

CHARACTERISATION OF SOME KAOLINS IN RELATIONSHIP WITH ELECTRIC INSULATOR CERAMICS MICROSTRUCTURE

MARIA GOREA, FERENC KRISTÁLY, DANA POP

Babeş - Bolyai University
1 Kogalniceanu str., 400084, Cluj Napoca, Romania
e-mail: mgorea@chem.ubbcluj.ro

ABSTRACT

Various types of kaolins as representative raw materials for electric insulator ceramics were investigated in order to establish their influence on ceramics' properties, defects and microstructure. The raw samples were chemically-investigated (AAS), and tested by X-ray diffraction (XRD) and thermal analysis (DTA and TG) in order to define their mineralogical composition and structural characteristics. The thermal treatment of the kaolins and of the ceramic mixture was carried out at 1300 °C. The microstructure resulted after firing was studied by optical and electron microscopy. The chemical composition of the amorphous phases of the ceramic body was studied by EDS; by processing the data acquired, some inhomogeneity in the microstructure of the ceramic body was established. It is concluded that the final microstructure, defects and properties of the ceramic products are influenced by the chemical and mineralogical composition of the raw materials. The impurities present (namely Fe-bearing phases) have a great influence on the electric properties of the ceramics. The mineral phases present in kaolins play a significant role in selecting the wet methods used for preparing the ceramic masses (presence of interstratified I/S increases the plasticity, but also the fired shrinkage), and the crystalline phase formation during thermal treatment (formation of poor- or well-crystallized mullite and cristobalite).

Key words: raw materials, ceramics, electric porcelain

INTRODUCTION

The increasing demand for high-quality electric insulators requires the improvement of their physical and mechanical characteristics, that are consequences of the ceramics' microstructure. The needed changes refer to both technological update and quality of the raw materials. A suitable formulae of the raw materials mixture and processing under fixed technological parameters should lead to a homogeneous microstructure of the ceramics showing the minimum possible internal stress (Isik Ece and Nakagawa 2002).

The electric porcelain for low-tension insulators is usually obtained from a mixture of kaolin, feldspar and quartz. Kaolin confers the required plasticity for forming and the ceramics' raw and dry strength. Feldspar is a flux used for decreasing the firing temperature and providing the reactive glassy/vitreous phase that dissolves some components of the mixture and enables the crystallisation of mullite from the melt.

The internal stress in ceramics is mainly caused by the presence of unreacted, or partly-reacted quartz grains (residual grains) into the vitreous phase. The larger quartz grains may enter the raw materials' mixture as components of kaolins, some of these naturally-containing up to 20 % quartz (Andreeva and Ordan'yan 2002). The replacement of quartz with α -Al₂O₃, besides the fact that increases the production costs, it does not completely solve this deficiency (Andreeva and Ordan'yan 2003).

Currently, most of the ceramics producers use the "classical" methods for characterising the raw materials and the final products, namely chemical composition. The mineralogical characterisation is not yet a standard procedure, in many cases it is implicitly assimilated to chemistry. The most frequently used industrial mineralogical

methods for raw materials and final products phase identification are X-ray diffraction (XRD) (Amigo et al. 2004), and thermal analysis.

Under these circumstances, the goals of this paper are the chemical (AAS) and mineralogical (XRD) characterisation of some commercial raw materials (kaolins) for silica-rich electric porcelain, the study of the thermal (DTA and TG) behaviour of kaolins and the investigation of the corresponding ceramics' microstructure and chemistry (by optical and electronic microscopy - SEM, and EDS) after specific processing and firing at 1300 °C.

RESULTS AND DISCUSSION

Characterisation of kaolins

Chemical composition

The clay raw materials used for the ceramic experiments are commercial kaolins commonly used for manufacturing electric porcelain:

Kaolin Z (from Czech Republic);

Kaolin KDH (from Germany);

Kaolin BO (from Bulgaria);

Kaolin Har (from Romania).

The chemical composition was investigated by using atomic absorption spectrometry (AAS). The results are presented in Table 1.

The relatively high Al₂O₃ content of Z kaolin provides a high strength to the ceramics. A low amount of Fe-containing phases in KDH and BO kaolins will lead to a higher whiteness of the final product. The Har "kaolin" is the richest in SiO₂ and Fe₂O₃ among the studied samples.

X-ray diffraction (XRD)

The mineralogical composition of the kaolin samples was investigated by the means of X-ray diffraction, on a TUR M

Table 1. Chemical composition of the investigated kaolins.

[%]	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃ *	MgO	CaO	Na ₂ O	K ₂ O	L.O.I.	Σ
Z	44.78	39.50	0.82	0.27	0.38	0.15	0.69	13.08	99.67
KDH	48.59	37.05	0.50	0.49	0.32	0.22	0.57	11.97	99.71
BO	47.65	37.60	0.68	0.33	0.27	0.32	0.84	11.85	99.54
Har	55.47	30.68	1.12	1.90	0.57	0.51	1.23	8.15	99.63

* Total Fe expressed as Fe₂O₃.

60 diffractometer with Co anticathode. The XRD patterns of the studied raw kaolins (unoriented samples) are presented in Fig. 1.

In samples Z, KDH and BO, the dominant mineral is kaolinite (K), well-crystallized (low defect) in Z kaolin and less-crystallized in the other two samples. Quartz (Q) and muscovite (Ms) are subordinated. In these samples illite (I) is absent or is present in small amounts, thus no influence of this phase is expected on the final and rheological properties of ceramics. On the other hand, "kaolin" Har is a mixture of several mineral phases: interstratified illite/smectite (I/S, basal spacing $d_{001} = 10.36 \text{ \AA}$) as the main component (~ 74 %), kaolinite (~ 6 %), quartz (11 %), feldspars (~ 4 %), pyrite (~ 1 %) and organic, amorphous material (~ 4 %). The presence of the non-clay minerals explains the high amounts of Si and Fe in this kaolin-type. The high amount of illite/smectite in this raw material explains the high plasticity of the raw mixture, but also the high dry and fired shrinkage, i.e. the cracks usually occurring after firing (Fig. 5). The black spots noticed in the ceramics are the consequence of the presence of Fe in phases such as pyrite, Fe oxides and hydroxides, as well as of the incomplete firing of organic matter. Muscovite (Ms) is present in the illite- and illite/smectite-containing samples, as the precursor of illite (especially in the Har "kaolin"; traces were identified also in BO and KDH kaolins). No muscovite is present in the Z kaolin.

In order to evidence the formation of mullite - the specific ceramic component that provides its suitable final properties (mainly the mechanical strength), the kaolin samples were thermally treated at 1300 °C, in a fast firing regime (a firing cycle of 10 hours) under conditions similar to those used for ceramics. The corresponding XRD patterns are presented in Fig. 2.

Many previous authors have studied the influence on the formation of cristobalite (C) besides mullite (M), of parameters such as natural kaolinite crystallinity, presence and nature of impurities, or temperature and oxidizing/reducing conditions during firing. According to Dubois et al. (1995) cristobalite usually forms below 1260 °C from poorly-crystallized kaolinite. The studied samples revealed the presence of dominant, well-crystallized mullite in sample Z and less well-crystallized in samples KDH and BO respectively. In sample Har besides mullite, less well-crystallized than in the previous samples, cristobalite occurs in relatively larger amounts. Under fast firing regime cristobalite occurred at 1300 °C, its formation being favoured by the presence of alkaline oxides. With the increase of temperature, muscovite is not significantly affected until 1100 °C, when it melts. However, under fast firing, the muscovite crystalline lattice may undergo some structural modification (Ms*), as proven by the XRD patterns.

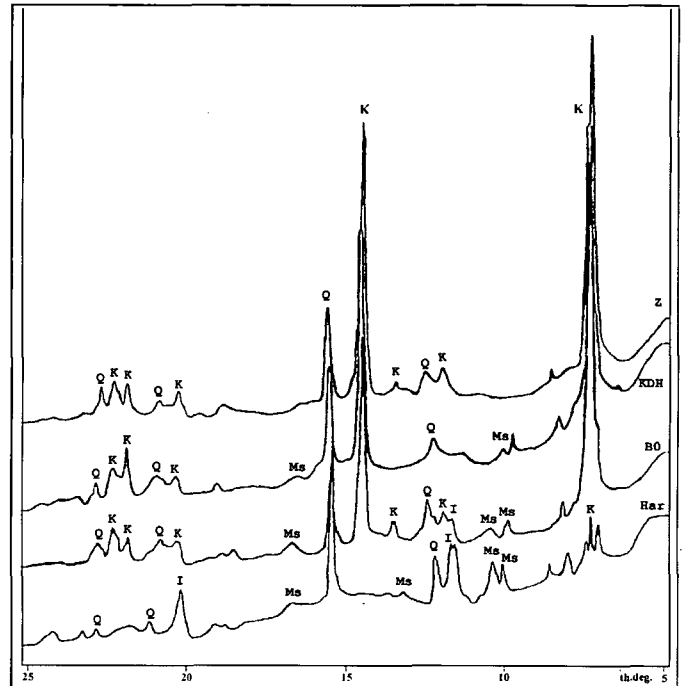


Fig. 1. XRD patterns of the studied raw kaolins. Legend: K = kaolinite; Ms = muscovite; I = illite; Q = quartz.

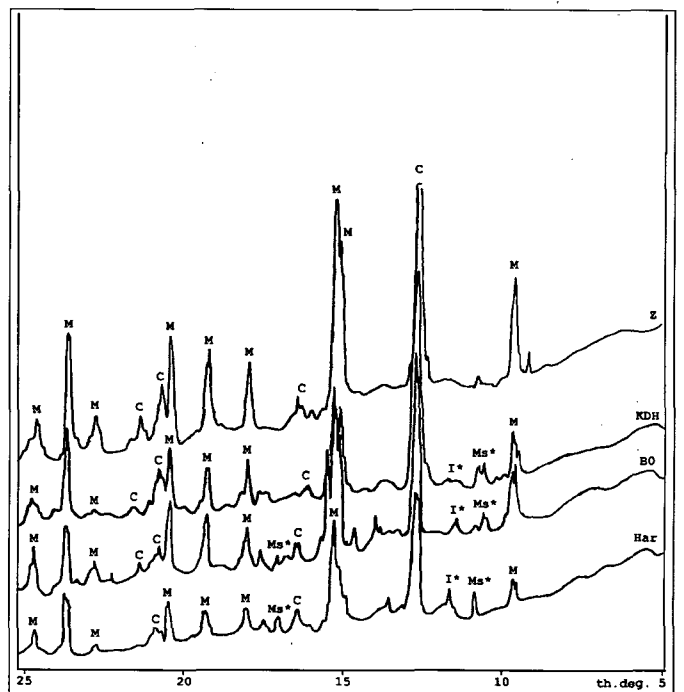


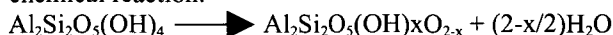
Fig. 2. XRD patterns of thermally-treated (1300 °C) kaolin samples. Legend: M = mullite; Ms* = structurally-modified muscovite; I* = structurally-modified illite; C = cristobalite.

Thermal analysis

Thermogravimetry (TG) and differential thermal analysis (DTA) were performed on the raw kaolins in the view of investigating the changes occurring during the thermal treatment. A MOM-C type derivatograph was used, and the temperature was increased up to 1100 °C. An amount of 200 mg of each sample was measured after drying at 105 °C for 2 hours. α -Al₂O₃ was used as reference material. The DTA and respectively TG curves of the studied samples are presented in Fig. 3 and Fig. 4.

The main reactions that occurred during the thermal treatment and which were evidenced by the DTA and TG curves are presented in Table 2.

The interpretation of the observed thermal effects (Todor 1976) is as follows: at around 100 °C, all the samples show a weak endothermic reaction accompanied by weight loss as a result of the desorption and dehydration (removal of pore water and water adsorbed in the interlayer of the poorly-crystallized clay minerals, i.e. illite/smectite); only in the case of sample Har, an exothermic reaction occurred around 440 °C accompanied by a minor weight loss, which is assigned to the oxidation of pyrite and the burnout of organic matter; between 560 - 595 °C a major endothermic effect was recorded, mainly due to dehydroxilation of kaolinite. Kaolinite was transformed into metakaolinite, following the chemical reaction:



where x = number of residual hydroxyl groups in the metakaolinite.

The dehydroxilation temperatures vary in each kaolin type, according to the particle size, amount of kaolinite and crystallinity. The BO kaolinite has a lower dehydroxilation temperature as compared to KDH and Z kaolins, as a consequence of its relatively reduced crystallinity degree and smaller particle sizes. The Har "kaolin" contains a smaller amount of kaolinite, this leading to a smaller and broader endothermic peak. In the same time, because of the significant amount of illite/smectite, dehydroxilation is in this case a gradual process taking place in the 400 - 900 °C temperature interval, that is accompanied by a continuous weight loss.

At about 990 - 1000 °C an exothermic reaction was recorded in all the samples, as a consequence of the debut of mullite formation process. The peak maximum and temperature interval for mullite formation show maximum values in the case of the Har "kaolinite", characterised by dominant illite/smectite and subordinate kaolinite.

The microstructure ceramics

Based on the analytical results obtained for the chemistry, and on the technological characteristics inferred from the specific mineralogical compositions, the four kaolin types were mixed in a suitable ratio for obtaining an optimum formulae for electric porcelain. The mixture contained besides kaolin (57 %), feldspar (25 %) and quartz (silica-rich sand) (18 %). The raw materials mixture was ground in a ball mill, then dried by atomisation thus a powder with the optimal grain size for semi-wet pressing was obtained. The samples were formed by pressing into metallic dies. The thermal treatment was performed in a furnace, at temperatures up to 1300 °C.

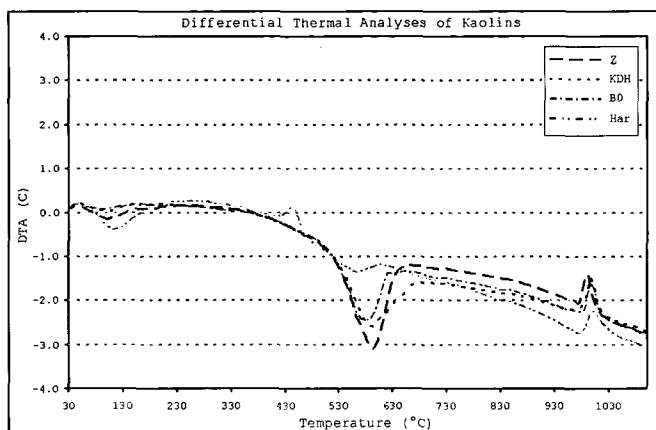


Fig. 3. DTA curves of the studied kaolins.

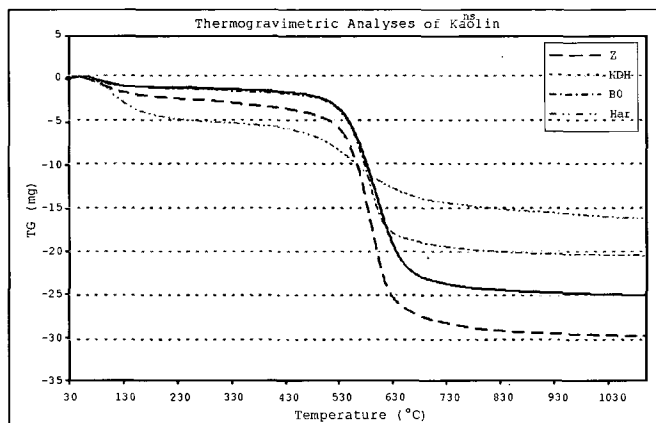


Fig. 4. TG curves of the studied kaolins.

Table 2. Thermal reactions in the studied kaolins.

Peak	Z	KDH	BO	Har	
1	Peak min.	101.52	105.27	92.09	112.69
	ΔT (°C)	102.59	89.4262	108.16	137.24
	ΔTG (mg)	-1.712	-0.861	-0.923	-4.183
	DTA min	-0.240	-0.143	-0.116	-0.560
2	Peak max.	/	/	/	443.38
	ΔT (°C)	/	/	/	33.3116
	ΔTG (mg)	/	/	/	-0.49
3	Peak min.	593.17	592.53	580.41	563.58
	ΔT (°C)	153.14	180.0663	144.9	110.1546
	ΔTG (mg)	-22.23	-20.6042	-15.89	-4.90
	DTA min	-2.056	-1.379	-1.356	-0.334
4	Peak max.	989.29	996.55	996.18	1000.99
	ΔT (°C)	55.876	64.9418	50.74	85.7069
	ΔTG (mg)	\	\	\	\
	DTA max	0.852	0.802	0.747	0.6433

Legend: Peak min./max. – the temperature corresponding to the minimum/maximum effect (°C); ΔT – temperature interval in which the effect takes place (°C); ΔTG – weight loss within the corresponding temperature interval (mg); DTA min, max – enthalpy changes corresponding to the peak reaction.



Fig. 5. Microstructure of the ceramics (1300 °C) (NII, 0.125mm bar).

The microstructure of the obtained ceramics was investigated by optical microscopy in thin sections, under plane polarised light by using a Zeiss-type polarising microscope (Fig. 5), as well as by scanning electron microscopy, SEM (Fig. 6 and Fig. 7) on a Jeol unit. Fig. 5 shows the presence of cracks elongated along the direction of pressing, and the stratified texture of the apparently homogeneous fine clayey material.

Irregular pores resulted from the decomposition of some minerals or from the burnout of organic matter used as forming lubricant are also noticeable. The quartz grains that were not melted are ubiquitous in the material.

The microstructure of thermally treated samples (before and after HF etching) is illustrated in Fig. 6 (single firing, 900 °C) and Fig. 7 (double firing, 1300 °C); the formation of secondary mullite is thus evidenced. Fig. 6 shows the presence of residual quartz and feldspar grains, as well as clay minerals' crystallites undergoing transformation into primary mullite.

Fig. 7A illustrates thermally treated ceramics fired at 1300 °C. A large amount of vitreous phase embeds the quartz

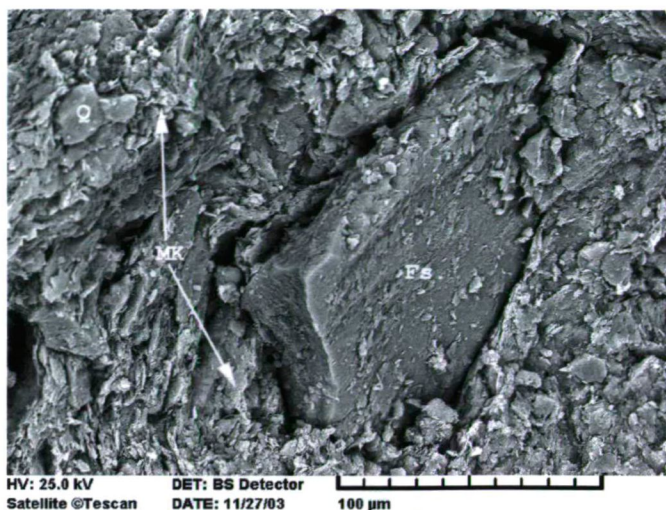


Fig. 6. Microstructure of ceramics fired at 900 °C (SEM, fractured surface, gold coating): quartz (Q), feldspar (Fs), clay minerals undergoing transformations (MK).

grains and the fissures that do not close even under thermal treatment at higher temperatures.

Fig. 7B shows the same sample after surface polishing and graphite coating (sample prepared for the EDS investigation). Besides pores and quartz grains, secondary acicular mullite crystallized from the melt is noticeable.

Chemistry of the vitreous phase in ceramics

The bulk composition of the ceramic body was determined by classical (wet chemistry) method as follows: SiO₂ 68.45 %; Al₂O₃ 25.69 %; Fe₂O₃ 0.53 %; CaO 1 %; Na₂O 2.02 %; K₂O 1.70 %.

The distribution of oxides within the vitreous phase was investigated by energy dispersive X-ray spectroscopy (EDS) on a Jeol JXA – 8600 SUPERPROBE-type unit on polished-surface samples (accelerating voltage 15 kV, probe current 20 nA, measuring time 40 s). Even if the recommended beam diameter for point analysis on Na-containing samples is 100 μm

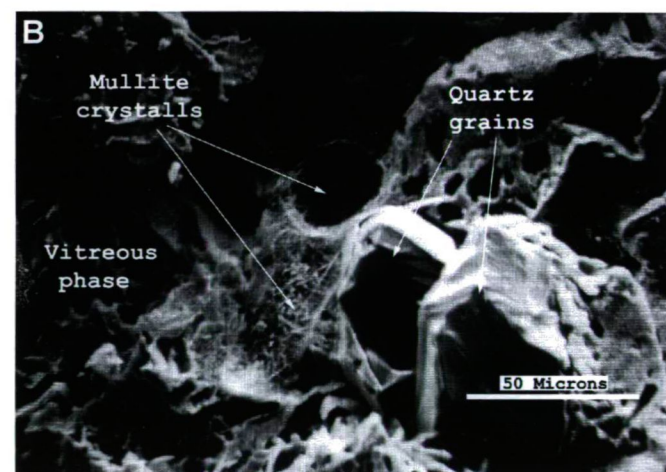
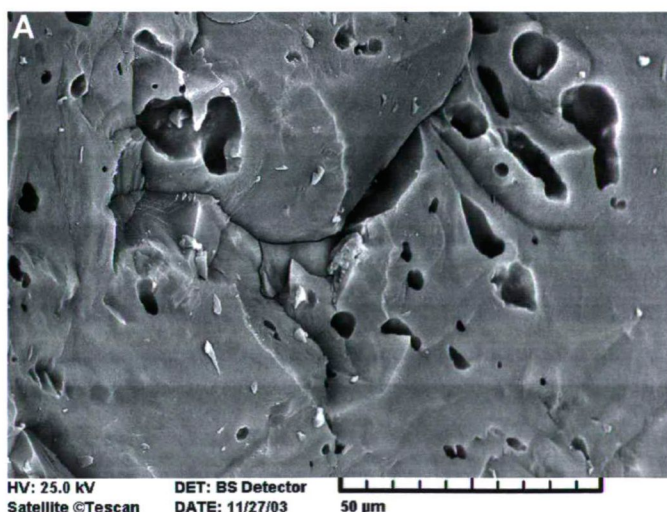


Fig. 7. (A) Microstructure of ceramics fired at 1300 °C (SEM, fractured surface, gold coating). (B) SEM image after HF etching (graphite coating), showing acicular mullite and quartz grains embedded in the vitreous phase.

(Taylor and Brown 1979), due to the short distance between the crystalline grains, our investigation was performed by using 1 micron spot size and a depth of penetration of 2-3 microns. The vitreous phase between the grains was evidenced by the means of SEI imaging. Data were collected along two profiles in the ceramic mass (12 locations/profile, at about 10 microns each); in each location three neighbouring spots were measured, the average value was calculated and plotted in Fig. 8 and Fig. 9. The average values obtained along the two profiles are presented in Table 3.

Chemically there is no major difference between the two studied profiles, both areas showing a composition similar to that of the bulk ceramics. Fig. 8 illustrates the SiO₂ and Al₂O₃ concentration patterns from the border (1) to the core (12) of the ceramic body in both investigated profiles.

The plot indicates a general, very slight trend of SiO₂ decrease from the border to the core, negatively correlated to the Al₂O₃ trend. This may be explained by the aggregation of quartz towards the external parts of the sample during pressing and its subsequent dissolution by the feldspar melt. Fig. 9A, B show the alkaline oxides (Na₂O and K₂O), and FeO patterns in the two profiles, from the border (1) to the core (12).

A heterogeneous distribution of the alkaline oxides and FeO within the ceramic vitreous phase is noticeable. In both profiles, K₂O concentration slightly decreases from the border to the core; Na₂O is almost constant along profile I and slightly increases along profile II, but the starting values are lower in the latter case. FeO content varies within the same limits, but opposite trends are noticeable in the two data sets.

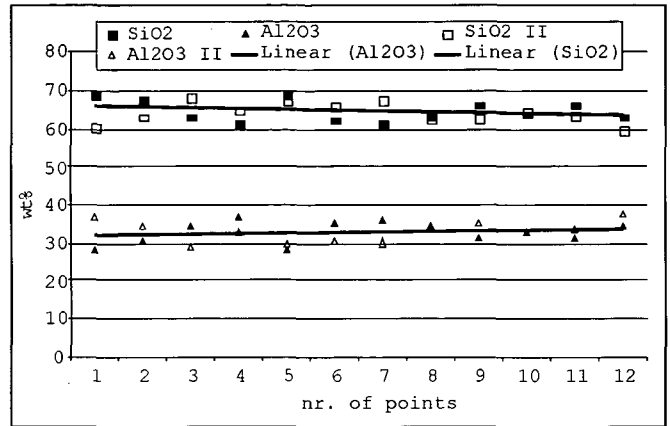


Fig. 8. SiO₂ and Al₂O₃ distribution in the vitreous phase of the ceramic body.

Table 3. Chemical composition of the ceramic vitreous phase

Profile	wt%	SiO ₂	Al ₂ O ₃	Na ₂ O	K ₂ O	FeO*	Σ
I	av. comp.	64.65	32.91	0.52	0.98	0.55	99.98
	st. dev.	2.74	2.77	0.25	0.15	0.15	
II	av. comp.	64.05	33.26	0.44	1.07	0.64	100
	st. dev.	2.64	2.78	0.19	0.10	0.13	

Legend: av. comp.=average composition, st. dev.=standard deviation.

* = total Fe expressed as FeO

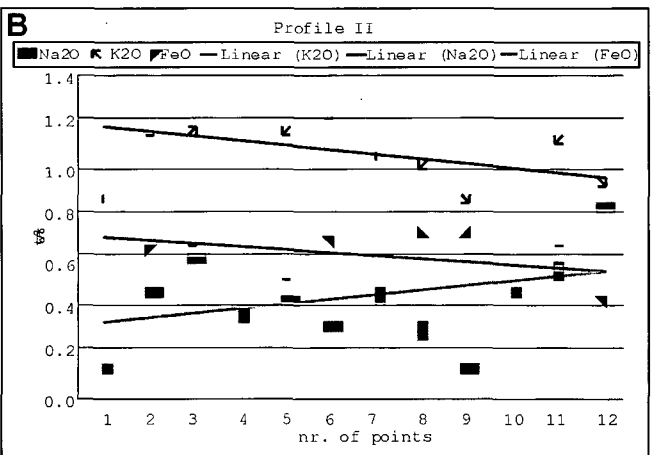
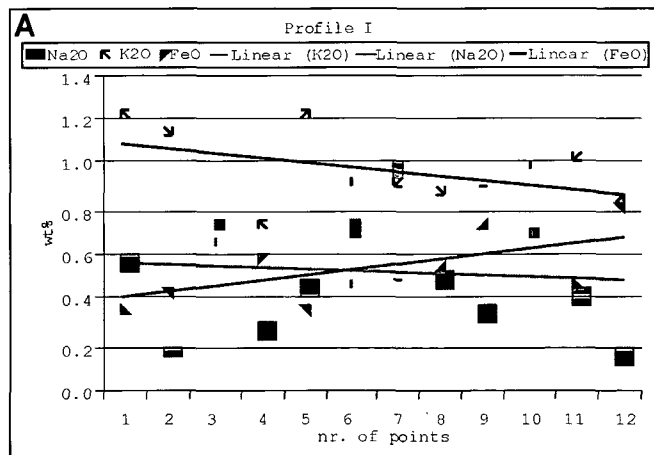


Fig. 9. (A) Na₂O, K₂O and FeO distribution along profile I. (B) Na₂O, K₂O and FeO distribution along profile II.

CONCLUSIONS

Obtaining high-quality ceramics, with optimal characteristics for components in electrical devices involves the usage of the suitable formulae of raw materials with well-defined chemical and mineralogical compositions that are stable in time and show a good behaviour under pre-established technological parameters.

High Al₂O₃ and low Fe₂O₃ contents of the clay minerals are recommended in order to avoid occurrence of defects (fissures and black Fe-spots). Well-crystallized as the main component of kaolins positively influences the formation of mullite and other properties of the ceramics. Taking these

into account, among the studied kaolins, the most recommendable types are Z, KDH and to a lesser extent, BO kaolins.

The thermal treatment of these kaolins at 1300 °C led to the formation of mullite and cristobalite. In the Har "kaolin" interstratified illite/smectite is the main component, which shows a continuous weight loss up to 1000 °C, as indicated by the thermal analysis. This involves a high contraction trend and, as a consequence, the high probability of occurrence of fissures. The thermal analysis evidenced the exothermic reaction (~ 440 °C) of pyrite associated with organic matter in kaolins. The corresponding peak (560 – 590 °C) and interval

of the dehydroxilation temperature (110 – 180 °C) provide information on the kaolinite amount, particle size and crystallinity.

Optical microscopy evidences the defects in the final products, mainly the occurrence of fissures related to the small grain size of the raw material mixture used for pressing, and to the relatively large amount of illite/smectite-rich clay.

Scanning electron microscopy (SEM) illustrates the crystalline and vitreous phases formed after single and double firing respectively. The primary mullite, resulted from the transformation of clay minerals is scarcely present after a single firing, at 900 °C, when most of the feldspar grains did not melt. The secondary, acicular mullite crystallizes from the feldspar-rich melt and sometimes preserves the shape of the feldspar original grain. The fissures occurring at the first firing do not close after the second firing, at higher temperatures.

The chemical study (by EDS) of the vitreous phase demonstrates its heterogeneity in the ceramic body, as concerns the major oxides. SiO₂ tends to decrease from the border to the core, in correlation with the increase of the Al₂O₃ content; the alkaline oxides and FeO show much heterogeneous distribution patterns, but within a narrow range.

REFERENCES

- AMIGO, J. M., CLAUSSELL, J.V., ESTEVE, V., DELGADO, J.M., REVENTOS, M.M., OCHANDO, E.L., DEBAERDEMAEKER, T., MARTI, F. (2004): X-ray powder diffraction phase analysis and thermomechanical properties of silica and alumina porcelains. *Journal of the European Ceramic Society*, **24**, 75–81.
- ANDREEVA, N. A., ORDAN'YAN, S. S. (2002): Technological implications in increasing the strength of porcelain. *Refractories and Industrial Ceramics*, **43**, 2–5.
- ANDREEVA, N. A., ORDAN'YAN, S. S. (2003): The role of component dispersity and molding pressure in the manufacturing technology of electric porcelain. *Refractories and Industrial Ceramics*, **44**, 17–21.
- DUBOIS, J., MURAT, M., AMROUNE, A., CARBONNEAU, X., GARDON, R. (1995): High-temperature transformation in kaolinite: the role of crystallinity and of the firing atmosphere. *Applied Clay Science*, **10**, 187–198.
- ISIK ECE, O., NAKAGAWA, Z. (2002): Bending strength of porcelains. *Ceramics International*, **28**, 131–140.
- TODOR, D., N. (1976): *Thermal Analysis of Minerals*. Tunbridge Wells, Kent, Abacus Press, 256.
- TAYLOR, M., BROWN, G. E. JR. (1979): Structure of mineral glasses – I. The feldspar glasses NaAlSi₃O₈, KAlSi₃O₈, CaAl₂Si₃O₈. *Geochimica et Cosmochimica Acta*, **43**, 61–75.

Received: October 03, 2005; accepted: February 10, 2006