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Evaluation of Dielectric Properties from the Cakes of Feldspathic Raw Material for Electrical Porcelain Production

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1. Introduction

Feldspars are anhydrous alumosilicates containing alkaline (Na^+, K^+) and alkaline-earth (Ca^{2+}) cations. The basic types of feldspars used in ceramic production are: potassic feldspar (microcline) $K_2O \bullet A1_2O_3 \bullet 6SiO_2$, sodic feldspar (albite) $Na_2O \bullet Al_2O_3 \bullet 6SiO_2$ and calcium feldspar (anorthite) $CaO \bullet A1_2O_3 \bullet 2SiO_2$. The dielectrical properties of electrical porcelain depend on the mineralogical composition, alkali ratio and total alkali content of feldspathic raw material [1].

To examine new sources of raw materials for electrical porcelain production, we have evaluated nonconventional types feldspathic rocks of Karelian. Feldspathic rocks such as alkaline and nepheline syenites from the Elisenvaara and Yeletozero deposits, aplite-like granite from the Louhi area and volcanics such as Kostomuksha halleflinta and Roza-Lambi quartz porphyry. On a chemical compound they represent Alumosilikate K, Na, Ca, less often Ba. Form isomorphic numbers, including Plagioclase [3]. In world practice, the above rocks are a common source of mineral products which has some advantages over pegmatite.

Nonconventional types of feldspathic raw materials were evaluated on cakes because the dielectrical and other properties of natural feldspars and their cakes are much the same, while the chemical bonds of natural feldspars persist after their melting and are inherited by the glass phase of the resulting ceramics [1,2].

Cakes (material in vitreous state, as in ceramics) were prepared from finely ground (particle size 0.063 mm) powders of deferrized feldspathic rocks by caking them in crucibles at 1350° C for 3 hr.

We have assessed the electrical properties (dielectrical permeability -ε, dielectrical loss angle tangent -tgδ and electrical resistance -lgρ), the thermal coefficient of linear expansion (TCLE) and pH of nonconventional types of feldspathic raw materials such as potassic halleflinta, quartz porphyry, syenite and granite-aplite and compared them with those of pegmatite, a common paw material for ceramics production. The compositions and physico-technical properties of feldspathic rocks are shown in Table 1.

2. Electrical characteristics of feldspathic raw material

To measure electrical properties, we prepared specimens of cakes. They were 20 - 25 mm in diameter and 2 - 3 mm in height. ε-, lgρ- and tg δ-values were measured using a bridge with a capacity E of 7-8 and a working frequency of 1000 Hz at 20°C.

Electrical properties were estimated by introducing an additional coefficient to account for additional capacity on the specimen zones not covered by electrodes using the formulas: dielectric permeability: $\varepsilon = \kappa_1 \kappa_2 c$, where $\kappa_1 = 1.14$ is the coefficient of the sensor, κ_2 is the coefficient of specimen thickness, c is specimen capacity; specific electrical resistance: $\lg\rho = \kappa/g \cdot l$, where $\kappa = 33.55$ is the sensor coefficient, g is conductivity, l is specimen thickness; dielectrical loss: $tg\ \delta = 0.175 \cdot g/s$, where c is specimen capacity and g is conductivity.

The results of the measurement of the dielectrical properties of feldspathic rocks are shown in Table 1, and the dependence of variations in ε, lgρ and tgδ on the quantities of microcline and plagioclase in the cake is shown in Figures 2.

Fig. 1. Cake from feldspathic raw material.

Dielectrical permeability, ε, is the electrical parameter of a mineral showing its ability to polarize in an electrical field. According to experimental data, the dielectrical permeability of the cakes of the rocks evaluated (Nos. 1 – 12) varies from 3.26 to 8.1. The dielectrical permeabilities of feldspathic rocks from other deposits (Nos. 13 – 18), shown in Table 1, range from 5.6 to 7.7, and according to E.V. Rozhkova's results presented in the literature [4,5] /(Golod et al., 1975), they vary from 5.6 – 6.3. This means that the variation range of ε of the cakes of nonconventional feldspathic rocks is within known values.

Analysis of the dielectrical permeability values obtained has shown that ε depends largely on mineralogical composition. Microcline and quartz were shown to have the greatest effect on dielectrical permeability. A high percentage of quartz (44 mass.%), in contrast to that of other rocks, in volcanics from the Roza-Lambi deposit (cake no. 7) contributes to a decline in ε of the cake to 5.4 dtn/cm^2.

The ε dielectrical permeability of plagioclase rock cakes (Nos. 10 – 12, Table) is lower than that microcline cakes (3.26-4.02), which seems to be due to the presence of large quantities of quartz and Ca^{2+} and Mg^{2+} ions in cakes 11-12 and Ba^{2+} ions in cakeв no. 10, because the electrical conductivity of K^+ and Na^+ ions in dielectrics is higher than that of Ca^{2+}, Mg^{2+} and Ba^{2+} ions [1,4].

Type of breeds	Feldspar deposits		Mineral structure, ***mass. %***				Dielectric properties			TKL $R \odot 10^{-6}$ 1/ grad	pH
	Area	Deposits	№пп	Q	Mi	Pl	E	$\rho \odot 10^{10}$ Ohm⊙ cm	tg δ	400^0C	
Pegmatite	Chaupino-Louhi	Hetolambino, Uracco, Civ-guba	1 2 3	2,5 28.6 24.2	70.0 64.1 61.3	27.5 7.3 14.5	7.70 7.53 7.35	- 0,94 1.00	- 0.148 0.062	7.70 7.93 7.72	9.67 9.08 9.85
	Priladozhye	Jccima Lypikko	4 5	27.2 27.8	49.8 46.6	23.0 25.6	6.20 6.73	0.95 1.00	0.900 0.127	8.10 8.51	9.83 9.82
	Uljlega	Cjryla	6	7.1	58.0	34.9	7.00	2.10	0.027	7.90	8.84
Volca-nic rock	White Sea	Roza-Lambi	7	44.0	44.2	11.8	5.40	0.85	0.160	8.08	7.10
	Kalevala	Kostomuksha	8	24.2	68.0	7.8	7.50	1.23	0.050	9.15	10.0
Syenite	Louhi	Yeletozero	9	23.1	53,5	31.4	6.65	1.51	0.032	7.83	9.80
	Priladozhye	Elisenvaara	10	2.8	43,0	54.2	3.26	2.00	0.025	8.00	8.25
Gra-nite-aplite	Louhi	Yeletozero	11	29.1	Or-30,8	40.4	3.87	0.85	0.207	7.89	7.98
		Slyudozero	12	22.0	Or-11,1	66.9	4.02	1.32	0.034	7.84	9.76
Pegmatite-granite	Mamsko-Chauiscoe	Mamskoe,B. Northern	13	9.0	71,0	20.0	7.5	-	-	7.78	-
	Enskoe	Rikolatva	14	10.1	69,5	26.4	7.0	-	-	7.52	8.4
	Central Asia	Ljngarskoe	15	15.5	47.7	36.8	5.6	-	-	7.82	-
	Kazakhstan	Karaotse-lgskoye	16	2.5	58,7	38.8	7.7	-	-	7.76	-
	Uralskoe	Malache-vskoye	17	43.6	29,3	27.1	5.6	-	-	7.80	
	Finland	Kemio (FFF)	18	8.0 50	37,0 50,0	55.0 450	-	-	-	-	8.3 83

Table 1. Mineral structure and properties of feldspar breeds.

Figure 2 shows that high microcline and plagioclase concentrations in feldspathic rocks are responsible for a low angle tangent of dielectrical loss in cakes: (no. 8) potassic halleflinta - 0,050, (no. 10) syenite - 0,025 – 0.032, (no. 6) and pegmatite (Cjryla) – 0.027- and increases their electrical resistance (Fig.3) -(1,23, 2,0, 2,10⊙10^{10} Ohm⊙cm), which is consistent with GOST parameters 2484-85 for electrical porcelain: dielectrical permeability not more than 7, the angle tangent of dielectrical loss – 0.030 and electrical resistance 1-2⊙10^{12}. Low dielectrical loss (0.025) and high electrical resistance (2.0⊙10^{10} Ohm⊙cm) are characteristic of Elisenvaara syenites which have a high total percentage of microcline and plagioclase (97 mass.%).

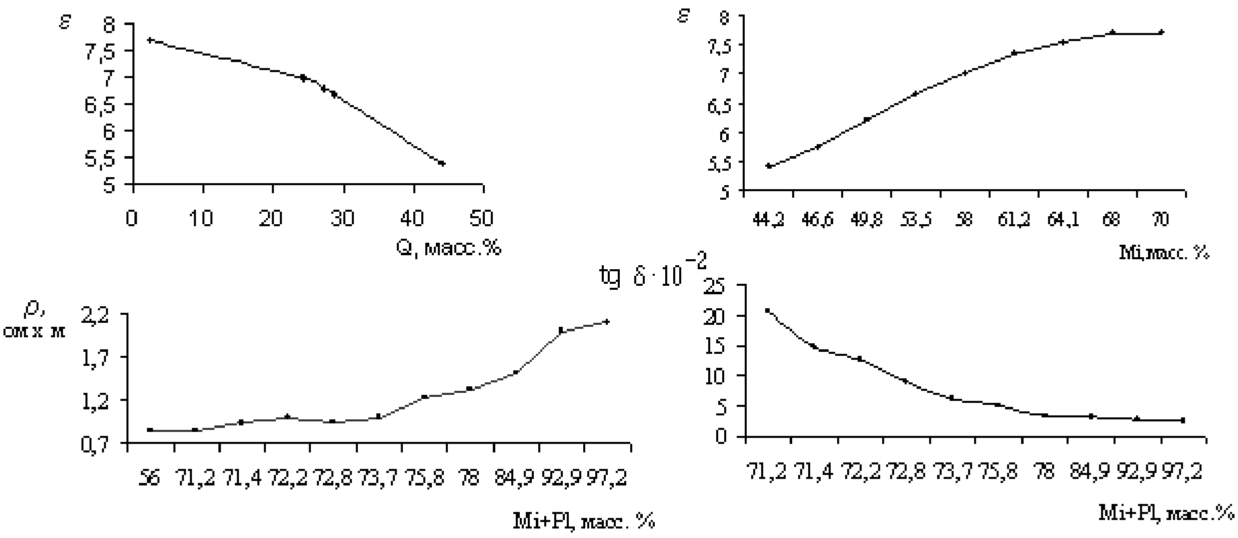

Fig. 2. Dependence of dielectric properties on feldspathic rock composition.

Elisenvaara syenites and Kostomuksha volcanics are most efficient feldspathic raw materials for electrical porcelain production in terms of their electrical properties.

3. Thermal Coefficient of Linear Expansion (TCLR)

Thermal coefficient of linear expansion (TCLR) is a parameter which shows thermal expansion upon burning of ceramic products.

TCLR was measured on a DKV- 4 quartz dilatometer on specimens, 55⊙ × 5 m in size, produced by pressing ground rocks to a grain size of 0.063 mm and subsequent burning in a silitic furnace at 1350°C to reach the maximum density of the specimens. TCLR was estimated using the formula: $\alpha = \frac{1}{l_0} \times \frac{l_t - l_0}{t_1 - t_0} + 55{,}5 \times 10^{-6} 1/\deg.$, where t_0 is initial measurement temperature, 20°C , t_l is final measurement temperature, 400, 700°C; l_0 is the original length of the specimen, mm, l_t is specimen lengthening, mm; 5.5⊙(10^{-6}- 1/deg. of the TCLR of quartz glass.

The highest TCLR values (9.15 and 11.75⊙10^{-6} 1/deg., respectively) are characteristic of halleflinta (cake no. 8) at 400° and 700°C, respectively. Halleflinta differs structurally from pegmatite in having finely dispersed quartz, which contributes to intense dissolution of quartz in a glass phase. Figure 3 shows that curves 1, 2 and 5 for the cakes of the rocks studied exhibit a non-uniform course of thermal expansion. A rapid increase in TCLR in the range 600 – 700° C is typical of compositions with a minimum quartz concentration and high microcline and plagioclase concentrations which form a less viscous liquid phase. Large quantities of quartz in rocks are responsible for the rectilinear course of the TCLR curves (3, 4, 6 and 7). A minimum TCLE value ($7.10 \cdot 10^{-6}$ 1/deg) in the range 600-700° C is observed in cake 7 with a minimum quartz concentration (44.0 mass.%), and a maximum TCLR value ($8.9 \cdot 10^{-6}$ 1/deg) in cake 1 with a quartz concentration of 2.5 mass. %.

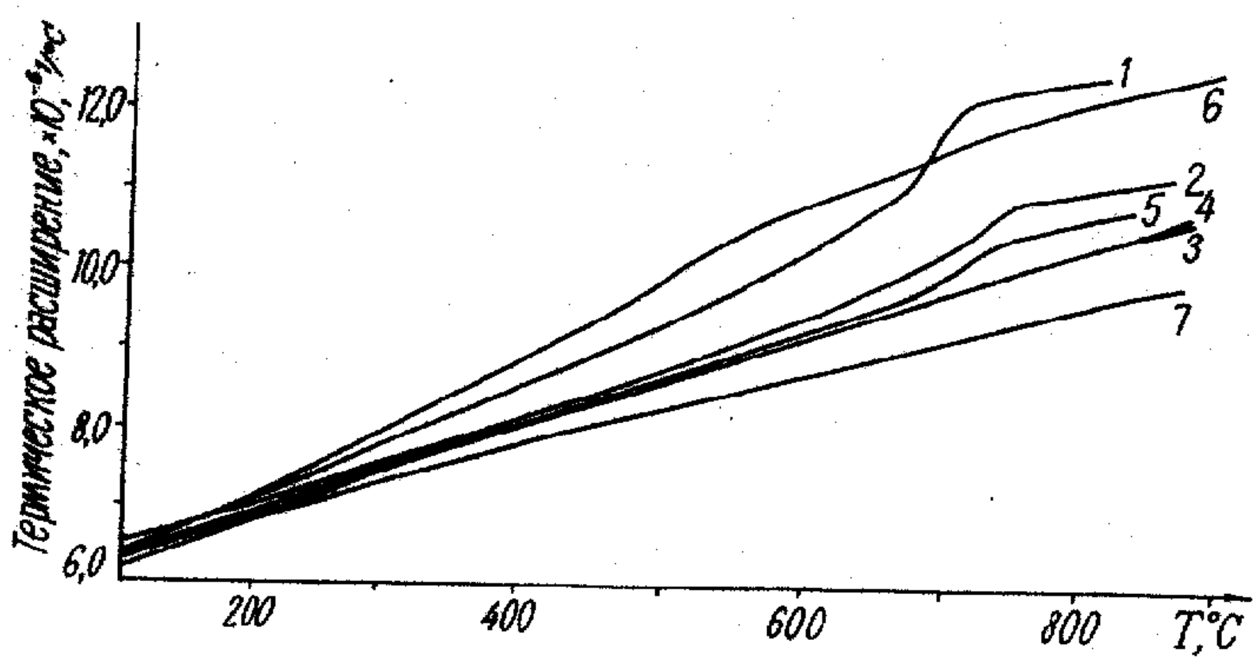

Fig. 3. Temperature dependence of the thermal coefficient of linear expansion: (numbers as in Table 1).

According to the literature [5] the dependence of TCLR on quartz concentration is due to a difference in the density of minerals. It is known that as mineral density increases, TCLR decreases. As the density of quartz (2.65 g/cm^2) is higher than that of albite (2.61 g/cm^2) and that of microcline (2.55 g/cm^2), low TCLR values in cakes with high quartz concentrations can well be expected. The dependence of TCLR on microcline-plagioclase ratio shows a more complex pattern. As quartz concentration rises with a decline in feldspar concentration [1], also observed in Roza-Lambi quartz porphyry, the porcelain burning expansion interval will expand to 100 ° C without deformation of products upon burning.

Quartz has thus been shown to decrease the TCLR of feldspathic rocks, as indicated by the absence of rapid changes in the curves (Fig.3) in the range 600 – 700 ^{o} C. High concentrations of feldspathic minerals (microcline, plagioclase - 95 – 97.5 mass. %), which form a less viscous glass phase, increase the TCLR of feldspathic rocks.

4. pH of feldspar suspension

pH is a parameter showing the acidity of feldspathic rocks and the engineering properties of clay slurry (viscosity, the density of clay slurry, tixotropy for molding ceramic products. As pH rises, the tixotropy of the clay slurry increases. Interacting with water, feldspathic minerals change the acidity of ceramic shlicker, depending on their constituent cations and anions. The optimum viscosity of clay slurry for refractory products is achieved at pH 5.5 and that for porcelain at pH 7.5–9. According to GOST 21119.3-91 for feldspathic fillers in varnish and paint production, pH is 6-9.

The pH of suspensions was measured using the potentiometer method on an I-120.1-type ionometer. Suspensions were prepared from из finely dispersed samples (grain size 0.063 mm) at solid:fluid ratio of 1:2.5 in accordance with the procedure described in [6,7]. The results of measurements of the pH of feldspar rock suspensions are presented in Table 1, and Figure 4 shows the dependence of pH on total microcline and plagioclase concentration in the rock.

Our results have shown that a common pattern of variations in the pH of feldspathic rock suspensions is a rise in pH with increasing alkaline oxide concentration.

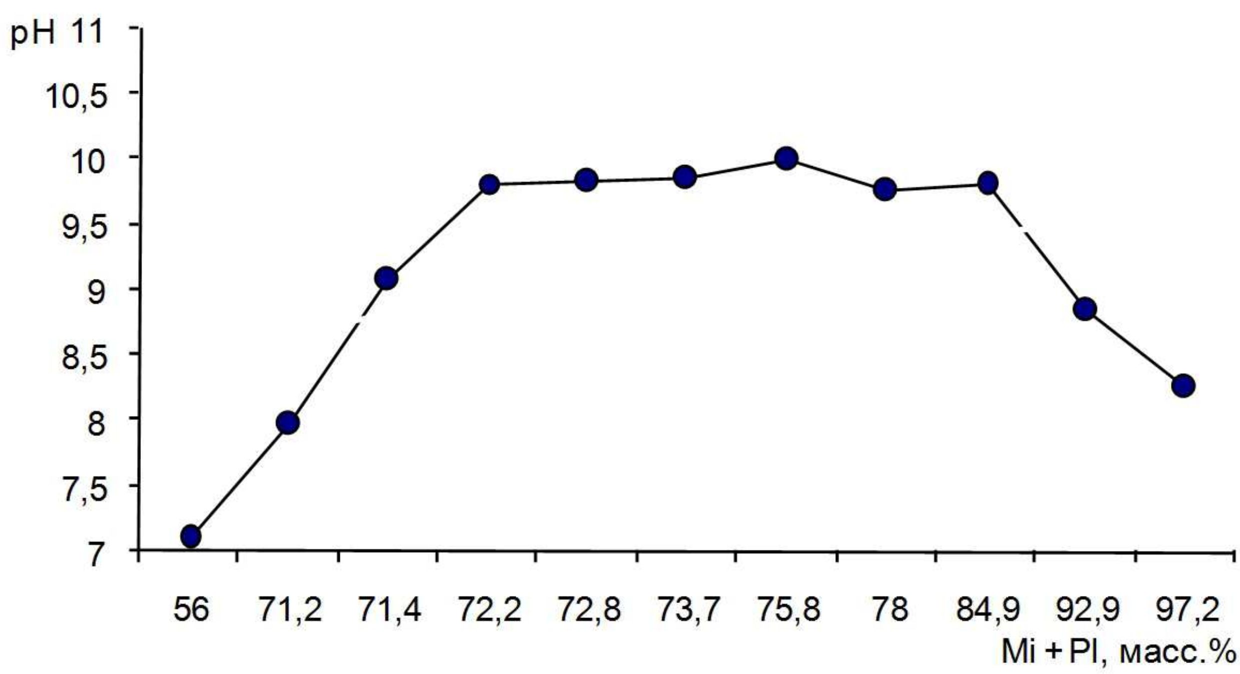

Fig. 4. Dependence of variations in pH on microcline and plagioclase.

Table 1 shows that suspensions of Khetolambino and Lupikko microcline pegmatites have the highest pH values: 9.67 and 9.82, respectively. Potassic halleflinta, a nonconventional type of feldspathic raw material, has a high pH (10.0). Comparison of the pH of quartz-feldspathic rock suspensions has shown that large quantities of quartz (pH of quartz is 6.4-6.9) decrease their pH considerably, as in Roza-Lambi volcanics (pH 7.1).

Figure 4 shows that rocks that contain a total microcline and plagioclase concentration of 75.8–78.0 mass. % and quartz concentration of 22.0–24.2 mass. % have the highest pH.

Thus, the pH of feldspar suspensions depends on total microcline and plagioclase concentrations and quartz concentration in the rock. The pH of Elisenvaara syenite is 8.25 is consistent with feldspathic raw material according to GOST 21119.3-91 (pH 6-9) and Kemio feldspar from Finland (pH 8.3).

5. Conclusions

The electrical properties ε , lg ρ, tg δ of the cakes of nonconventional types of feldspathic rocks and conventional types, such as pegmatite, are basically affected by alkaline oxides and quartz. Dielectrical permeability depends more on microcline and quartz concentrations in rocks. The angle tangent of dielectrical loss and electrical resistance depend on total microcline and plagioclase concentration. Elisenvaara syenites, which contain high microcline and plagioclase concentrations (97 mass.%), typically show lower tg δ values (0.025) and higher electrical resistance ($2.0\cdot10^{-12}$ Ohm·cm) than other rocks. Their TCLR is consistent with that of microcline pegmatite. The pH of the suspensions of nonconventional feldspathic raw material depends on total microcline and plagioclase concentration and quartz concentration. Elisenvaara alkaline syenites are a promising feldspathic raw material for electrical porcelain production.

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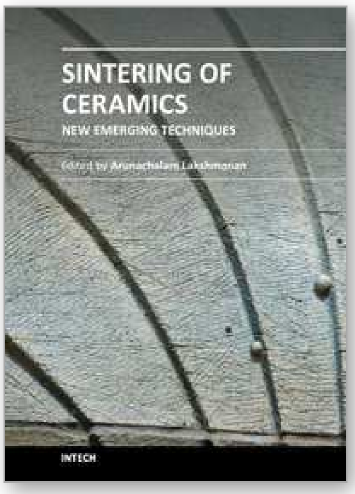

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The chapters covered in this book include emerging new techniques on sintering. Major experts in this field contributed to this book and presented their research. Topics covered in this publication include Spark plasma sintering, Magnetic Pulsed compaction, Low Temperature Co-fired Ceramic technology for the preparation of 3-dimesinal circuits, Microwave sintering of thermistor ceramics, Synthesis of Bio-compatible ceramics, Sintering of Rare Earth Doped Bismuth Titanate Ceramics prepared by Soft Combustion, nanostructured ceramics, alternative solid-state reaction routes yielding densified bulk ceramics and nanopowders, Sintering of intermetallic superconductors such as MgB2, impurity doping in luminescence phosphors synthesized using soft techniques, etc. Other advanced sintering techniques such as radiation thermal sintering for the manufacture of thin film solid oxide fuel cells are also described.