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Ceramic composites with improved thermo-mechanical properties

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The ceramic composites from the quaternary Al_2O_3-SiO_2-MgO-ZrO_2 system, with the major compounds: mullyte, cordyerite, zircone silicate and silica have important applications for the dental technics, because of their interesting thermo-mechanical properties. There can be obtained materials of high purity, good homogeneity, fine precision and also very good thermo-mechanical properties (the thermal expansion coefficient α from 20 to 920 ^oC between 2.5 and 4 x 10^{-6} K^{-1}), extremely good chemical stability, without risc related to toxic inclusions in dental materials. Several thermal treatement programs are proposed for the obtaining of the samples from ceramic composite materials of four different compositions and there is determined the influences of thermal history on the properties of the studied samples. The chemical composition influence on the thermo-mechanical properties is also studied, especially for the systems with different proportions of cordyerite.The samples are investigated through the determinations of the physical and chemical properties comprising: density, porosity, water absorbtion, mechanical strenght, thermal expansion coefficient, thermal schock resistance, chemical resistance, X-ray diffraction, Raman and FTIR Spectroscopy, Scanning Electronic Microscopy-SEM.

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Keywords: Ceramic composites, Mullite, Cordierite, Zirconium silicate, Raman, SEM, XRD, FTIR

1. Introduction

For dental uses, the ceramic composites must be an ideal compromise between an excellent thermal shock resistance and good physico-chemical and mechanical characteristics.

The composites based on silica contain the SiO_2 glass as major phase, proving excellent properties of thermal shock resistance and also contain amounts of other oxides, such as Al_2O_3, which improve the thermo-mechanical and chemical properties at high temperatures. The ceramic composites mullite-cordierite are made from a major mullite phase (the ceramic matrix) and variable amount of cordierite. The mullite phase improves the mechanical characteristics and increases the maximum utilisation temperature for the products. The products obtained from those composites will combine harmonious the excellent thermal shock resistance, given by the cordierite phase (compound with very low thermal expansion coefficientα), and the superior mechanical characteristics of the mullite phase (compound with high value for the elastic modulus). The composites based on zirconium silicate together with alumina or kaolin proves also very good thermo mechanical properties.

2. Experimental

The experiments were made for four composite types, two based on silica and mullite, code S and MS, the third based on mullite and cordierite, code MC and the forth on zirconium silicate with alumina and kaolin additives, code ZSC and ZSA. The chosen compositions are presented in Table 1.

Table 1. The compositions, in gravimetric %.

Sample code	Composition [wt. %]						
	SiO_2	Al_2O_3	CaO	Na_2O	P_2O_5	MgO	ZrO_2
S	88-90	5-6	4-5	0.5-1	0-1		
MS	53-57	35-37	1-2	2-3		3-4	
MC	35-40	53-60				4-7	
ZSC	33-35	4-5					60-63
ZSA	15-17	49-51					33-35

For slurry moulding there were added additives, sodium silicate, 3-7 % and sodium polyphosphate 0.2-0.5 %, over 100%. The raw materials were dried in electric stove, China and weighted on a 2 kg technical balance, Sibiu, ± 1 % precision. The homogenisation was realised on humid route, in a stainless homogenizer, provided with one helicoidal stirrer.

The gypsum moulding was manually made. Four hours after the moulding, the products were manually taken out. The samples were dried in the electric stove, at 120 ºC ± 5 ºC, for 24 hours. After the drying, the samples

were burned in an electrical chamber four, Nabertherm, provided with molybdenum disilicon elements, at temperatures between 1350 and 1450 ºC.

The mullite-cordierite samples were prepared in two steps: the first one comprises the cordierite fired preparation, from who, in the next step, it was realised the ceramic composite material. The homogenization of fired cordierite with the mullite was made by humid way, in plastic mills, in a planetary mill, for 6 hours. The ceramic material was prepared for semi humid pressing (humidity of 8-10 %). The used binder was an aqueous solution of polyvinyl alcohol of 5 % concentration. From this material they were realised the samples, with the aid of a hydraulic press, at 5 tone/camp. The samples were dried in the stove, at 110ºC ± 5ºC, for 12 hours. After the drying, the samples were burned in the electrical chamber four, at 1350-1430ºC.

The preparation of ceramic composite materials based on zirconium silicate was similar with the technics utilised for the samples made from mullite-cordierite. They were prepared two types of materials based on zirconium silicate: ZSA base on zirconium silicate anda alumina; ZSC base on zirconium silicate and kaolin. The final burning temperatures for these ceramic materials were between 1350 and 1430 °C.

For the sintered samples they were measured the density, porosity and contraction measurements, for the determination of burning parameters, through the usual methods.

The thermal expansion measurements were made with the aid of a LINSEIS L75 apparatus.

They were also made measurements of Raman spectroscopy, Raman System 2001 Ocean Optics apparatus, XRD, Dron 3, FTIR, Shimadzu and scanning electronic microscopy SEM, Philips Quanta 5 apparatus.

3. Results and discussion

The material and textural characteristics (density, porosity and absorbtion), are given in Table 2.

Table 2. The characteristics, at different burning temperatures.

The composite sample; sintering temperature [°C]	Apparent density, ρ_a [g/cm^3]	Apparent porosity, P_a [%]	Absorbtion [%]
S; 1450	1.51	33.18	17.97
S; 1400	1.50	33.63	18.22
MS; 1450	2.08	20.22	8.82
MS; 1400	2.06	20.63	9.04
MS; 1350	2.04	21.64	9.55
MC; 1430	2.56	9.50	
MC; 1400	2.08	28.35	
MC; 1375	2.03	30.17	
ZSC; 1430 ºC	3.245	23.90	
ZSC; 1400 ºC	3.165	25.55	
ZSC; 1350 ºC	3.14	26.60	
ZSA; 1430 ºC	3.255	16.75	
ZSA; 1400 ºC	3.225	16.875	
ZSA; 1350 ºC	3.21	19.95	

The thermal linear expansion index for the composite ceramic samples realised are presented in Table 3.

Table 3. The thermal linear expansion index, for several sintering temperatures, for the composite obtained samples.

The composite sample	The sintering temperature	The thermal linear expansion index $\alpha_{20\text{-}920^\circ C}$ x 10^6 [grd^{-1}]
S	1400 ºC	1.9
MS	1400 ºC	3.8
MC	1430 ºC	3.3
	1400 ºC	3.4
	1375 ºC	3.6
ZSC	1430 ºC	4.4
	1400 ºC	4.5
	1350 ºC	4.6
ZSA	1430 ºC	5.0
	1400 ºC	5.1
	1350 ºC	5.3

The Raman spectra, for composite ceramic samples are presented in Fig. 1- Fig. 9.

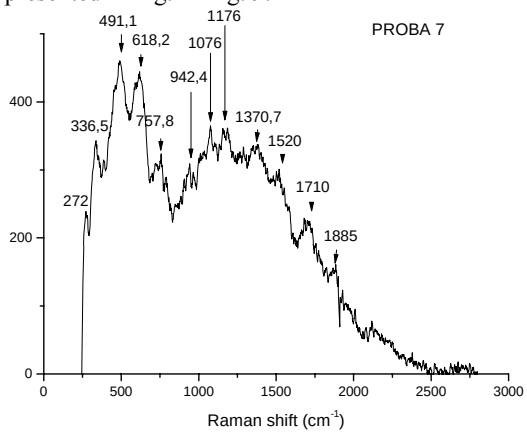

Fig. 1. The Raman spectra for the S sample.

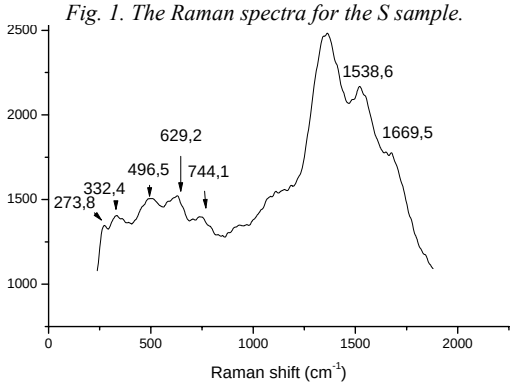

Fig. 2. The Raman spectra for the MS sample.

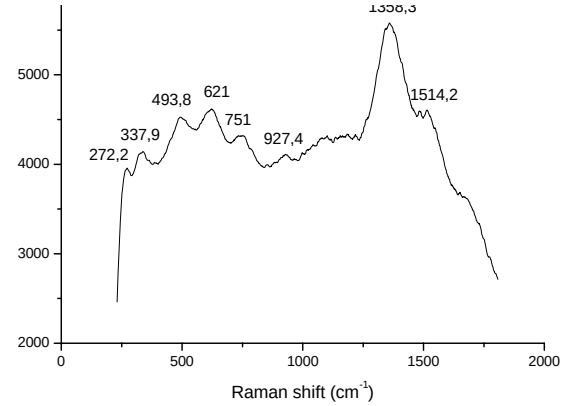

Fig. 3. The Raman spectra for the MC type sample, sintered at 1430 °C.

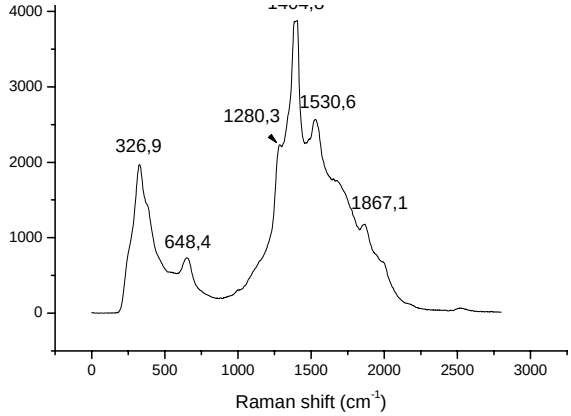

Fig. 6. The Raman spectra, for the ZSC type sample, sintered at 1400 °C.

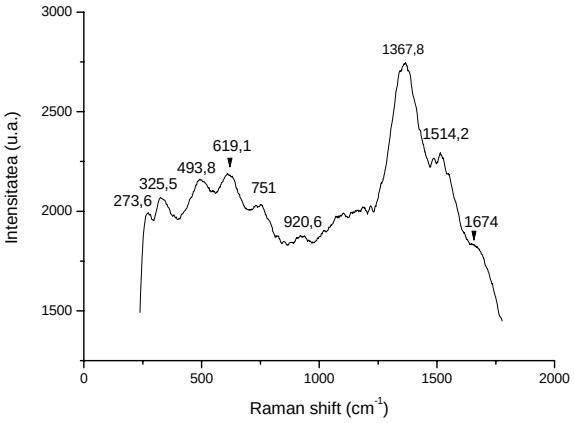

Fig. 4. The Raman spectra for the MC type sample, sintered at 1400 °C.

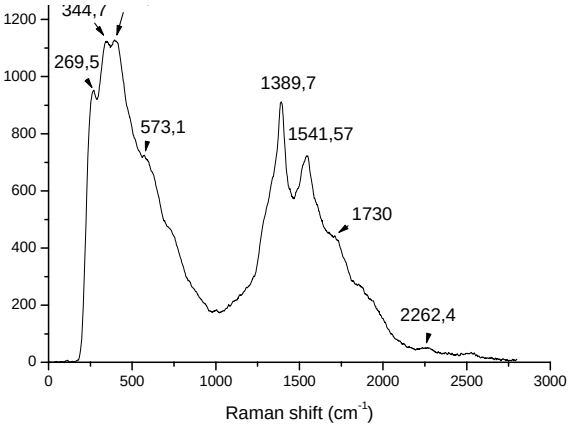

Fig. 7. The Raman spectra for the ZSA type sample, sintered at 1430 °C.

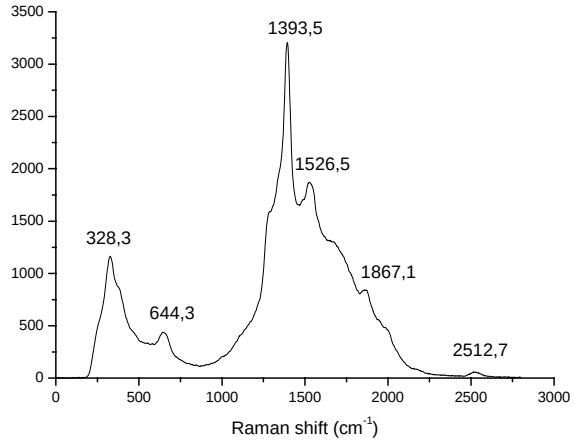

Fig. 5. The Raman spectra for the ZSC type sample, sintered at 1430 °C.

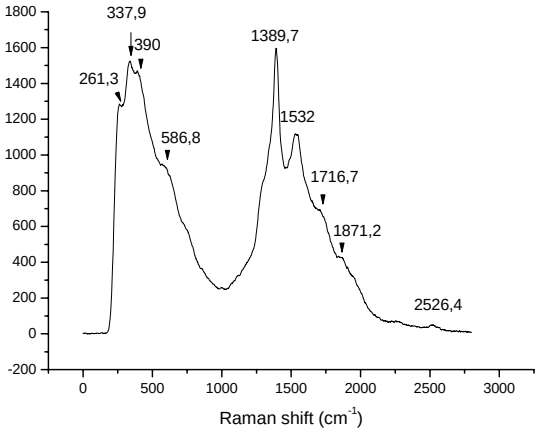

Fig. 8. The Raman spectra for the ZSA type sample, sintered at 1400 °C.

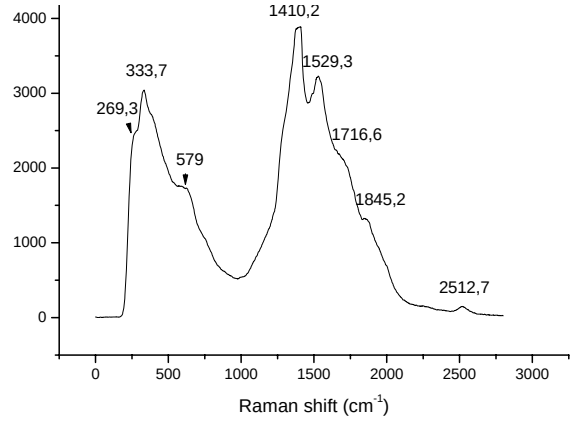

Fig. 9. The Raman spectra for the ZSA type sample, sintered at 1350 ^oC.

The Raman spectra for the S sample is specific for a vitreous structure, which is normally, because this sample have as major compound the silica. The Raman spectra for the MS sample put in evidence the maximum specific to alumina, with the dominant structure associated to the maximum at 1358 cm^{-1}, and also the maximum for the mullite and for an amorphous phase of SiO_2.

The Raman spectra for the MC type samples put in evidence the maximum specific for the alumina, for two types of structure, from whom the dominant is the one associated to the maximum at 1358 cm^{-1}, and also the maximum for the magnesium.

For the ZSC samples, the spectra put in evidence the contribution of two phases of ZrO_2 (monoclinic and tetragonal. For the ZSA samples, it appears as dominant the zirconium phases, with a little shift, due to eutectics formation.

The XRD curves are presented in Fig. 10- 13: for the samples MC type – Fig. 10- 11, in the first case being added free Al_2O_3, in the second case with no free Al_2O_3; for the ZSA type – Fig. 12, and for the ZSC type - Fig. 13.

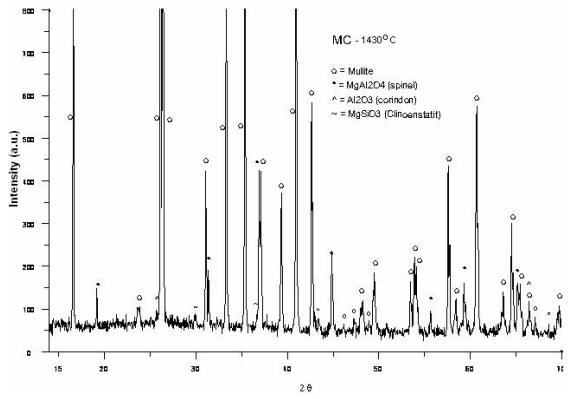

Fig. 10. The XRD curve for the MC composite, treated at 1430^oC, with free Al_2O_3.

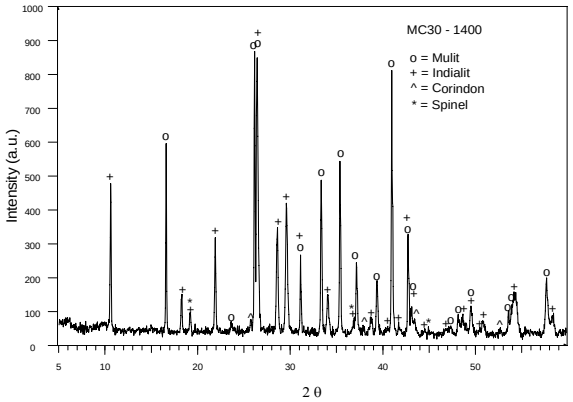

Fig. 11. The XRD curve for MC composite, treated at 1400 ^oC, without free Al_2O_3.

In the Fig. 10 there appear the characteristic peaks for mullite- intense and Al_2O_3. The MC sample with no free alumina presents intense peaks for cordierite and mullite, smaller quantity- Fig. 11. The treatment temperature is decreased in the second case, and it appears that the cordierite decomposition doesn't take place.

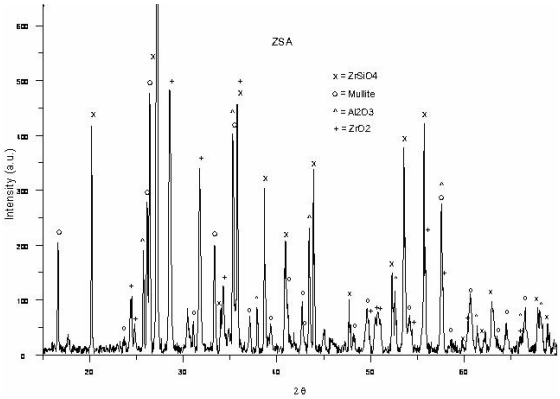

Fig. 12. The XRD spectra for the ZSA composite.

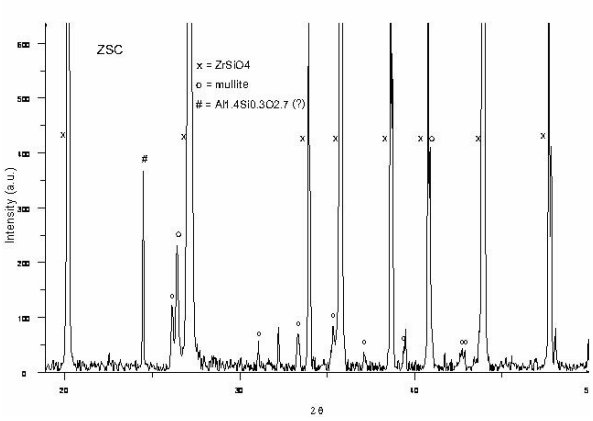

Fig. 13. The XRD spectra for the ZSC composite.

In the case of the ZSA and ZSC composites, it appears the characteristic peaks for zirconium silicate and mullite in both cases. The peaks for Al_2O_3 and ZrO_2 are present

only for the ZSA type sample, showing partial decomposition of the zirconium silicate, under the alumina influence.

The FTIR spectra are presented in Fig. 14- 17.

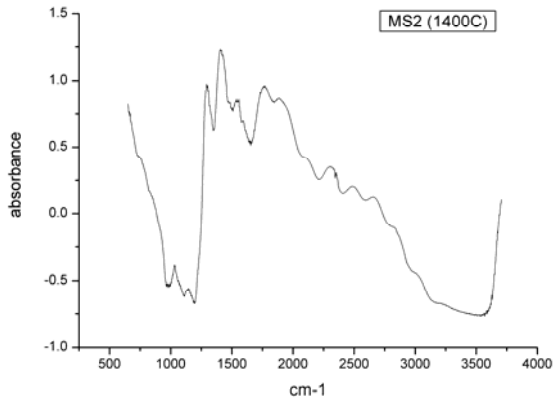

Fig. 14. The FTIR spectra for the MS sample, burned at 1400 °C.

The MS samples spectra - Fig. 14, put in evidence the absorption maxima characteristic to condensed [SiO_4], in the domain 1200-1100 cm^{-1}. The shoulders at 750-850 cm^{-1} seams to indicate the presence of condensed [AlO_4] groups. It also appears the characteristic maxima for water, in the domain 2000-2500 cm^{-1}.

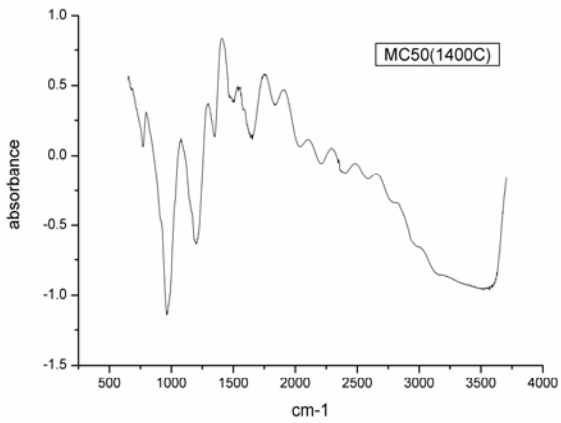

Fig. 15. The FTIR spectra for the MC sample, thermal treated at 1400 °C.

The FTIR spectra, for composites MC type - Fig. 15, put clearly in evidence the maxima at 800 cm^{-1}, attributed to condensed [AlO_4], the maxima at 1200 cm^{-1}, for polymeric [SiO_4] and the maxima for water, above 2000 cm^{-1}.

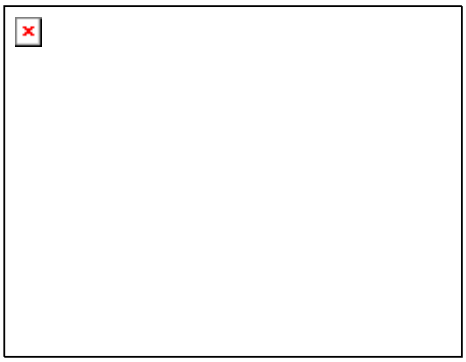

Fig. 16. The FTIR spectra for the ZSA sample, thermal treated at 1400 °C.

The shoulder at 800 cm^{-1}, due to condensed [AlO_4] appears more pronounced in the case of ZSA samples - Fig. 16 than in the case of the ZSC composite - Fig. 17. That fact proves the free corundum existence in the system, in the first case. They are put in evidence the condensed [SiO_4] maxima, at 1200 cm^{-1}, more pronounced in the case of the ZSA composite. This can signifies that the silicon enter in mixed network, with zirconium and aluminium oxides, more for the ZSC samples than for the ZSA ones.

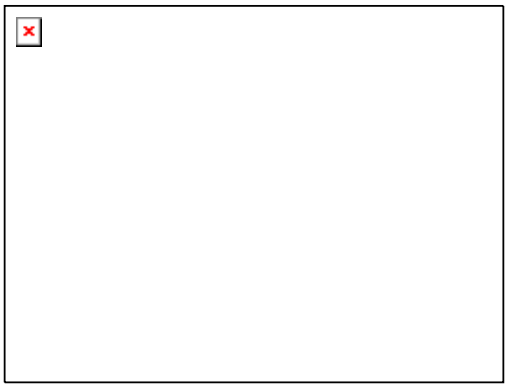

Fig. 17. The FTIR spectra for the ZSC sample, thermal treated at 1400 °C..

It was studied the morphology for the composites type MS, MC, ZSC, ZSA, by SEM (Fig. 18 - Fig. 21).

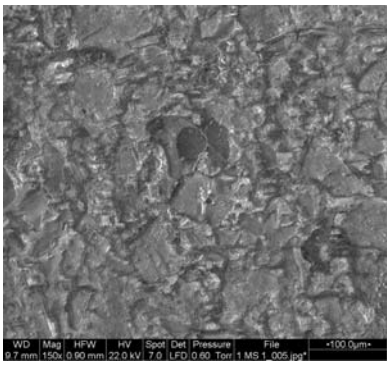

Fig. 18. SEM image for the MS type sample, burned at 1400 °C.

For the MS sample it can be seen the mullite particles distributed in the vitreous phase. The sintering is advanced. For the MC composite it appear an uniform distribution, without large pores and it can be observed the advanced sintering of the composite particles.

The SEM image for the ZSC and ZSA type samples, thermal treated at 1400 ^{o}C are presented, respectively, in Fig. 20 and 21. For the ZSC sample, it can be observed large particles of zirconium silicate, together with long particles of mullite. The structure appears relatively homogeneous, without large pores. For the ZSA composite the particles distribution is more homogeneous than in the case of ZSA, no large pores appears and it can be observed the two type of particles, of zirconium silicate and mullite.

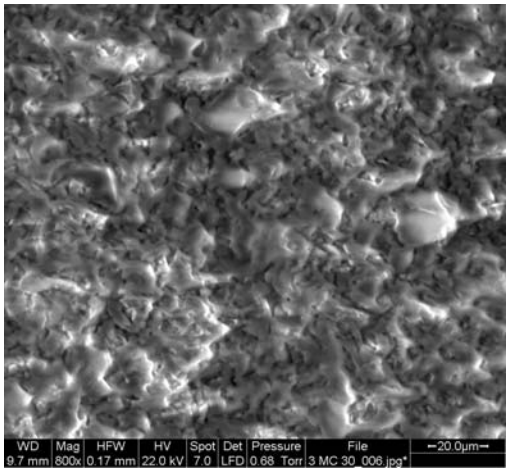

Fig. 19. SEM image for the MC type, sample, burned at 1400 ^{o}C.

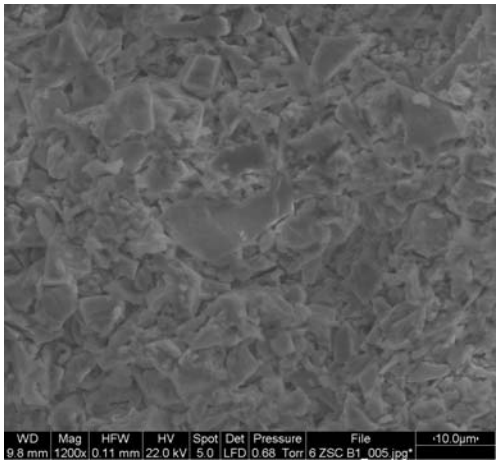

Fig. 20. SEM image of the ZSC type sample, burned at 1400 ^{o}C.

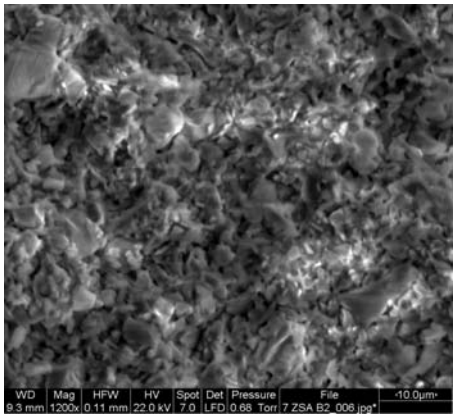

Fig. 21. SEM image of the ZSA type sample, burned at 1400 ^{o}C.

4. Conclusions

The best values, respectively the lowest, for the thermal linear expansion index, were those for samples S, MC and MS type, in which both major components have low expansion. The ceramic composite materials MC type are composed mainly from mullite (of 8-10 µm particles dimension) and cordierite (~5 µm). For the MC type sample, the temperature of 1430ºC, represents the optimal sintering temperature.

For the ZSC and ZSA type samples, the principal mineralogical compounds are the zirconium oxid, the aluminium oxid and the enstatite. The thermo-mechanical characteristics, characterised by the thermal expansion measurements, in the temperature range from 20 to 920 ºC, and the flexural strenght, presents normal values, known from literature from such ceramic materials, for dental technical applications.

For optimal working conditions (sintering temperature of 1430 ºC), the medium values for the thermal linear expansion index lies between 1.9 and 5.2×10^{-6} cm^{-1}, and for the bending resistance the results were within 66 and 93 MPa.

The Raman spectroscopy showed for the S type sample an amorphous structure, and diffuse spectra. For the MC type sample, burned at 1430 ^{o}C, they were revealed specific maximum for alumina and mullite, two structures type, from whom that associated to the 1358 cm^{-1} maximum is the dominant. For the MS type sample, it was observed a structure similar to that for the MC sample, but in which the SiO_2 is in amorphous phase. The Raman spectra for ZSC type samples, sintered at 1430, respectively 1400 ^{o}C put in evidence the contribution of two phases of ZrO_2 (monoclinic and tetragonal). The ZSC and ZSA type samples, thermal treated at 1430, 1400 and 1350 ^{o}C presents dominant maximum for the zirconium oxide phases, with some displacements and plates, due to eutectics formation.

The increase of the raport cordierite/mullite has benefic influences on the thermo-mechanical properties of the composites. The XRD peaks characteristic to the

cordierite are signifiant more intense for the increased cordierite amount, and the thermal expansion is lower.

The FTIR spectra reveal the possibility of mixed network, formed by the silicon together with zirconium and aluminium oxides, in the case of ZSC samples. For the MS and MC composites, it appears the characteristic maxima attributed to condensed [AlO_4], at 800 cm^{-1}. In this case, it is possible that the mixed network is formed by the silicon and aluminium oxides

The scanning electronic microscopy SEM revealed, for the ZSC and ZSA samples, sintered at 1400 ^oC, the mixture of large zirconium silicate particles together with thin mullite ones, in homogeneous and good sintered bodies. For the MS composites, the mullite particles are sintered in vitreous siliceous environment. The MC composites are also good sintered. All the composites show no large pores.

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