is weakest. It is also important to be the thermal expansion coefficient of individual ceramic layers in agreement so as to attain high strength in the multiple layer arrangement. In addition, repeated heat treatments are known to push dental porcelain thermal expansion to lower values.

Leucite

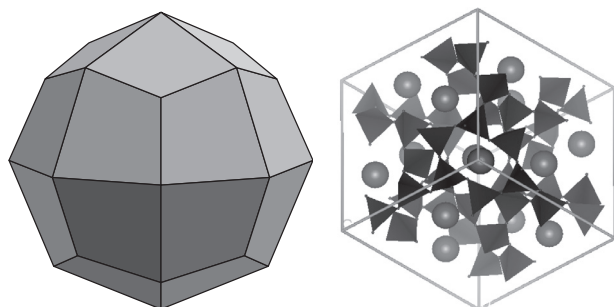


Figure 2. The single leucite crystal (left) and the crystal structure of tetragonal leucite (right); spheres – K^+ ions, tetrahedra – $[\text{SiO}_4]^{4-}$, $[\text{AlO}_4]^{5-}$.

Leucite (KAlSi_2O_6) is a potassium aluminium silicate mineral formed by $(\text{Si},\text{Al})\text{O}_4$ tetrahedra, each of which shares all its oxygens with its neighbours [5-7], see Figure 2. Leucite exists as two polymorphs. The stable form of leucite at high temperature is cubic (high leucite), and as it cools, there is a phase transformation to the tetragonal form (low leucite) in a temperature range of 500-600°C. This transformation is rapid, reversible and continuous (a transformation of the 2nd order). Figure 3 shows XRD line patterns of tetragonal [01-085-1626] and high temperature cubic [01-085-1420] leucite.

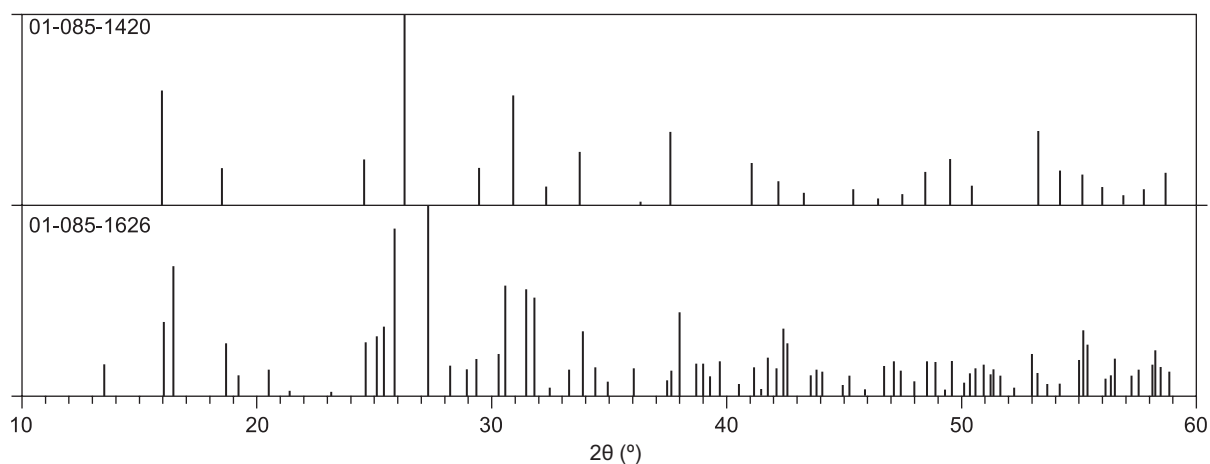


Figure 3. The X-ray diffraction lines of tetragonal [01-085-1626] and cubic [01-085-1420] leucite.

te (8) and corundum (9), see Figure 4a. These phases are separated by heavy curves with arrows, which indicate the direction of the falling temperature. In the leucite field, the lowest temperature is $810 \pm 5^\circ\text{C}$, which rises up to $1686 \pm 5^\circ\text{C}$, a congruent melting point of leucite. Tie lines divide the $\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system into triangular areas. The composition of leucite for dental applications commonly lies in the ternary subsystem of silica–potassium disilicate–leucite ($\text{SiO}_2-\text{K}_2\text{O}\cdot 2\text{SiO}_2-\text{K}_2\text{O}\cdot \text{Al}_2\text{O}_3\cdot 4\text{SiO}_2$). Leucite-glass compositions mostly lie either in compatibility triangles of silica–potassium tetrasilicate–potash feldspar or of potassium tetrasilicate–potassium disilicate–potash feldspar. The first mentioned triangle of $\text{SiO}_2-\text{K}_2\text{O}\cdot 4\text{SiO}_2-\text{K}_2\text{O}\cdot \text{Al}_2\text{O}_3\cdot 6\text{SiO}_2$ becomes completely crystalline at $710 \pm 20^\circ\text{C}$ (ternary eutectic E_1) and consists of crystals of potassium tetrasilicate, quartz and potash feldspar. The second triangle of $\text{K}_2\text{O}\cdot 4\text{SiO}_2-\text{K}_2\text{O}\cdot 2\text{SiO}_2-\text{K}_2\text{O}\cdot \text{Al}_2\text{O}_3\cdot 6\text{SiO}_2$ becomes crystalline at $695 \pm 5^\circ\text{C}$ (ternary eutectic E_2) and consists of potassium tetrasilicate, potash feldspar and potassium disilicate. The crystallisation paths on the cooling of the compositions lying in these areas are shown in Figure 5b. The initial composition for the triangle of $\text{SiO}_2-\text{K}_2\text{O}\cdot 4\text{SiO}_2-\text{K}_2\text{O}\cdot \text{Al}_2\text{O}_3\cdot 6\text{SiO}_2$ lies in the primary field of leucite and is characterised by Point A. During cooling, the first leucite crystals appears at 1300°C . The crystallisation path continues by Line AB, which is an extension of the line $\text{K}_2\text{O}\cdot \text{Al}_2\text{O}_3\cdot 4\text{SiO}_2 - \text{A}$. As soon as Point B reaches the boundary curve, potash feldspar appears as the second solid phase. The composition of the liquid runs along this boundary curve in the direction of the arrow (Line BC). At Point C, all the leucite is resorbed and the crystallisation path leaves the boundary curve and crosses the field of potash feldspar in the direction of $\text{K}_2\text{O}\cdot \text{Al}_2\text{O}_3\cdot 6\text{SiO}_2 - \text{C}$ (Line CD). At Point D, potassium tetrasilicate appears as the second

solid phase and the crystallisation path continues to the eutectic Point E_1 , where feldspar, quartz and potassium tetrasilicate are in equilibrium. The crystallisation path for the triangle of $\text{K}_2\text{O}\cdot 4\text{SiO}_2-\text{K}_2\text{O}\cdot 2\text{SiO}_2-\text{K}_2\text{O}\cdot \text{Al}_2\text{O}_3\cdot 6\text{SiO}_2$ is characterised by curve PQRSE2 and is analogous to path ABCDE1.

Due to the high viscosity of liquidus in this system, it is very difficult to obtain equilibrium. During the crystallisation of the compositions of any of the previously discussed areas (where leucite is the primary phase), leucite can be obtained by a rapid cooling of the melt. Metastable leucite is then accompanied by a desired amount of the amorphous phase and/or by other phases like potash feldspar, quartz, and potassium tetrasilicate. According to the ternary-phase diagram, potash feldspar must be present as an equilibrium phase at low temperatures (below 900°C) and leucite at high temperatures.

The preparation of leucite or leucite porcelains

The preparation of leucite porcelain from a glass has conventionally consisted of several steps described approximately as follows: raw materials are blended by ball milling and then fused to form a glass at a temperature of about 1300°C and usually higher. After the fusion, the material is quenched (in water) and then reheated to an elevated temperature (of e.g. 1000°C) for several hours to form the desired amount of leucite. After that, the glass comprising leucite particles is quenched, crushed and reduced to a fine powder. Alternately, the reheating process can be skipped with the cooling process being continued at a lower temperature for a few hours to crystallise leucite. Each step requires several hours to complete. As is evident from the description above,

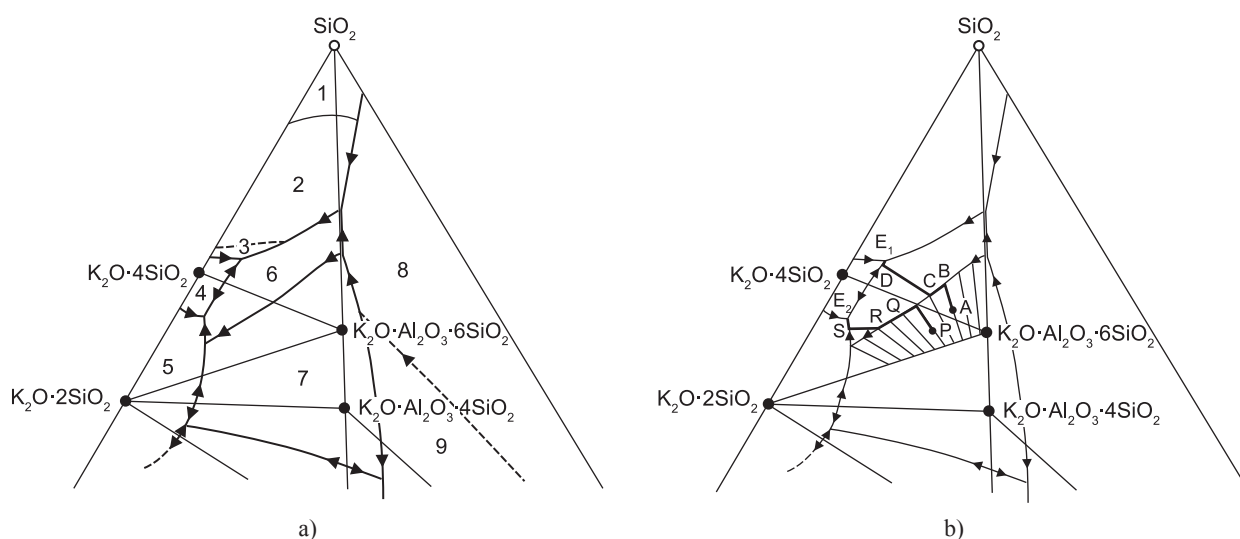


Figure 5. The primary fields of the crystalline phases in the $\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system (a). The crystallisation paths in the $\text{SiO}_2-\text{K}_2\text{O}\cdot 4\text{SiO}_2-\text{K}_2\text{O}\cdot \text{Al}_2\text{O}_3\cdot 6\text{SiO}_2$ triangle (1) and in the $\text{K}_2\text{O}\cdot 4\text{SiO}_2-\text{K}_2\text{O}\cdot 2\text{SiO}_2-\text{K}_2\text{O}\cdot \text{Al}_2\text{O}_3\cdot 6\text{SiO}_2$ triangle (2) (b).

crystallisation of leucite from alkali aluminosilicate glasses is very demanding in terms of energy. Often, crystallisation processes occur via uncontrolled nucleation mechanisms, which leads to crystals of different sizes and a microstructure that is not uniform. These problems are why research has focused for the past few decades on finding new methods of preparing leucite, or leucite porcelains.

Since Weinstein prepared porcelain consisting of a glassy matrix and tetragonal leucite in 1962, many scientists have prepared leucite or leucite porcelain by different methods, resulting in various properties.

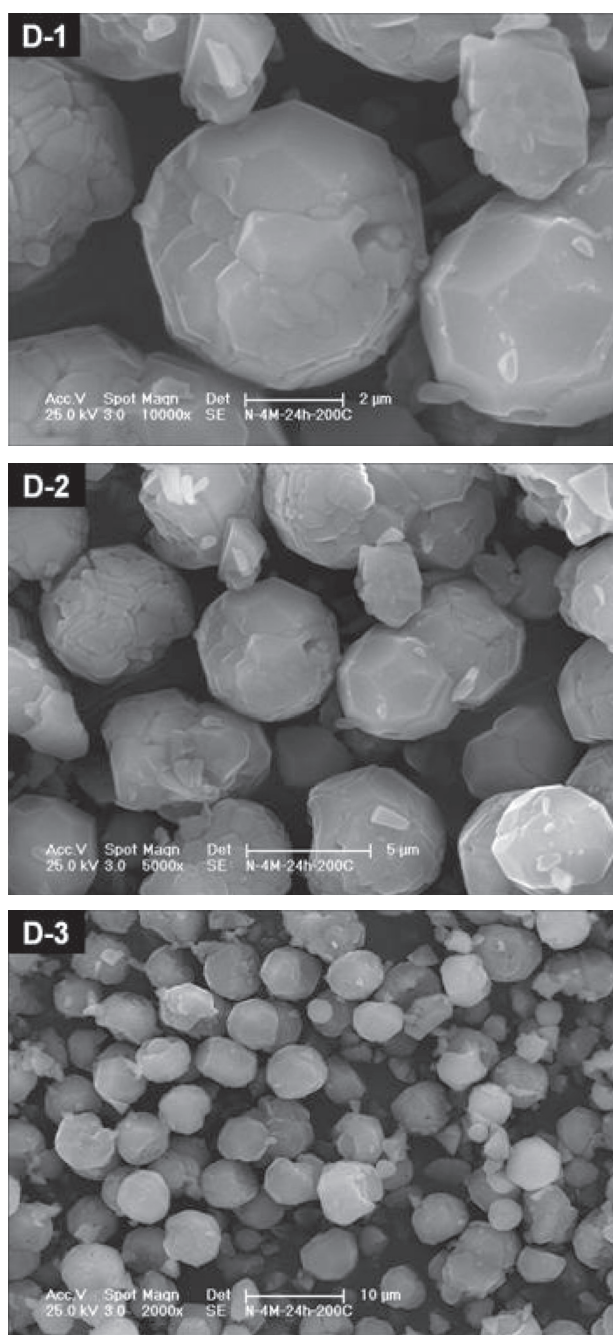


Figure 6. The SEM micrographs of tetragonal leucite prepared by the hydrothermal method at 200°C.

Originally, research focused on the crystallisation of leucite from a melt, which led to numerous patents [12, 13, 20, 21, 22]. Further, it was discovered that tetragonal leucite can also improve the mechanical properties of the final porcelain [23-26]. Nevertheless, the crystallisation process is not quite optimal for the preparation of leucite porcelain. Acceptable leucite porcelain requires an optimal microstructure created by a homogeneous dispersion of leucite ‘submicron’ particles in a glassy matrix. To prepare material with such a structure, it is desirable to replace the classical technology when leucite was crystallised from a melt with a preparation procedure for a composite material. The reason to prepare leucite ceramic as a composite material is therefore the tendency to simplify manufacturing process as well as to improve properties of leucite ceramic – especially to increase the value of fracture toughness. At present, several different experimental methods like sol-gel, co-precipitation, hydrothermal etc. for leucite preparation can be found in literature. In 1994, Sheu et al. [27] prepared porous specimens containing leucite particles employing the co-precipitation method. The powders were sintered at 1200°C. In 1997, Erbe et al. [9] prepared congruently crystallised tetragonal leucite using only pure components in dispersion (i.e. using no mineral sources such as feldspar). They found that the coefficient of thermal expansion of some of the leucite powders was greater than the α of leucite derived from feldspathic minerals using conventional thermal processing. ‘Unfortunately’, many of the samples had a kalsilite phase as an impurity. Liu et al. [28] used the sol-gel method to synthesise leucite at a relatively low temperature of 900°C, although their final leucite specimens contained a high amount of amorphous phase. In 2006, Zhang et al. [29] prepared high-purity leucite powders at 850°C employing the sol-gel method and using CaF_2 as a modifier. In 2003, Novotná et al. [30] firstly synthesised highly pure tetragonal leucite using the hydrothermal method in a two-step process at the lowest temperature ever. Homogeneous leucite powders with a particle size of 3 μm were prepared by an ion exchange of hydrothermally synthesised analcime at 200°C. The reaction occurred in a solution of KCl in a teflon-lined stainless steel autoclave [31, 32], see Figure 6. One year later (2004), Novotná et al. [33] hydrothermally synthesised leucite from an amorphous precursor, followed by a subsequent high temperature treatment at 1000°C.

The fusing process

The fusing temperature of the leucite porcelains is always limited by the melting temperature of the metal and must occur below this value. In terms of temperature, dental porcelains can be classified as ‘high’ and ‘low’ fusing porcelains [1]. The high-fusing porcelains fuse

above 950°C and have been found to be more resistant to thermal and mechanical shock as well as to erosion by mouth fluids. Low-fusing porcelains (650°C-950°C) are less desirable but are preferred in dentistry because of their workability. However, the leucite crystal phase is instable in low-fusing porcelains [34]. It has been stated that if leucite porcelain is maintained at a temperature of 950°C or lower, or if it is slowly cooled, it has a tendency to devitrify or to change its coefficient of thermal expansion. More specifically, when leucite ceramic is fused to a metal, Na-K feldspatic crystals start to appear after a certain period. Leucite crystals begin to decrease and finally may even disappear, because the leucite crystal phase is metastable. The precipitation of feldspatic crystals is undesirable, because it lowers the coefficient of thermal expansion and causes opacification of the porcelain. This may be the reason why most of the commercially manufactured leucite porcelains at present are coated to a metal frame at a temperature of 900°C or higher.

CONCLUSIONS

Leucite dental porcelains are currently made by admixing a glass frit (imparting a low α and low sintering temperature and optionally providing pigments and fluorescence) and a leucite-containing frit (having a high α and high sintering temperature) in appropriate ratios. From the discussion above, it is quite clear that the preparation of leucite by some other method than by the high temperature process would be more suitable in future. In addition, it is obvious that leucite ceramics still need to be improved to satisfy all the requirements of dental restorations (a low-processing temperature, high coefficient of thermal expansion, fine-grain and uniform leucite particles in the matrix etc.). This implies firstly a knowledge of the material and then its correct technical application.

Acknowledgement

This work was a part of the project No. 2A-ITP1/063, 'New glass and ceramic materials and advanced concepts of their preparation and manufacturing', implemented with the financial support of the Ministry of Industry and Trade of the Czech Republic. This study was also a part of the research programme MSM 6046137302 preparation and research of functional materials and material technologies using micro and nanoscopic methods

References

- Weinstein M. et al.: US Patent No. 3,052,982 (1962).
- Weinstein M. et al.: US Patent No. 3,052,983 (1962).
- Kelly J. R. et al.: J. Prosthet. Dent. 75, 18 (1996).
- Hahn C., Teuchert K.: Ber. Dent. Keram. Ges. 57, 208 (1980).
- Šatava V., Kloužková A., Ležal D., Kohoutková M.: Ceramics-Silikáty 46, 37 (2002).
- Liebau F.: *Structural Chemistry of Silicates*, Springer-Verlag, Berlin 1985.
- Palmer D. C., Dove N. T., Ibberson R. M., Powell B. M.: Am. Mineral. 82, 16 (1997).
- Ota T., Takahashi M., Zamai J., Suzuki H.: J. Am. Ceram. Soc. 76, 2379 (1993).
- Erbe E. M. et al.: US Patent No. 5,622,551 (1997).
- Denry I. R., Meckert J., J. Dent. Res. 77, 1928 (1996).
- Rouf M. A., Hermansson L., Carlsson R.: Trans. J. Br. Ceram. Soc. 77, 36 (1978).
- Panzera C.: US Patent No. 4,455,383 (1984).
- Katz B.: US Patent No. 4,798,536 (1989).
- Holand W., Frank M., Rheinberger V.: J. Non-Cryst. Solids 180, 292 (1995).
- Holand W., Frank, Rheinberger V.: Quintessenz Zahnarzt 44, 761 (1993).
- Brodkin D. et al.: US Patent No. 6,120,591 (2000).
- Levin E. M. et al.: *Phase Diagrams for Ceramics*, The American Ceramics Society INC, Ohio 1964.
- Schairer J. F., Bowen N. L.: American Journal of Science 253, 681 (1955).
- Barreiro M. M., Rlesgo O., Vicente E. E.: Dent. Mater. 5, 51 (1989).
- Burk B., A. P. Burnett: US Patent No. 4,101,330 (1978).
- Bedard H. L., Flanigen E. M.: US Patent No. 5,071,801 (1991).
- Brodkin D.: US Patent No. 6,086,662 (2000).
- McLean et al.: US Patent No. 3,464,837 (1969).
- Morena R., Lockwood P. L.: J. Am. Ceram. Soc. 64, C 74 (1986).
- Mackert J. R.: Dental Mater. 2, 32 (1986).
- Rasmussen T. et al.: Dental Mater. 14, 202 (1998).
- Sheu T., O'Brien W. J., Rasmussen S. T., Tien T.: J. Mater. Sci. 29, 125 (1994).
- Liu C., Komarneni R.: J. Am. Ceram. Soc. 77, 3105 (1994).
- Zhang Y., Wu J., Rao P., Lv M.: Mater. Lett. 60, 2819 (2006).
- Novotná M., Šatava V., Ležal D., Kloužková A., Kostka P.: Solid State Phenomena 90, 377 (2003).
- Novotná M., Kloužková A., Maixner J., Šatava V.: Ceramics-Silikáty 49, 252 (2005).
- Kohoutková M., Kloužková A., Maixner J., Mrázová M.: Ceramics-Silikáty 51, 9 (2007).
- Novotná M., Šatava V., Kostka P., Ležal D., Maixner J., Kloužková A.: Glass Technol. 45, 105 (2004).
- Hoshikawa et al.: US Patent No. 6,797,048 (2004).