

## PREPARATION OF LEUCITE-BASED COMPOSITES

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Submitted August 28, 2012; accepted November 26, 2012

**Keywords:** Leucite ceramics, Hydrothermal, Dilatation, Coefficient of thermal expansion

*The aim of this study was to prepare leucite dental composites from two separately synthesized components - tetragonal leucite and glassy matrix. The newly developed procedure is based on the preparation of crystalline tetragonal leucite powder by relatively low temperature synthesis under hydrothermal conditions. Matrix powder was prepared by a classical melting process and subsequent milling of the quenched glass. The dental composites were prepared by mixing of 10 wt. %, 20 wt. % and 30 wt. % of synthesized tetragonal leucite with glass powder followed by pressing and firing. The sintering process was observed by optical microscope and the optimal firing temperature for each composite was determined. Optical and electron microscopy was used to characterise the microstructure of the composites, especially the distribution of the leucite particles in the matrix. Dilatometric measurements proved that the coefficient of thermal expansion of the composites increased up to 44 % in comparison with the basic matrix.*

### INTRODUCTION

In the last few years leucite ( $\text{KAlSi}_2\text{O}_6$ ) and leucite ceramics have become the aim of many scientific studies, especially in the field of dental prosthetics. The reason for its extension was the fact that the leucite crystals presented in dental ceramics increased the coefficient of thermal expansion and so allowed the ceramics to be fused with a metal reinforcement. This feature enabled the production of metal-ceramic dental prostheses with satisfactory mechanical properties. Nowadays, metal-ceramic systems are the most extensive dental restorations in dental prosthetics and occupy 70 - 80 % of the total number of all dentures. In addition, leucite ceramics with a higher content of leucite crystals > 40 wt. % is used for all-ceramic systems.

As mentioned above, the coefficient of thermal expansion is one of the most important properties, especially for metal-ceramic systems. The mismatch in CTE of a metal framework and of a ceramic material after the firing process causes the formation of tension, which can lead to the scaling of these materials from each other.

It was reported by Ong et al. [1] that the addition of 15-25 % of t-leucite to the glassy matrix increased the CTE of the resulting composite materials from

17 to 29 %. Yang et al. [2] published a significantly lower increase in the CTE of the composite materials containing 5 - 25 % of t-leucite. The highest addition of leucite (25 %) to the glassy matrix composite caused a CTE increase of 14.5 %. Moreover, it was found that the increasing amount of leucite crystals in composite materials increased the CTE values linearly.

The CTE values of some selected commercial dental materials are provided in the following Table 1. Leucite ceramics suitable for metal-ceramic restorations are represented by the following systems: IPS Classic, IPS d.Sign, Empress I and Ceramco II (containing up to 25 wt. % of leucite crystals). The two systems OPC and Vitadur-N are used for all-ceramic restorations and contain a higher amount of crystalline phase. The aforementioned system OPC contains ~ 41 wt. % of t-leucite, whereas the system Vitadur-N represents leucite-free ceramics with ~ 55 wt. % of  $\text{Al}_2\text{O}_3$ . For comparison it should be noted that the CTE of commercially available Ni-Cr alloys and alloys of rare metals for metal-ceramic systems ranges from 12.0 to  $15.7 \times 10^{-6} \text{ K}^{-1}$  [3-5].

The aim of this work was to prepare a leucite dental composite from hydrothermally synthesised t-leucite and glassy matrix and to measure its coefficient of thermal expansion with respect to its possible use for metal or all-ceramic restorations.

Table 1. Values of CTE of some selected commercial dental materials.

	IPS Classic [6]	IPS d.Sign [6]	Empress I [7]	Ceramco II [7]	OPC [4]	Vitadur-N [4]
CTE $\times 10^{-6} \text{ K}^{-1}$	12.6 $\pm$ 0.5	12.0 $\pm$ 0.5	14.4	13.4 $\pm$ 0.1	19.2 $\pm$ 0.6	7.1 $\pm$ 0.1
	[20-600°C]	[20-600°C]	[25-500°C]	[25-500°C]	[25-500°C]	[25-500°C]

## EXPERIMENTAL

Dental leucite composites were produced from two separately prepared components – tetragonal leucite and glassy matrix. Leucite powders were prepared by a hydrothermal method in two steps [8]. The first step comprises the synthesis of analcime ( $\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$ ) from aluminate and silicate solutions, which had been prepared separately by dissolving silica and aluminium raw materials in a 4M sodium hydroxide solution while being stirred permanently. In the second step, t-leucite was prepared by ion exchange of  $\text{Na}^+$  ions from analcime for  $\text{K}^+$  ions from a 4M solution of KCl. Both syntheses were carried out under hydrothermal conditions in Teflon-lined autoclaves at 200°C. The prepared powders were washed by boiling distilled water, vacuum filtered and dried in an oven at 100°C.

A leucite-free glass frit of the composition 60.9  $\text{SiO}_2$ , 9.4  $\text{Al}_2\text{O}_3$ , 11.8  $\text{K}_2\text{O}$ , 8.6  $\text{Na}_2\text{O}$ , 2.3  $\text{CaO}$ , 6.6  $\text{B}_2\text{O}_3$ , 0.1  $\text{BaO}$  (all in wt.%) was prepared by melting in a Pt crucible placed in a laboratory furnace heated to 1500°C for 2 hours. After being melted, the specimens were quenched and crushed to pass through a sieve with mesh size 1.5 mm. Crushed samples were grinded in planetary mill to obtain an average particle size of 27  $\mu\text{m}$ .

As-prepared powders of t-leucite and the frit containing 5 wt. % of water were well homogenized in a tilting mixer equipped with corundum balls for 1 hour and subsequently pressed into the bars using the pressure 50-60 MPa. These bars having 12.7 mm in diameter were fired in a laboratory vacuum furnace (Clasic, Czech Republic) according to the temperature calculated from the commercial software Sci Glass. The sintering process was observed by optical microscopy, and the optimal firing temperature for each composite was determined. The heating rate was 30°C/min and the sintering temperature was held for 1-2 minutes (Table 2).

The microstructure of the specimens was characterized using optical (Olympus BX 51P) and electron (Hitachi S-4700) microscopy. The surface of the bars

was grinded, polished and etched in 3 % HF for 10 s to increase the contrast between amorphous and crystalline phases.

XRD measurements of powder samples were performed on the X'Pert PRO powder diffractometer by means of parafocusing Bragg-Brentano geometry using  $\text{Cu K}\alpha$  radiation ( $k = 1.5418 \text{ \AA}$ ,  $U = 40 \text{ kV}$ ,  $I = 30 \text{ mA}$ ). Data evaluations were performed in the software package X'Pert High Score Plus.

Thermal expansion coefficients (CTEs) were obtained from thermomechanical analysis. The blocks of samples 5 $\times$ 5 $\times$ 3 mm were heated (heating rate 5  $\text{K min}^{-1}$ ) in the TMA CX04 equipment (R.M.I. Pardubice, Czech Republic). From the thermal expansion curves using the slope intercept method the values of CTE were determined.

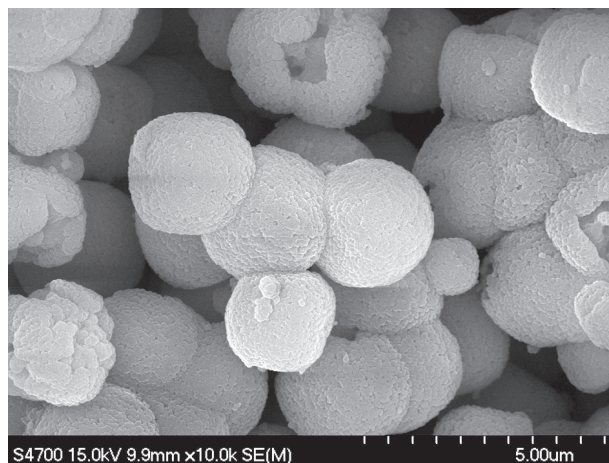
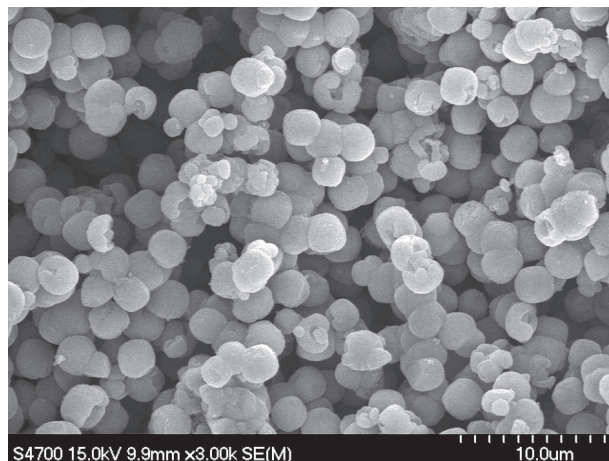


Figure 1. SEM images of t-leucite.

Table 2. Firing schedules.

Initial temperature (IT) (°C)	500
Drying time on IT (min)	10
Vacuum (mbar)	1-10
Heating rate (°C/min)	30
Maximum temperature (°C)	800-1150
Vacuum off temperature (°C)	= max. temperature

## RESULTS AND DISCUSSION

Leucite powders for dental composites were prepared by hydrothermal synthesis. Figure 1 shows SEM images of the analcime obtained in the first step of the preparation procedure. The resulting t-leucite is shown in Figure 2. It can be seen, that homogenous leucite powders with a uniform particle size of 4 $\mu$ m have been prepared. These spherical particles of leucite are composed of much smaller crystallite grains of 100 nm (Figure 2 c, d).

Figure 3 shows the diffraction pattern of the amorphous matrix and of the composite powders containing 10, and 20 wt. % of t-leucite. The left image clearly demonstrates the loss of the amorphous phase at the expense of crystalline phase. The second figure shows the angular range 24-32.5° (2 $\theta$ ) in greater detail, clearly indicating an increase of the amount of crystalline phase (tetragonal leucite).

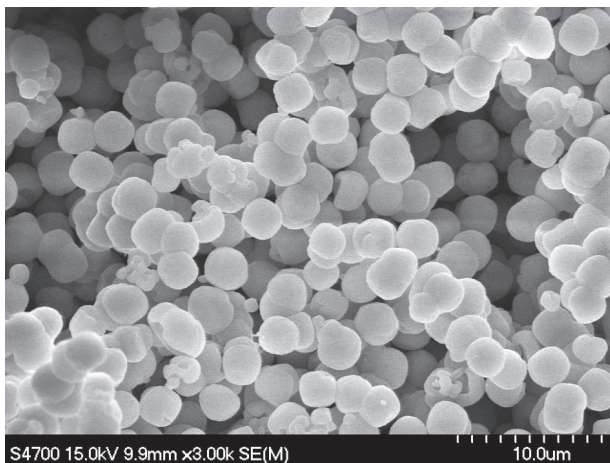
The powders of the basic matrix and of the composites containing up to 30 wt. % of leucite were pressed into bars and sintered in a vacuum furnace. The sintering process was observed using an optical microscope.

Figure 4 shows an insufficiently sintered sample of the matrix material fired at 720°C and a sintered sample fired at 750°C. It was found that the increasing amount of crystalline phase increased the temperature required for sintering of the composite material. Optimal firing temperatures of the composites are listed in Table 3.

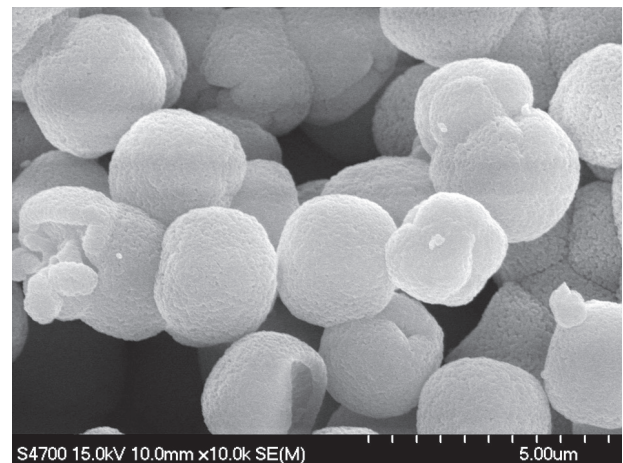
Microscopic analysis (Figures 5 and 6) demonstrates that a relatively well (homogeneously) dispersed composite material was prepared at temperatures from 800°C to 1000°C, depending on the content of the crystalline phase. Figure 5 shows images of the sintered samples of the basic matrix and of the composites containing 10, 20 and 30 wt. % of t-leucite obtained by optical microscopy.

Table 3. Firing temperatures of the prepared samples.

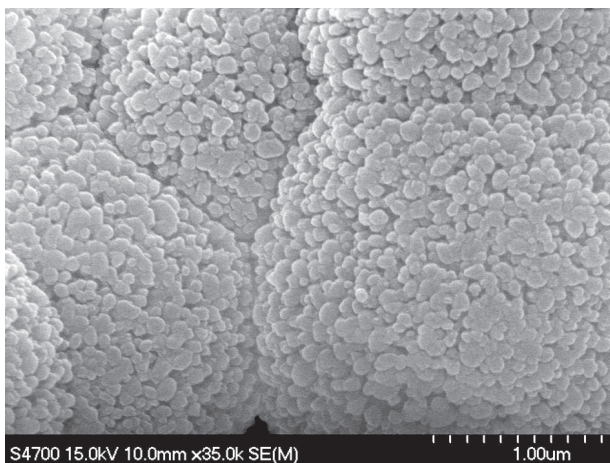
Sample	Amount of t-leucite (wt.%)	Firing temperature (°C)
M	0	750
M_10t	10	800
M_20t	20	870
M_30t	30	1000



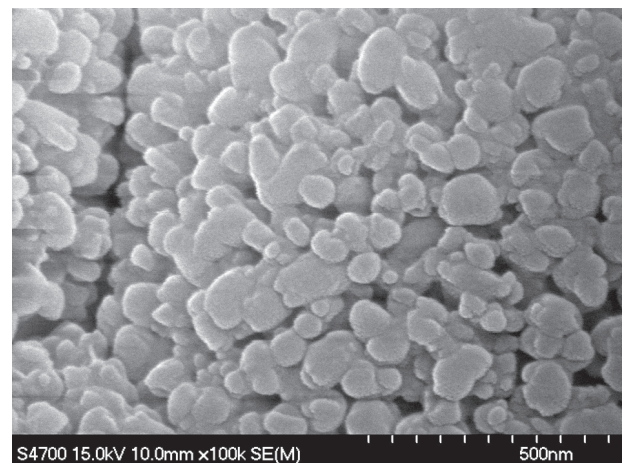
a)



b)



c)



d)

Figure 2. SEM images of t-leucite.

The microstructure of the prepared composites was also characterised by scanning electron microscopy (see Figure 6). The first image shows the distribution of leucite particles in the dark matrix (Figure 6a). In the second image etched surface of the spherical leucite particle composed of crystallite grains having average size of 100nm can be seen (Figure 6b).

The thermal expansion coefficient values (CTE) were obtained from dilatometric measurements and are listed in Table 4. The value of CTE increased from  $10.08 \times 10^{-6} \text{K}^{-1}$  for the basic matrix to  $14.52 \times 10^{-6} \text{K}^{-1}$  for the composite M\_30t in the temperature range 50-450°C. The addition of 30 wt. % of t-leucite caused the increase of CTE of 44 %. In case of the composite M\_20t the increase was 39 % to a CTE value  $14.01 \times 10^{-6} \text{K}^{-1}$ .

### CONCLUSIONS

Dental leucite composites consisting of two separately synthesized components (tetragonal leucite and glassy matrix) were prepared. Homogenous leucite

Table 4. CTE values of the prepared samples.

Sample	Amount of t-leucite (wt. %)	CTE ( $\times 10^{-6} \text{K}^{-1}$ )
M	0	10.08
M_10t	10	12.24
M_20t	20	14.01
M_30t	30	14.52

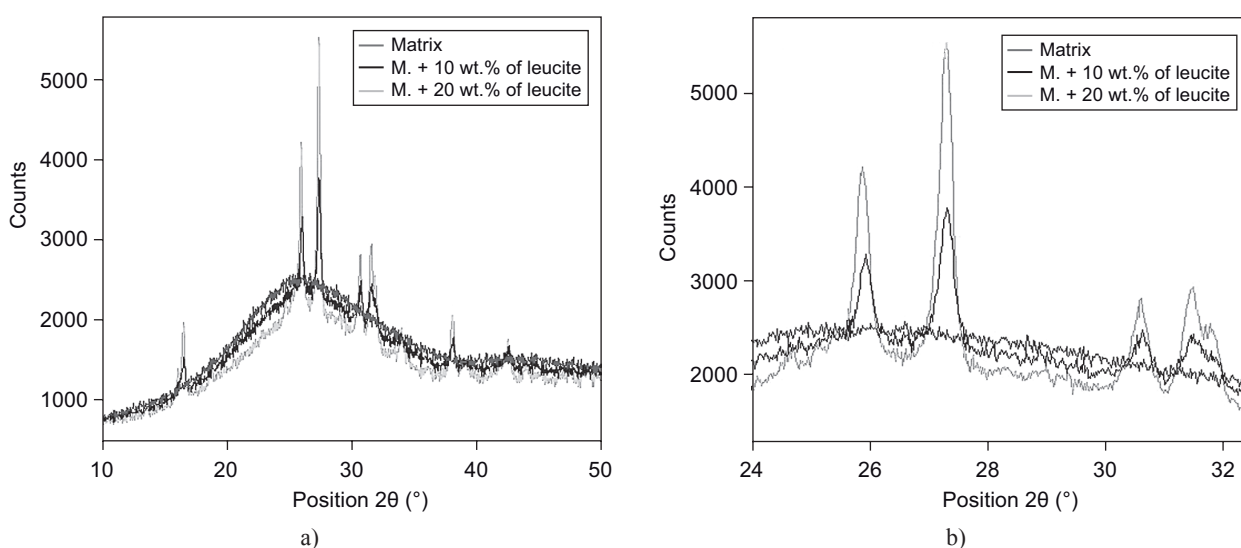


Figure 3. XRD patterns of the matrix and of the composites containing 10 and 20 wt. % of t-leucite.

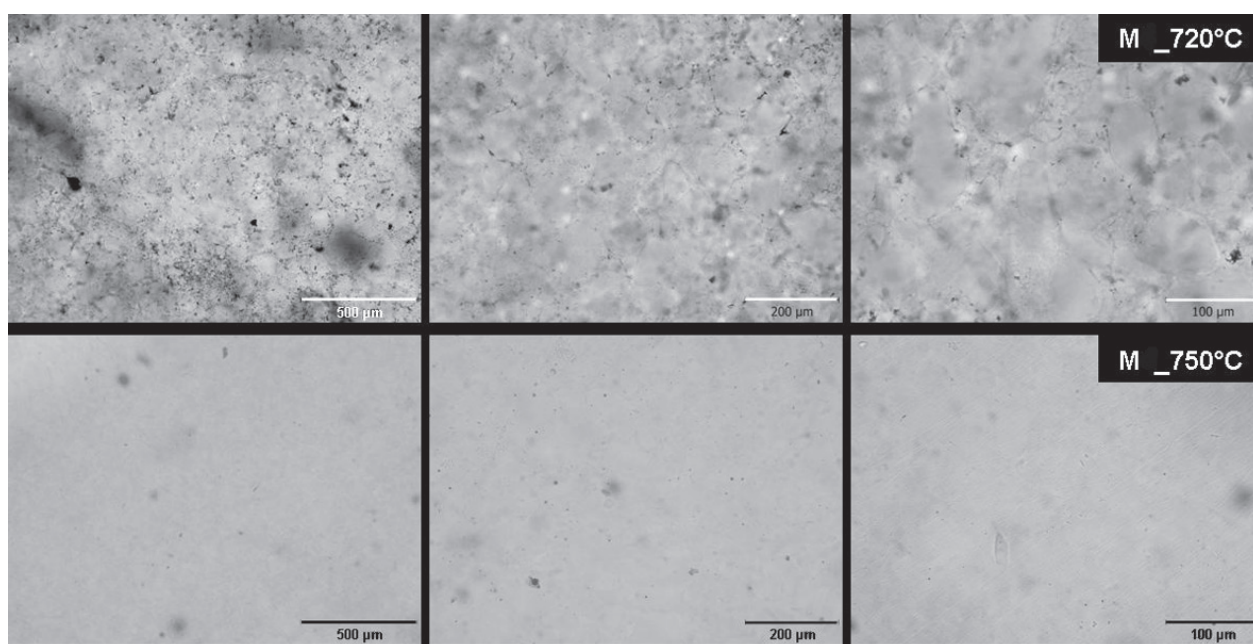


Figure 4. OM images of the matrix fired at 720 and 750°C.

powders having a uniform particle size of 4  $\mu\text{m}$  were synthesized at 200°C under hydrothermal conditions. The matrix powder was prepared by a classical melting process and subsequent milling of the quenched glass. The dental composites were obtained by mixing of 10 wt. %, 20 wt. % and 30 wt. % of the synthesized tetragonal leucite with glass powder followed by pressing and firing. Microscopic analysis showed that relatively

well-homogeneously dispersed composite material was prepared at temperatures from 800°C to 1000°C, depending on the content of the crystalline phase. Dilatometric measurements proved that the coefficient of thermal expansion of the composites increased up to 44 % in comparison with the basic matrix. Prepared composite materials containing 20 wt. % and 30 wt. % of the t-leucite and having the CTE values  $14.01 \times 10^{-6} \text{K}^{-1}$  and

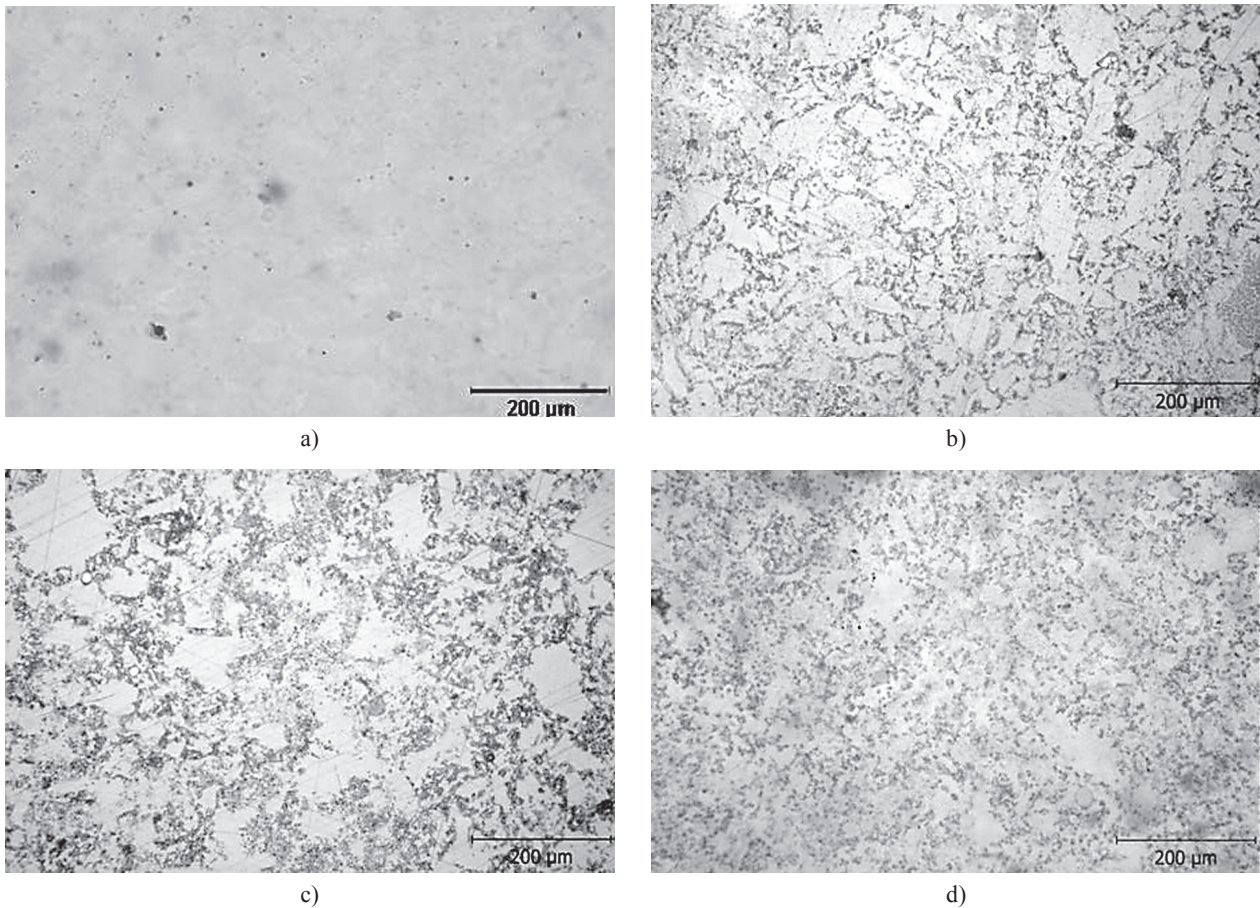


Figure 5. OM images of the matrix (a) and of the composites containing 10 wt. % (b), 20 wt. % (c) and 30 wt. % (d) of t-leucite.

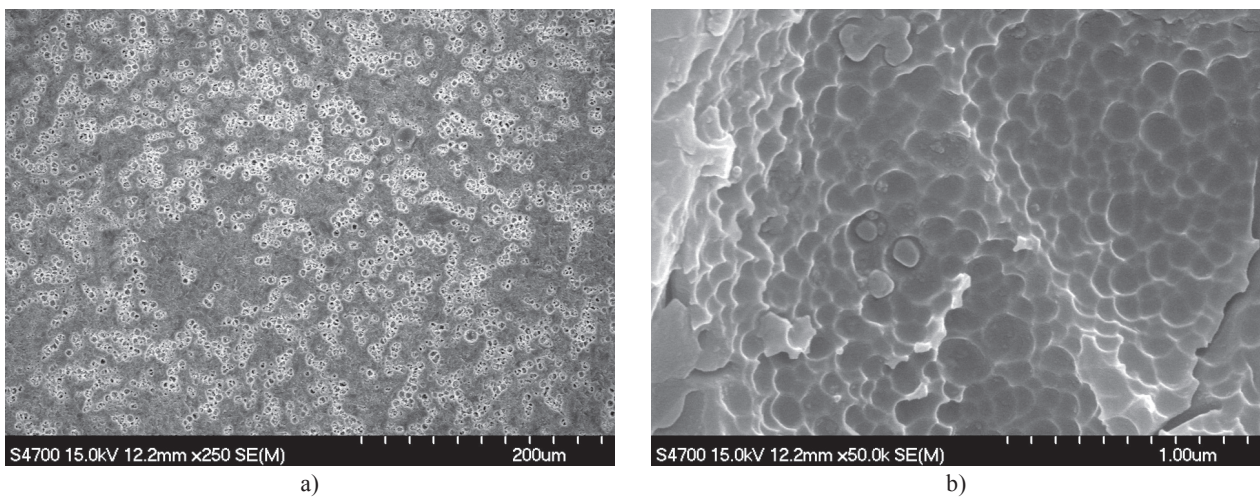


Figure 6. SEM images of the composite M\_30t containing 30 wt.% of t-leucite.

$14.52 \times 10^{-6} \text{ K}^{-1}$ , respectively, in the temperature range 50-450°C are suitable materials for metal or all-ceramic restorations.

#### Acknowledgement

*This work was part of the project No 2A-1TP1/063, "New glass and ceramic materials and advanced concepts of their preparation and manufacturing", supported by the Ministry of Industry and Trade, Czech Republic and by Grant MSM 6046137302.*

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