

Microstructural Properties of Leucite-type Glass-ceramics for Dental Use

*Svetozar Musić,^a Jasenka Živko-Babić,^b Ketij Mehulić,^b
Mira Ristić,^a Stanko Popović,^{a,c} Krešimir Furić,^a
Dunja Selinger-Kocijan,^d Stojan Čelap,^d and Tomislav Ivanišb^b*

^a*Ruder Bošković Institute, P. O. Box 1016, 10001 Zagreb, Croatia*

^b*Faculty of Dentistry, University of Zagreb, 10000 Zagreb, Croatia*

^c*Department of Physics, Faculty of Science, University of Zagreb,
P. O. Box 162, 10001 Zagreb, Croatia*

^d*INA-NAFTAPLIN, 10000 Zagreb, Croatia*

Received February 20, 1996; revised May 16, 1996; accepted May 27, 1996

Microstructure of leucite-type dental glass-ceramics was investigated using X-ray diffraction, Fourier transform infrared spectroscopy, laser Raman spectroscopy, scanning electron microscopy and energy dispersive X-ray spectrometry. The main features of the FT-IR and laser Raman spectra were similar to those of silicate glasses containing Al^{3+} or other M^{3+} ($\text{M} = \text{metal}$) as network forming ions. Two weak IR bands at 640 and 543 cm^{-1} were typical of all leucite glass-ceramics. These IR bands disappeared with the conversion of leucite glass-ceramics to the glass state. The laser Raman spectrum of leucite-type glass exhibited one unusual band centred approximately at 4600 cm^{-1} possessing the fluorescence/luminescence spectral feature together with two luminescence sharp peaks at 5037 and 5007 cm^{-1} . The effects of quenching (cooling) on the morphological and chemical properties of leucite-type dental glass-ceramics were monitored.

INTRODUCTION

Glass-ceramics are polycrystalline solids that can be produced by partial crystallization of glass under controlled conditions. They have found very different applications as engineering materials. Glass-ceramics have also be-

come important materials in dental restoration due to their chemical inertness combined with high mechanical strength and appropriate thermal and physical properties.¹ For example, glass-ceramics composed largely of β -quartz were proposed for use in dental restorations.² The glass-ceramics with β -quartz microcrystals were obtained by partial crystallization of the glass containing Li_2O , Al_2O_3 , SiO_2 , ZnO , MgO , TiO_2 , ZrO_2 , P_2O_5 and CeO_2 . The colours of this material were similar to those of natural teeth. Wolf *et al.*³ investigated the properties of alumina-glass dental composites. Tzeng *et al.*⁴ investigated the effects of ZrO_2 and Al_2O_3 additions on the mechanical properties of DICOR glass-ceramics. DICOR-related glass-ceramics exhibit a property of machinability. Appropriate additions of Al_2O_3 led to increased bending strength, because Al_2O_3 stabilizes and strengthens the DICOR-related glass-ceramics by being incorporated into the silicon network. Extra ZrO_2 addition to DICOR formulation resulted in an opposite effect.

Recently, the industry of dental materials has been paying significant attention to leucite glass-ceramics for use in dentistry. Seven dental materials made by different manufacturers were tested for their leucite content.⁵ Fischer *et al.*⁶ investigated a procedure for increasing the flexural strength of leucite dental material VMK 68. Sodium ion exchange in NaCl at 830 °C for 8 min increased the flexural strength of this dental material. A high sodium content favourably stabilized the cubic phase of the persisting leucite down to room temperature, which also reduced thermal expansion of thus treated ceramics. When the surface of leucite glass-ceramics (Empress®)⁷ was exposed to 5% HF, after etching for 120 s most of the surface layer was removed, revealing a fine grained pattern characteristic of this type of glass-ceramics. Since mechanical removal of the surface layer by grinding is not recommended, the pressed glass-ceramics should be etched for 120 s or longer to achieve an optimal bond strength to the luting composite. Wakasa *et al.*⁸ examined the glass-transition, dehydration, crystallization and melting temperature of several dental porcelains and kaolinite/feldspar mixtures.

In the present study, structural, chemical and morphological properties of leucite-type glass-ceramics were investigated. The aim was to obtain information on the changes of microstructure of leucite-type glass-ceramics in dependence on the treatment of these materials. Knowledge of the microstructure of leucite-type glass-ceramics is specially important in tailoring the material with better properties for the application in dentistry.

EXPERIMENTAL

The original dental ingots (IPS-Empress®) were obtained by courtesy of Ivoclar-Vivadent, FL-9494 Schaan, Liechtenstein. The manufacturer of these dental materials gave the initial chemical composition of glass as shown in Table I. The ingots were used for preparation of samples by the so-called »Schicht« (layering) or »Mal«

(tinting) technique.^{9,10} A description of the samples investigated in this study is given in Table II. The production and shaping of leuciteglass ceramics for dental restorations have been described in detail elsewhere^{9,10} and the procedures described in these references were used during the preparation of samples L5 to L12.

X-ray powder diffraction (XRD) measurements were performed at room temperature, using a Philips counter diffractometer, model MPD 1880, with monochromatized Cu-K α radiation (graphite monochromator).

TABLE I
Initial chemical compositions of IPS-Empress[®]
glass-ceramics ($w \times 100$) used in preparation of
leucite-type dental glass-ceramics

Oxide	Ingot 1	Ingot 2
SiO ₂	59.0–63.0	59.0–61.0
Al ₂ O ₃	12.5–16.7	17.0–21.0
K ₂ O	10.0–14.0	10.0–14.0
Na ₂ O	5.8–8.0	3.5–6.5
B ₂ O ₃	0.5–2.0	0.0–1.0
CeO ₂	0.5–2.0	0.0–1.0
CaO	1.0–3.5	0.5–2.5
BaO	0.5–3.0	0.0–1.5
TiO ₂	0.0–0.5	0.0–0.5

TABLE II
Description of the samples investigated in the present study

Sample	History of the samples
L1	Glass-ceramic ingot for »Schicht« technique, as supplied by Ivoclar-Vivadent
L2	Sample L1 heated at 1300 °C in air for 2 h and cooled in furnace to room temperature
L3	Glass-ceramic ingot for »Mal« technique, as supplied by Ivoclar-Vivadent
L4	Sample L3 heated at 1300 °C in air for 2 h and cooled in furnace to room temperature
L5	Glass-ceramic crown pressed for »Schicht« technique
L6	Glass-ceramic crown pressed for »Mal« technique
L7	Sample pressed for »Mal« technique and quenched in water
L8	Sample pressed for »Schicht« technique and quenched in water
L9	Sample pressed for »Mal« technique and cooled to room temperature
L10	Sample pressed for »Schicht« technique and cooled to room temperature
L11	Sample pressed for »Mal« technique and cooled in furnace
L12	Sample pressed for »Schicht« technique and cooled in furnace

FT-IR spectra were recorded at room temperature with a Perkin-Elmer spectrometer, model 2000. The spectrometer was coupled with a personal computer loaded with the IR Data Manager (IRDM) program. The specimens were pressed in discs using spectroscopically pure KBr for measurements in the mid IR region. The FT-IR spectra were also recorded in the far IR region and in this case a polyethylene matrix was used.

Raman scattering experiments were performed through standard geometry at 90 °C. A Coherent Innova-100 laser with $\lambda = 514.5$ nm served as an excitation source and the scattered light was analyzed using a DILOR Z-24 Raman spectrometer.

The samples were also investigated by a scanning electron microscope, model 515, manufactured by Philips. Energy dispersive X-ray spectrometry was performed by the EDAX system, 9900 A North American Philips Co. The samples were not surface polished or treated with HF before the electron microscopic work. The samples were coated with gold.

RESULTS AND DISCUSSION

X-ray diffraction patterns of samples L1 to L4 are shown in Figure 1. The diffraction pattern of sample L1 contained diffraction lines of leucite and a broad maximum due to an amorphous component. The diffraction pattern of sample L3 also corresponded to leucite, but the amorphous fraction was much smaller than in L1. Leucite, α -KAlSi₂O₆, belongs to the feldspathoid group of minerals.¹¹ A high temperature polymorph, β -KAlSi₂O₆ (cubic form), is also known. After heating sample L1 to 1300 °C in air, the diffraction lines of leucite decreased in intensity (sample L2). However, the diffraction pattern of sample L4, obtained by heating sample L3 to 1300 °C, showed only a broad amorphous maximum, thus indicating the glass nature of sample L4. X-ray diffraction patterns (Figure 2) of the crowns made by »Schicht« and »Mal« techniques corresponded to the leucite-type glass-ceramics.

FT-IR spectra of the selected samples are shown in Figures 3 and 4. The spectrum of sample L1 was characterized by three broad bands at 1170–1020, 769–715 and 454 cm⁻¹. Two weak bands at 640 and 543 cm⁻¹ were also visible. Heating sample L1 at 1300 °C in air caused no changes in the corresponding FT-IR spectrum (sample L2). However, after heating sample L3 at 1300 °C in air (sample L4), the weak bands at 640 and 543 cm⁻¹ in the FT-IR spectrum were not visible. The weak IR bands at 640 and 543 cm⁻¹ were also observed in the FT-IR spectrum of crowns (samples L5 and L6). These two IR bands were found to be typical of all leucite-type glass-ceramics. Handke and Mozgawa¹² suggested that the bands at approximately 630 and 540 cm⁻¹ could be related to six-membered ring vibrations, observed for tridymite and kalsylite.

Vibrational spectroscopic results, obtained for silica and silicate glass, can be used as reference in the interpretation of vibrational spectra of leucite glass-ceramics. The precipitated (amorphous) silica¹³ showed a very

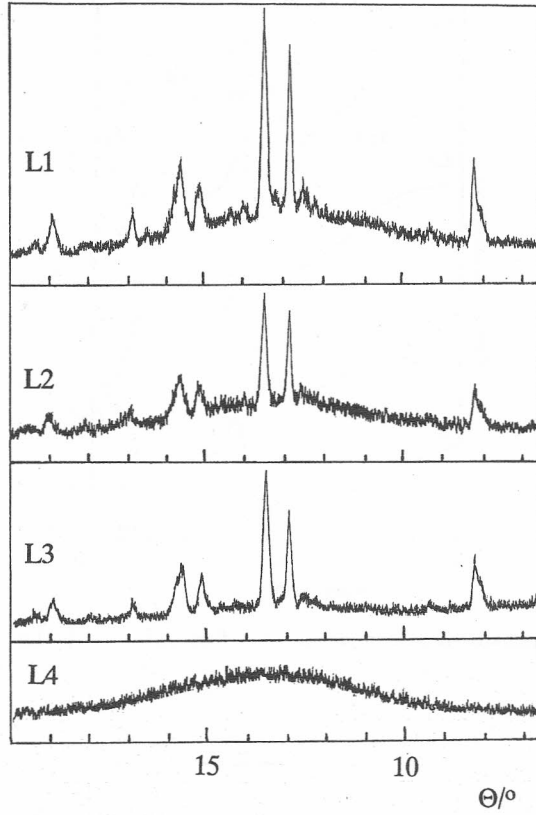


Figure 1. X-ray diffraction patterns of samples L1 to L4, recorded at room temperature.

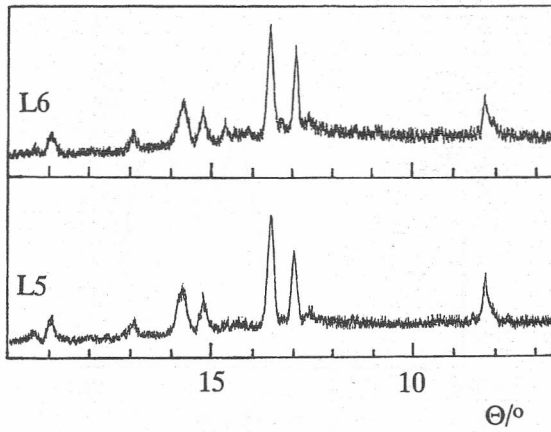


Figure 2. X-ray diffraction patterns of samples L5 and L6, recorded at room temperature.

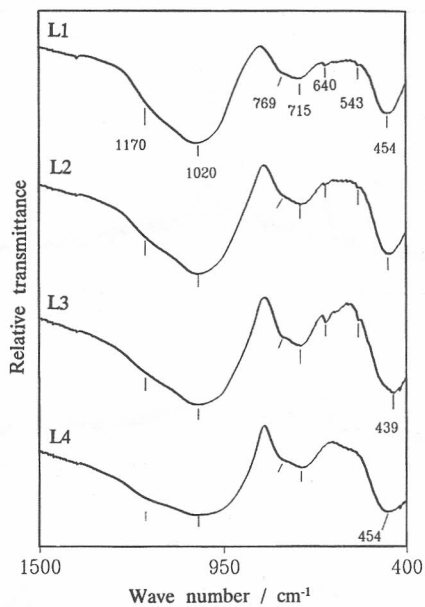


Figure 3. Fourier transform infrared spectra of samples L1 to L4, recorded at room temperature.

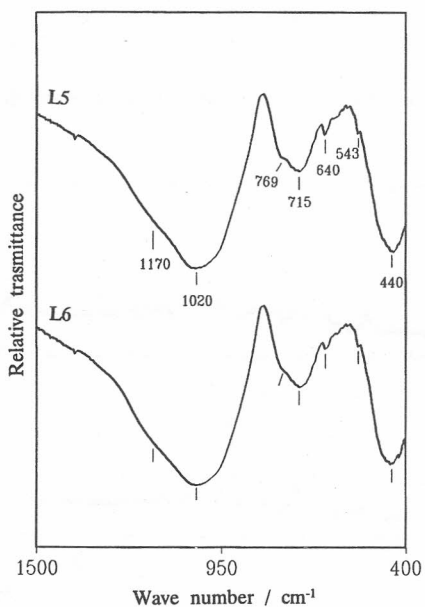


Figure 4. Fourier transform infrared spectra of samples L5 and L6, recorded at room temperature.

strong IR band at 1090 cm^{-1} with a shoulder at $\approx 1200\text{ }^\circ\text{C}$, bands at 900 and 800 cm^{-1} and also a very intense band at 470 cm^{-1} with a shoulder at $\approx 550\text{--}600\text{ cm}^{-1}$. In the IR spectrum of pure SiO_2 glass film, three distinct absorption bands were observed.¹⁴ The strongest band at 1060 cm^{-1} was assigned to asymmetric vibration of the silicon sublattice against oxygen sublattice, and the shoulder on the high frequency side to symmetric vibration of the Si-O sublattices. The bands at 810 and 440 cm^{-1} were interpreted as bond bending motions of three-atom centres of the O-Si-O and Si-O-Si type in the quasilattice.

Structural incorporation of metal cations into SiO_2 glass, possessing the network forming or/and modifying properties, influences the corresponding vibrational spectra. Mezbacher and White¹⁵ investigated the structure of alkaline earth aluminosilicate glass by vibrational spectroscopy. Raman modes at $\approx 1200, 1100, 950, 900$ and 850 cm^{-1} were associated with silicate tetrahedra with 0, 1, 2, 3, and 4 NBOs (NBOs = non-bridging oxygens), respectively, in simple binary silicate glass. The structural incorporation of tetrahedral aluminium was correlated with a shift of the high frequency envelope to longer wavelengths. The intense Raman band at $525\text{--}540\text{ cm}^{-1}$, assigned to Al-O symmetric stretching in CaAl_2O_4 , might contribute to the broad mid-frequency Raman band in the Mg-aluminosilicate spectrum. The strong IR band between 700 and 900 cm^{-1} , characterizing condensed AlO_4 framework units, could be assigned to the 908 cm^{-1} TO mode. The 1025 cm^{-1} band is close to the IR mode for pure SiO_2 . Bands in the mid-frequency region of $500\text{--}600\text{ cm}^{-1}$ were assigned to bending and rocking motions of the aluminosilicate network, while the low frequency bands (below $\approx 400\text{ cm}^{-1}$) could be related to M-O vibrations (M = alkaline earth cation).

Raman spectra¹⁶ of barium gallosilicate glasses ($x_{\text{SiO}_2} < 0.40$) showed that Ga-O-Ga bonding was dominant, as monitored by a single major peak at $\approx 530\text{ cm}^{-1}$. Konijnendijk and Stevels¹⁷ concluded that Al^{3+} ions in alkali borosilicate glasses were only present in AlO_4 tetrahedra. Addition of Al^{3+} ions caused disappearance of the band at 780 cm^{-1} , typical of BO_4 tetrahedra in six-membered borate rings. Tarte *et al.*¹⁸ observed in the IR spectrum of sinhalite, MgAlBO_4 , a strong band at 700 cm^{-1} , which was assigned to Al-O vibration.

Ellisson and Hess¹⁹ investigated the incorporation of R = La, Gd or Yb in potassium silicate glasses. The increase of the R_2O_3 concentration produced partially-polarized Raman bands at $1030, 940$ and 860 cm^{-1} , which were assigned to the symmetric stretching modes of SiO_4 tetrahedra containing 1, 2 and 4 non-bridging oxygens, respectively, in which the non-bridging oxygens were coordinated primarily by R atoms. The most prominent feature in the mid-frequency region of IR spectra was the absorption band at $\approx 770\text{ cm}^{-1}$, presumably a counterpart of the Raman band at 780 cm^{-1} . The relative intensity of the band near 590 cm^{-1} increased with R_2O_3 concentration.

Musić *et al.*¹³ observed in the IR spectra of sodium borosilicate glass doped with iron ions that the shoulder at 800 cm^{-1} did not change its intensity and position, while the shoulder at 710 cm^{-1} changed to a well-resolved peak at the same position, on increasing the iron content. The shoulder at 710 cm^{-1} was also observed after incorporation of Eu^{3+} in sodium borosilicate glass.²⁰ This effect was interpreted as a consequence of the incorporation of Fe^{3+} or generally M^{3+} ($\text{M} = \text{metal}$) into the borosilicate glass network. In analogy to the above results, it could be suggested that the IR band at 715 cm^{-1} , observed in the present study, was due to the incorporation of Al^{3+} ions into the silicate network. Similarly, the IR band at 769 cm^{-1} could be attributed to Si–O–Si bending vibrations.

The main characteristics of the laser Raman spectra of leucite glass-ceramics for dental use can be compared with those known for aluminosilicate glass containing M^{3+} as network forming ions. Figure 5 shows the laser Raman spectra of powdered samples L2 and L4. The positions of Raman bands in these spectra were almost identical, and only slight differences in relative intensities of the bands were present. The Raman spectrum of sample L4, recorded by laser beam scattering on the glass monolith, is shown in Figure 6. Two well pronounced bands at 52 and 480 cm^{-1} were observed. Also, the band at 1084 cm^{-1} with a shoulder at 954 cm^{-1} , and the bands at 772 and 576 cm^{-1} were visible, which is in agreement with the spectra shown in Figure 5. In the Raman spectrum of sample L4 (Figure 6),

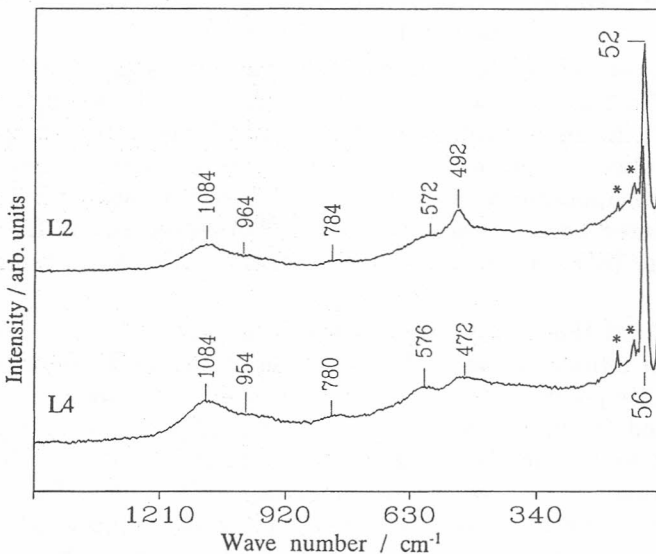


Figure 5. Raman spectra of samples L2 and L4, recorded at room temperature. Samples L2 and L4 were powdered before the Raman spectra recording. (*) denotes plasma lines.

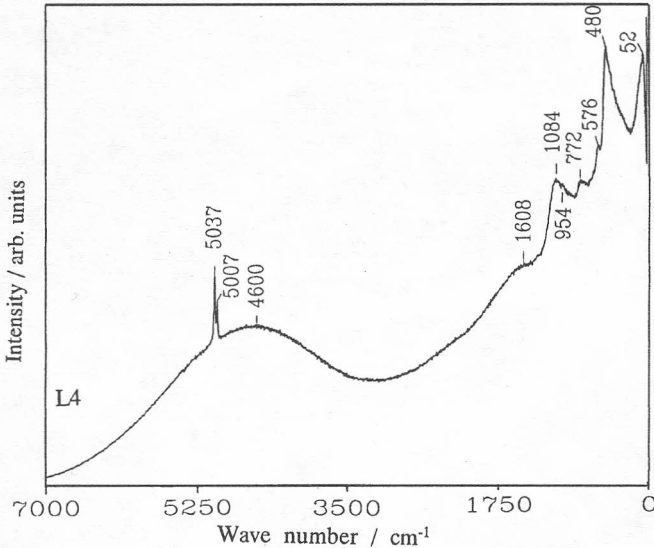


Figure 6. Raman spectrum of sample L4, recorded by laser beam scattering on the glass monolith at room temperature.

one extra broad band was observed around 4600 cm^{-1} . We attribute it to a fluorescence/luminescence spectral feature. Two joint sharp luminescent peaks at 5037 and 5007 cm^{-1} could belong to some dopant.

The samples were also analyzed by SEM and EDAX in order to obtain information on the morphology and elemental composition of the materials in dependence on their treatment. The results of these measurements indicated a strong influence of the treatment of the samples on their microstructure. These results are specially important to those involved in the technology of leucite-type dental glass-ceramics.

Figures 7 and 8 show SEM pictures of sample L2 with the corresponding EDAX patterns. Sample L2, obtained by heating sample L1 at a maximum temperature of $1300\text{ }^{\circ}\text{C}$, was powdered after cooling to room temperature in order to obtain information on the chemical composition inside the sample. EDAX patterns were obtained for particular points and for the total observed surface (the «total screen»). EDAX patterns undoubtedly showed that, there was a pronounced increase of potassium concentration (Figure 8) on the surface of some grains. Naturally, the $\text{Au-M}\alpha$ peak is present due to gold coating.

Figures 9 and 10 show the effect of quenching in water on the chemical and morphological properties of leucite-type glass-ceramics. Sample L7 made by the «Mal» technique and quenched in water showed pores on the surface of the material (Figure 9), because degassing could not be achieved

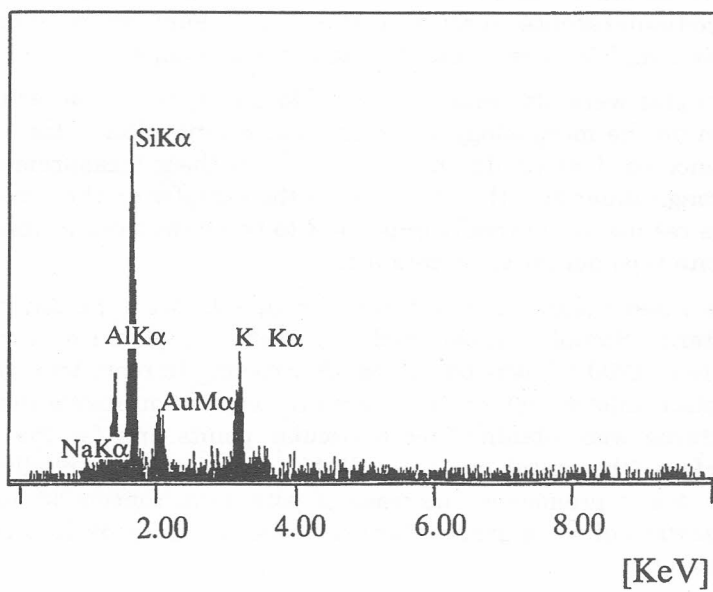
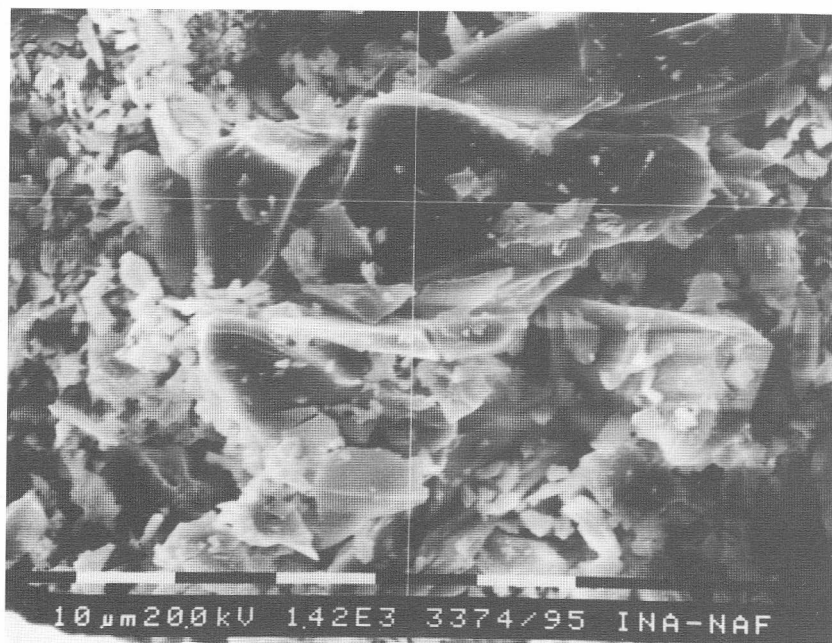


Figure 7. Scanning electron micrograph of sample L2. Sample L2 was powdered before SEM work. The cross shows the first »point« of EDAX pattern.

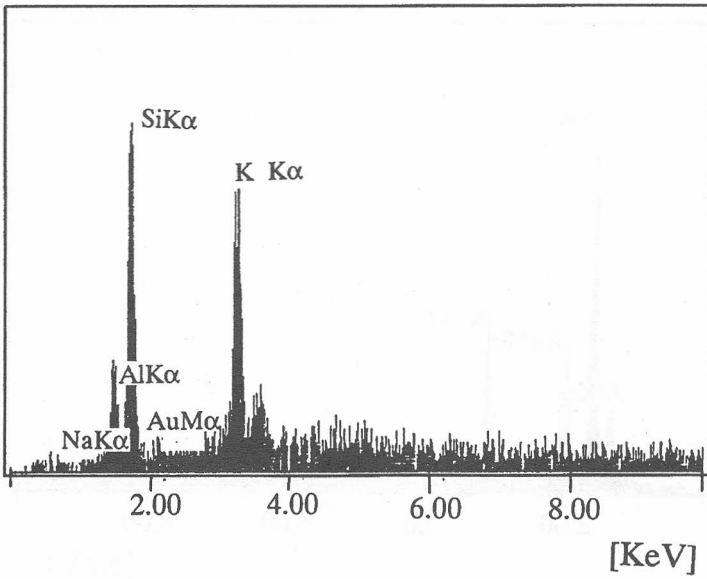
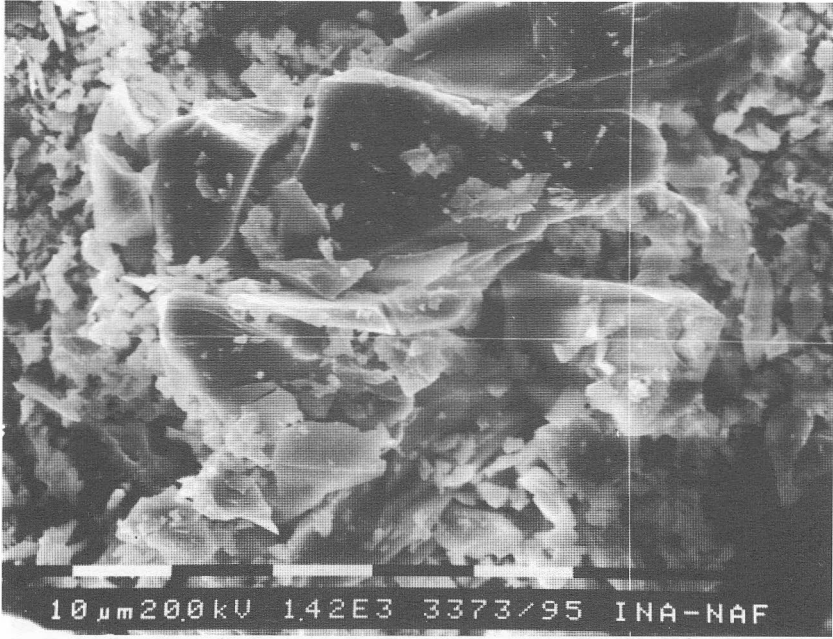


Figure 8. Scanning electron micrograph of sample L2. Sample L2 was powdered before SEM work. The cross shows the second »point« of EDAX pattern.

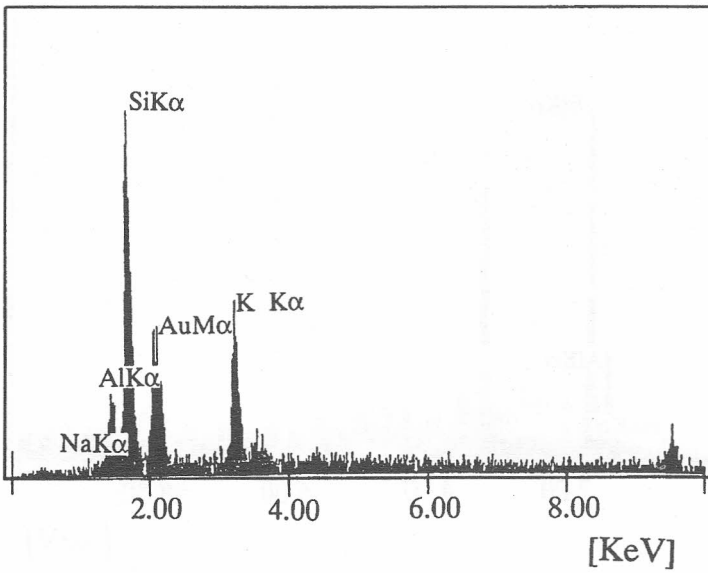
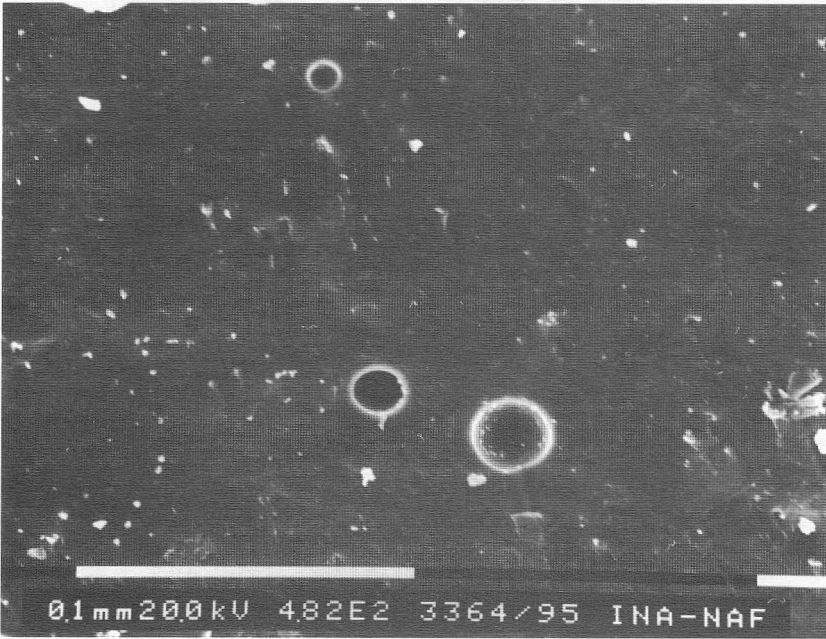


Figure 9. Scanning electron micrograph of sample L7 with EDAX pattern of the »total screen«.

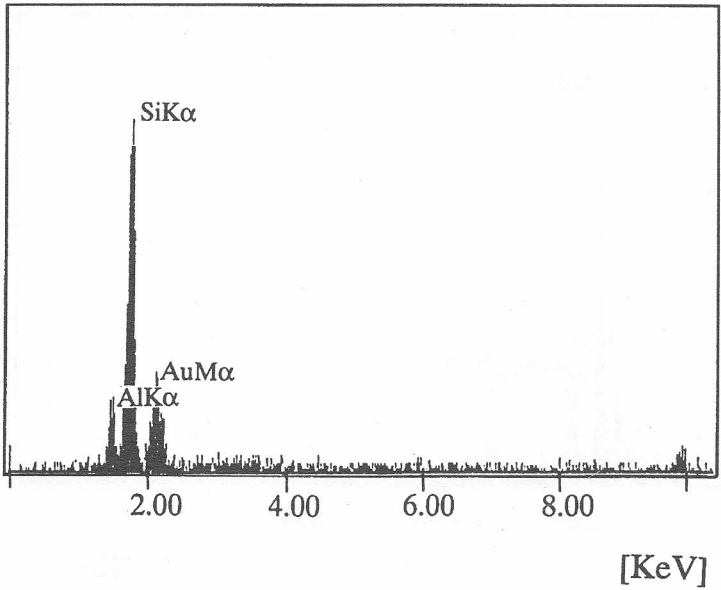
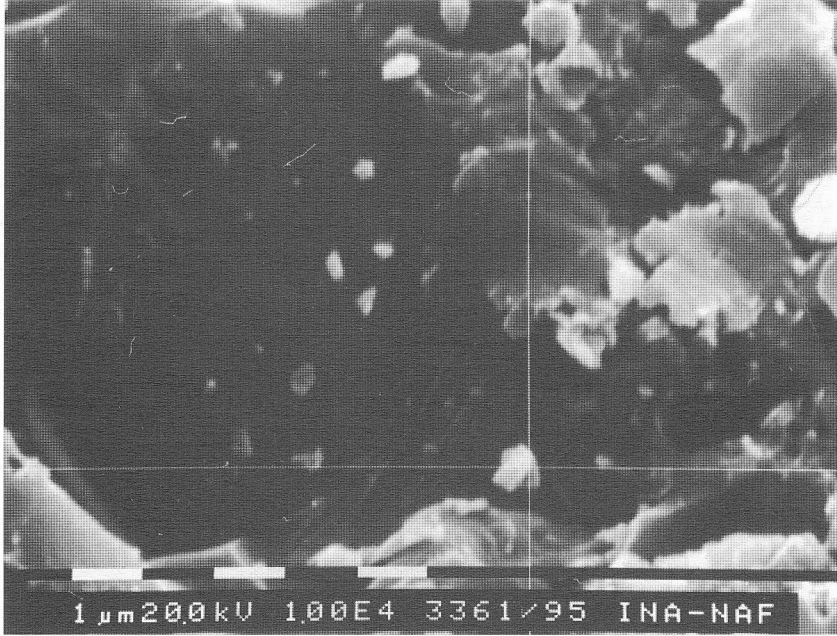


Figure 10. Scanning electron micrograph of sample L8 with EDAX pattern for the point marked by the cross.

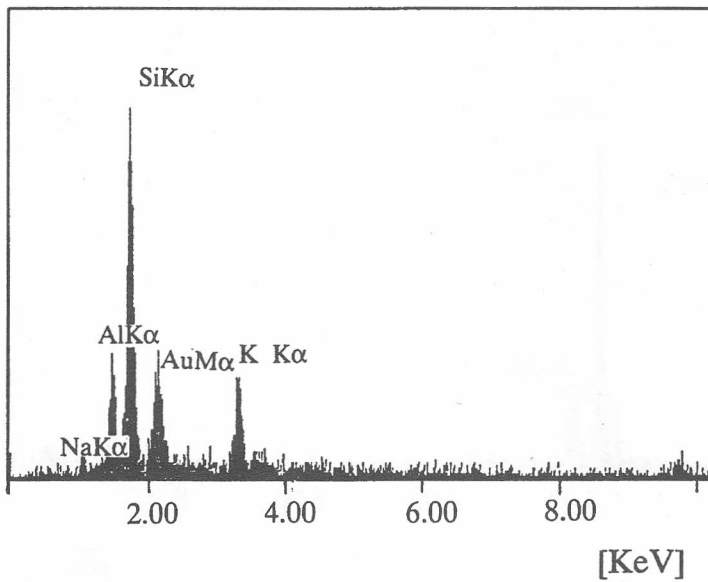
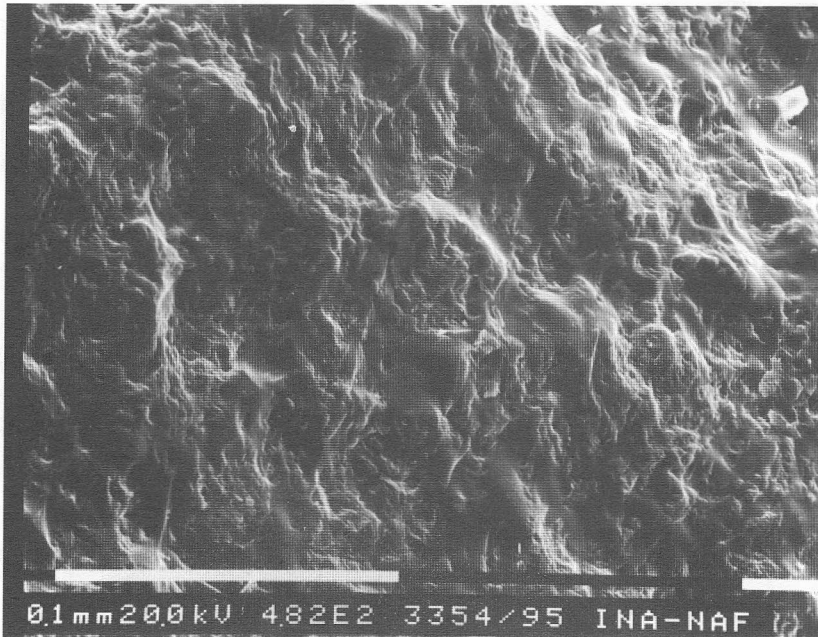


Figure 11. Scanning electron micrograph of sample L12 with the corresponding EDAX pattern.

with this mode of quenching. Figure 10 shows the results obtained for sample L8 made by »Schicht« technique and quenched in water. The EDAX pattern in the point of the grain marked with the cross showed the absence of potassium and sodium. It could be suggested that quenching in water of this sample caused formation of aluminosilicate grains (rich in silicon), in addition to the KAlSi_2O_6 phase. On the other hand, slow cooling of sample L12 in the furnace gave a satisfactory surface morphology (Figure 11), with the ratio of relative intensities of Na, K, Al and Si corresponding to leucite-type dental glass-ceramics.

CONCLUSION

Leucite-type glass-ceramics represent an important material in dental restoration due to their chemical inertness combined with a high mechanical strength and appropriate thermal and physical properties. The structural and chemical properties, as well as the surface morphology of leucite-type glass-ceramics, IPS-Empress[®], were investigated using the X-ray diffraction, Fourier transform infrared spectroscopy, scanning electron microscopy and energy dispersive X-ray spectroscopy. The samples were thermally treated under different conditions. The main features of the FT-IR and laser Raman spectra were similar to the analogous spectra of silicate glass containing Al^{3+} or other M^{3+} ($\text{M} = \text{metal}$) as network forming ions. All leucite-type glass-ceramics were characterized by two weak IR bands at 640 and 543 cm^{-1} . These IR bands disappeared with the conversion of leucite-type glass-ceramics to the glass state. The laser Raman spectrum of leucite-type glass exhibited one unusual band centred approximately at 4600 cm^{-1} . This band was attributed to a fluorescence/luminescence spectral feature. Two joint luminescent peaks at 5037 and 5007 cm^{-1} could belong to some of the dopant cations. EDAX patterns showed that the factors, such as the heating temperature and mode of cooling or quenching affected the distribution of elements in leucite-type glass-ceramics. Slow cooling of the sample in the furnace gave a satisfactory surface morphology with the ratio of relative intensities of Na, K, Al and Si corresponding to leucite-type dental glass-ceramics. The findings of the present work are of importance for the specialists involved in the technology of leucite-type dental glass-ceramics.

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SAŽETAK

Mikrostruktura leucitnih staklokeramika za dentalnu primjenu

Svetozar Musić, Jasenka Živko-Babić, Ketij Mehulić, Mira Ristić, Stanko Popović, Krešimir Furić, Dunja Selinger-Kocijan, Stojan Čelap i Tomislav Ivaniš

Mikrostruktura leucitnih staklokeramika istraživana je primjenom rentgenske difrakcije, FT-IR i Ramanove spektroskopije te pretražne elektronske mikroskopije. Kemijska elementna analiza izvedena je uzorak tehnikom EDAX. FT-IR i Ramanovi spektri proučavanih staklokeramika bili su slični spektrima silikatnih stakala, koja su sadržavala umrežene metalne ione M^{3+} ($M^{3+} = Al, Fe$). U svim uzorcima staklokeramike opažene su dvije IR vrpce malog intenziteta pri 640 i 543 cm^{-1} . Te IR vrpce nestale su nakon pretvorbe staklokeramike u leucitno staklo. Ramanov spektar leucitnog stakla pokazao je široku vrpcu s maksimumom pri $\approx 4600 cm^{-1}$, zbog fluorescence/luminescencijskog svojstva materijala te dva oštra luminescencijska vrha pri 5037 i 5007 cm^{-1} . Motreni su učinci brzog i sporog hlađenja na morfološka i kemijska svojstva leucitnih staklokeramika.