

DIELECTRIC PROPERTIES OF FILLED GLASS-CERAMIC

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Experimental methods are reported and a method is suggested for calculating the dielectric properties of glass-ceramics for electronics.

FORMULATION OF THE PROBLEM

In the design of modern electronic equipment many resources and much effort are expended on the solution of problems of increasing the speed and integration. In view of this more stringent requirements are put on the materials of substrates for electronic circuits. Many corporations and firms such as NEC, Toshiba, and Murata (Japan), DuPont (USA), and others have been working on this problem.

A ceramic or a composite based on it is customarily used in the development of a new electronic material. Creation of a material with predetermined properties is a multi-parameter problem, which can be solved only by employing analytical methods that allow different variants to be calculated.

Below we describe a glass-ceramic for electronic-circuit substrates with parameters that meet present-day requirements and also present a method for calculating the frequency-concentration dependences of the dielectric properties of filled glass-ceramics on the physical properties of the components and structural parameters of the glass-ceramic.

STRUCTURAL MODEL OF GLASS-CERAMICS

The glass-ceramic studied consisted of a mixture of a powdered ceramic filler ($\alpha\text{-Al}_2\text{O}_3$) and glass of the $\text{BaO-SiO}_2\text{-ZnO}$ system. Using x-ray phase analysis, differential thermal analysis, and electron-probe x-ray spectral microanalysis, we studied the sintering kinetics of this composite (see Table 1) and used the results to choose the sintering temperature time for forming 20-30 vol. % of α -celsian in the glass-ceramic.

Elsewhere [1] we proposed a glass-ceramic structural model which takes into account the result of percolation theory [2], clustering (aggregation of filler particles), the properties of the interphase layer, and other structural parameters (see Fig. 1).

The effective dielectric properties of a glass-ceramic are determined on the basis of this structural model in two stages: first the properties of a cluster of aggregated particles are determined on the basis of the averaged-element model (Fig. 1d) and then the effective properties of the entire glass-ceramic are found on the basis of the percolation model (Fig. 1f).

The structure of a filled glass-ceramic can be represented by three phases: a filler, a matrix, and an interphase layer. The change that occurs in the structure as the volume concentration v_f of filler particles increases can be described qualitatively as follows. First isolated clusters of aggregated particles (CAP's) are formed in the continuous binder (matrix), then as the filler volume concentration rises they combine into an infinitely large cluster of aggregated particles (see Fig. 1a, b, c). A further increase in concentration causes the CAP volume to increase and at some concentration $v_f = v^*$ the entire volume V of the composite is occupied by the CAP.

The filler particles in the composite usually come into contact with each other through thin interlayers of the matrix material. This feature of the contact between the particles affects the transport processes in the composite and should be taken into account in the model ($\Delta l = 0$).

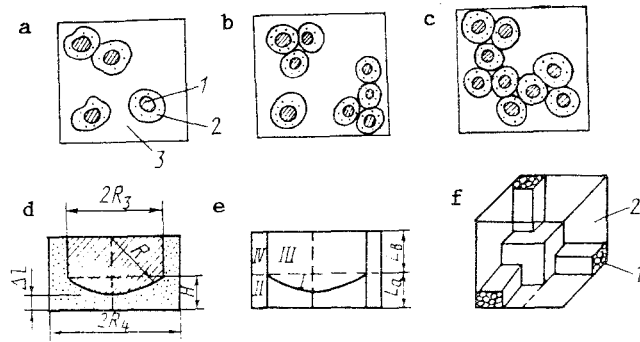


Fig. 1. Contribution to the structural model of a filled ceramic: a, b, c) structure with interphase layer at various filler concentrations [1) matrix; 2) filler; 3) interphase layer]; d) cross section of an averaged element; d) arbitrary division of the averaged element into regions; e) unit cell of the percolation model at $v_C < v_C < 0.5$ [1) cluster aggregated particles; 2) matrix].

TABLE 1. Results of Study of the Glass-Ceramic Sintering Kinetics

Crystallizing phase	Phase-initiation temperature, °C	Temperature of phase disappearance, °C
BaO·SiO ₂	680	850
α-celsian	720	Does not disappear
BaO·6Al ₂ O ₃	1100	1300

We determine the CAP properties by using the averaged-element model. In the case under consideration (Fig. 1d) the geometrical parameters of the averaged element (\bar{R}_3 , \bar{R}_4 , \bar{H}) are determined by the formulas [3]

$$\bar{R}_3 = 2(N_c)^{-1} \sqrt{N_c - 1}; \quad (1)$$

$$\bar{R}_4 = \bar{R}_3 / \sqrt{1 - v_{mc}}; \quad (2)$$

$$\bar{H} = 1 + \Delta\bar{l} - \sqrt{1 - \bar{R}_3^2}; \quad \bar{H} = H/R, \quad (3)$$

where N_c is the average coordination number of the particles in the CAP; v_{mc} is the volume concentration of the binder material in the CAP ($v_{mc} = 1 - v^*$); and $\Delta\bar{l}$ is the relative interlayer thickness at the points of contact.

The coordination number N_c is uniquely related to the concentration v_{mc} :

$$N_c = (v_{mc} + 3 + \sqrt{v_{mc}^2 - 10v_{mc} + 9}) / 2v_{mc}. \quad (4)$$

We find the complex admittance $\hat{\sigma}_e$ of the averaged element by the integral method of sections. We divide the averaged element into regions I-IV as shown in Fig. 1e. The complex admittance $I(\hat{\sigma}_I)$ is determined by the formula

$$\hat{\sigma}_I = S^{-1} \int_S \hat{\sigma}_{ser} dS, \quad (5)$$

where S is the area of the base of region I and σ_{ser} is calculated for series-connected elementary regions.

Going over to polar coordinates ρ , φ and bearing in mind that $S = \pi R_3^2$, where R_3 is the radius of the region I, we obtain

$$\hat{\sigma}_I = \pi^{-1} R_3^{-2} \int_0^{R_3} \hat{\sigma}_{ser} \rho d\rho \int_0^{2\pi} d\varphi = 2R_3^{-2} \int_0^{R_3} \hat{\sigma}_{ser} \rho d\rho. \quad (6)$$

Here the value $\hat{\sigma}_{ser}$ is determined from the formula [1]

$$\hat{\sigma}_{\text{ser}} = \sigma_{\text{ser}} + i\omega\varepsilon_{\text{ser}}, \quad (7)$$

where

$$\sigma_{\text{ser}} = \sigma_2 \frac{1 + \bar{L}_1(a_1 - 1) + \omega^2\tau_1^2[1 + \bar{L}_1(b_1 - 1)]}{[1 + \bar{L}_1(a_1 - 1)]^2 + \omega^2\tau_1^2[1 + \bar{L}_1(b_1 - 1)]^2};$$

$$\varepsilon_{\text{ser}} = \varepsilon_1 \frac{1 + \bar{L}_1(a_1^2 - b_1) + \omega^2\tau_1\tau_2 b_1[1 + \bar{L}_1(b_1 - 1)]}{[1 + \bar{L}_1(a_1 - 1)]^2 + \omega^2\tau_1^2[1 + \bar{L}_1(b_1 - 1)]^2}. \quad (8)$$

Subscripts 1 and 2 pertain to the first and second component; L_i is the thickness of the layer of i -th component; $\bar{L}_i = L_i/L$; L is the thickness of the layered system; $a_1 = \sigma_2/\sigma_1$; $b_1 = \varepsilon_2/\varepsilon_1$; $\tau_1 = \varepsilon_1/\sigma_1$; $\tau_2 = \varepsilon_2/\sigma_2$; σ_i is the electrical conductivity, and ε_i is the dielectric constant of the i -th component.

We isolate the real and imaginary parts of the integrand:

$$\sigma_I = 2R_3^{-2} \int_0^{R_3} \frac{\sigma_{\text{IPL}}\sigma_f(\bar{L}_f\sigma_{\text{IPL}} + \bar{L}_{\text{IPL}}\sigma_f) + \omega^2(\varepsilon_f^2\bar{L}_{\text{IPL}} + \varepsilon_{\text{IPL}}^2\bar{L}_f\sigma_f)}{(\bar{L}_f\sigma_{\text{IPL}} + \bar{L}_{\text{IPL}}\sigma_f)^2 + \omega^2(\bar{L}_f\varepsilon_{\text{IPL}} + \bar{L}_{\text{IPL}}\varepsilon_f)} \rho d\rho, \quad (9)$$

$$\varepsilon_I = 2R_3^{-2} \int_0^{R_3} \frac{\bar{L}_f\varepsilon_f\sigma_{\text{IPL}}^2 + \bar{L}_{\text{IPL}}\varepsilon_{\text{IPL}}\sigma_f^2 + \omega\varepsilon_{\text{IPL}}\varepsilon_f(\bar{L}_f\varepsilon_{\text{IPL}} + \bar{L}_{\text{IPL}}\varepsilon_f)}{(\bar{L}_f\sigma_{\text{IPL}} + \bar{L}_{\text{IPL}}\sigma_f)^2 + \omega^2(\bar{L}_f\varepsilon_{\text{IPL}} + \bar{L}_{\text{IPL}}\varepsilon_f)^2} \rho d\rho, \quad (10)$$

where σ_f , ε_f , and σ_{IPL} , ε_{IPL} , respectively, are the electrical conductivity and dielectric constant of the filler and the interphase layer (IPL); \bar{L}_f and \bar{L}_{IPL} are determined from the geometry of the average element:

$$\bar{L}_f = (V\sqrt{1-\bar{\rho}^2} - \sqrt{1-\bar{R}_3^2})/\bar{H}, \quad \bar{L}_{\text{IPL}} = (1 + \Delta\bar{l} - \sqrt{1-\bar{\rho}^2})/\bar{H}; \quad (11)$$

$\bar{\rho}$ is the relative polar radius,

or

$$\sigma_I = 2\bar{H}\bar{R}_3^{-2} \left\{ \frac{A_1}{A} (1 - k_2) + \frac{B_1A - A_1B}{2A^2} \ln \frac{A + B + C}{Ak_2^2 + Bk_2 + C} + \frac{A_1B^2 - 2ACA_1 - B_1AB}{2A^2} [I_\Delta(1) - I_\Delta(k_2)] \right\}; \quad (12)$$

$$\varepsilon_I = 2\bar{H}\bar{R}_3^{-2} \left\{ \frac{A_2}{A} (1 - k_2) + \frac{B_2A - A_2B}{2a^2} \ln \frac{A + B + C}{Ak_2^2 + Bk_2 + C} + \frac{A_2B^2 - 2ACA_2 - B_2AB}{2A^2} [I_\Delta(1) - I_\Delta(k_2)] \right\}. \quad (13)$$

Here we have introduced the notation

$$A = \sigma_f^2 [(a_m - 1)^2 + \omega^2\tau_m^2 (1 - b_m^2)];$$

$$B = 2\sigma_f^2 [(a_m - 1)(k_1 - a_mk_2) + \omega^2\tau_m^2 (1 - b_m)(b_mk_1 - k_2)];$$

$$C = \sigma_f^2 [(k_1 - a_mk_2)^2 + \omega^2\tau_m^2 (b_mk_1 - k_2)^2];$$

$$A_1 = \sigma_f^3 [a_m(a_m - 1) - \omega^2\tau_m^2 (1 - b_m^2 a_m)];$$

$$B_1 = \sigma_f^3 [a_m(k_1 - a_mk_2) + \omega^2\tau_m^2 (b_m^2 a_m k_1 - k_2)];$$

$$A_2 = \sigma_f^2 \varepsilon_{\text{IPL}} [b_m a_m^2 - 1 + \omega^2\tau_m b_m (1 - b_m)];$$

$$B_2 = \sigma_f^2 \varepsilon_{\text{IPL}} [k_1 - b_m k_2 a_m + \omega^2\tau_m^2 b_m (b_m k_1 - k_2)].$$

The generalized function $I_\Delta(x)$ introduced into (12) is

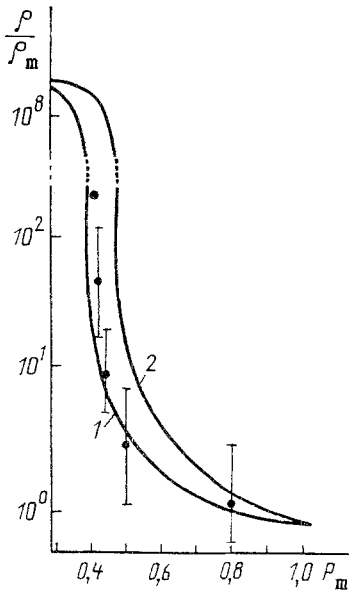


Fig. 2

Fig. 2. Dependence of the relative resistivity of the glass-ceramic on the mass concentration of the glass: 1) calculation at $v^* = 0.75$; 2) at $v^* = 0.6$; the points represent experimental data.

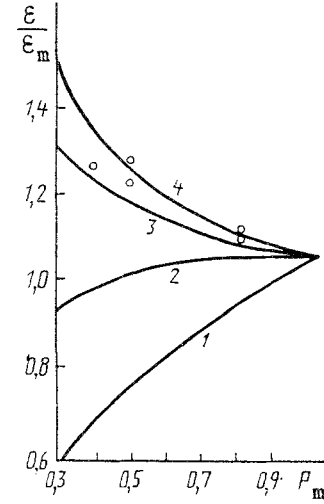


Fig. 3

Fig. 3. Dependence of the relative dielectric constant of the glass-ceramic on the mass concentration of the glass: 1) calculation at $\epsilon_{IPL} = 1$; 2) $\epsilon_{IPL} = 0.5 \epsilon_m$; 3) $\epsilon_{IPL} = 0.7 \epsilon_m$; 4) $\epsilon_{IPL} = \epsilon_m$; the points represent experiment.

$$I_{\Delta}(x) = \begin{cases} \frac{2}{\Delta} \operatorname{arctg} \frac{2Ax + B}{\sqrt{\Delta}}, & \text{if } \Delta > 0; \\ -\frac{1}{Ax + B/2}, & \text{if } \Delta = 0, \end{cases}$$

where $\Delta = 4AC - B^2$, $a_m = \sigma_{IPL}/\sigma_f$; $b_m = \epsilon_f/\epsilon_{IPL}$; and $\tau_{IPL} = \epsilon_{IPL}/\sigma_{IPL}$.

The effective conductivity $\hat{\sigma}_a$ of region a consisting of parallel-connected regions I and II (see Fig. 1e) is calculated from the formulas [1]

$$\hat{\sigma}_{\text{par}} = \sigma_{\text{par}} + i\omega\epsilon_{\text{par}} \quad (14)$$

where

$$\sigma_{\text{par}} = \sigma_1 \bar{S}_1 + \sigma_2 \bar{S}_2; \quad \epsilon_{\text{par}} = \epsilon_1 \bar{S}_1 + \epsilon_2 \bar{S}_2; \quad (15)$$

$$\hat{\sigma}_a = \sigma_a + i\omega\epsilon_a; \quad (16)$$

$$\sigma_a = \sigma_f \bar{R}_3^2 / \bar{R}_4^2 + \sigma_{IPL} (\bar{R}_4^2 - \bar{R}_3^2) / \bar{R}_4^2; \quad (17)$$

$$\epsilon_a = \epsilon_1 \bar{R}_3^2 / \bar{R}_4^2 + \epsilon_{IPL} (\bar{R}_4^2 - \bar{R}_3^2) / \bar{R}_4^2.$$

A similar equation is valid for the effective conductivity of region b ($\hat{\sigma}_b$), consisting of regions III and IV:

$$\hat{\sigma}_b = \sigma_b + i\omega\epsilon_b, \quad (18)$$

where

$$\sigma_b = \sigma_f \bar{R}_3^2 / \bar{R}_4^2 + \sigma_{IPL} (\bar{R}_4^2 - \bar{R}_3^2) / \bar{R}_4^2; \quad (19)$$

$$\varepsilon_b = \varepsilon_f \bar{R}_3^2 / \bar{R}_4^2 + \varepsilon_{\text{TPL}} (\bar{R}_4^2 - \bar{R}_3^2) / \bar{R}_4^2. \quad (19)$$

The effective conductivity $\hat{\sigma}_e$ of the entire averaged element is found from the formula for series-connected regions a and b:

$$\sigma_e = \sigma_b \frac{1 + \bar{L}_b(a_{11} - 1) + \omega^2 \tau_{11}^2 [1 + \bar{L}_a(b_{11} - 1)]}{[1 + \bar{L}_a(a_{11} - 1)]^2 + \omega^2 \tau_{11}^2 [1 + \bar{L}_a(b_{11} - 1)]^2},$$

$$\varepsilon_e = \varepsilon_a \frac{1 + \bar{L}_a(a_{11}^2 + b_{11}) + \omega^2 \tau_{11} \tau_{22} b_{11} [1 + \bar{L}_a(b_{11} - 1)]}{[1 + \bar{L}_a(a_{11} - 1)]^2 + \omega^2 \tau_{11}^2 [1 + \bar{L}_a(b_{11} - 1)]^2}, \quad (20)$$

where $a_{11} = \sigma_b / \sigma_a$; $b_{11} = \varepsilon_b / \varepsilon_a$; $\tau_{11} = \varepsilon_a / \sigma_a$; $\tau_{22} = \varepsilon_b / \sigma_b$; $\bar{L}_a = k_2 / k_1$; $\bar{L}_b = 1 - \bar{L}_a$; $k_1 = 1 + \Delta \bar{l}$; $k_2 = \sqrt{1 - \bar{R}_3^2}$.

From formulas (20), therefore, we can determine the electrical conductivity σ_e and the dielectric constant ε_e of the CAP. Now, considering the system as a two-component system, we can determine the effective conductivity σ_{eff} and the dielectric constant ε_{eff} of the entire system on the basis of the percolation model (Fig. 1f). The volume concentration of the CAP is determined from the formula

$$v_c = v_m / v^*, \quad (21)$$

where $v^* = 1 - v_{\text{mc}}$ is the volume concentration of the filler at maximum filling for the given glass-ceramic.

PERCOLATION MODEL

The effective electrical conductivity σ and dielectric constant ε obtained on the basis of the percolation model have the form

$$\sigma = \sigma_e [\bar{S}_1^{(\sigma)} + a_e (S_2 x_1 + S_3 x_2 + S_4)], \quad (22)$$

$$\varepsilon = \varepsilon_e [\bar{S}_1^{(\varepsilon)} + S_2 y_1 + S_3 y_2 + S_4], \quad (23)$$

where

$$x_1 = \frac{1 + (a_e - 1) l_2 + \omega^2 \tau_e^2 [1 + (b_e - 1) l_2]}{[1 + (a_e - 1) l_2]^2 + \omega^2 \tau_e^2 [1 + (b_e - 1) l_2]^2};$$

$$x_2 = \frac{1 + (a_e - 1) l_1 + \omega^2 \tau_e^2 [1 + (b_e - 1) l_1]}{[1 + (a_e - 1) l_1]^2 + \omega^2 \tau_e^2 [1 + (b_e - 1) l_1]^2}; \quad (24)$$

$$a_e = \sigma_m / \sigma_e; \quad b_e = \varepsilon_m / \varepsilon_e; \quad \tau_e = \varepsilon_e / \sigma_e; \quad \tau_m = \varepsilon_m / \sigma_m,$$

$$y_1 = \frac{\bar{l}_2 a_e^2 + (1 - \bar{l}_2) a_m + \omega^2 \tau_e \tau_m a_m [1 + k_m - 1] \bar{l}_2}{[1 + (a_e - 1) \bar{l}_2]^2 + \omega^2 \tau_e^2 [1 + (k_m - 1) \bar{l}_2]^2},$$

$$y_2 = \frac{\bar{l}_1 a_e^2 + (1 - \bar{l}_1) a_m + \omega^2 \tau_e \tau_m a_m [1 + (a_m - 1) \bar{l}_1]}{[1 + (a_e - 1) \bar{l}_1]^2 + \omega^2 \tau_e^2 [1 + (a_m - 1) \bar{l}_1]^2}, \quad (25)$$

$\bar{S}_1^{(\sigma)}$, $\bar{S}_1^{(\varepsilon)}$, \bar{S}_2 , \bar{S}_3 , \bar{S}_4 , \bar{l}_1 , and \bar{l}_2 are the geometrical parameters of the percolation model, which are given in Table 2.

If $v_c > 0.5$, then when calculating \bar{S}_1 , \bar{S}_2 , \bar{S}_3 , \bar{S}_4 , \bar{l}_1 , \bar{l}_2 we must make the exchange $v_c \rightleftharpoons v_{2c}$ in Table 2 and change the subscripts e \rightleftharpoons m in formulas (22)-(25).

COMPARISON OF CALCULATION WITH EXPERIMENTAL DATA

In Figs. 2 and 3 the calculation of the resistivity and dielectric constant of a glass-ceramic (glass + Al_2O_3) is compared with the experimental data.

X-ray structural analysis of the given material showed that an interphase layer, celsian, is formed on the surface of the filler (Al_2O_3) particles. The value of the resistivity of celsian is close to that of the filler while its dielectric constant is smaller than that of the glass (ε_m) by a factor of 1.3 to 2. In our calculations of the effective

TABLE 2. Geometrical Parameters of the Percolation Model*

Range of variation	\bar{S}'_1	\bar{S}_2	\bar{S}_3	\bar{S}_4	\bar{l}_1	\bar{l}_2
$0 < v_c \leq v$	0	$v_c^{2/3}$	0	$1 - v_c^{2/3}$	0	$v_c^{1/3}$
$v_c \leq v_c \leq 0.5$	$\frac{1}{3} \frac{v_c - v_c}{1 - v_c^{1/3}}$	$v_c^{2/3} - \bar{S}'_1$	$2 (\bar{S}'_1)^{1/2} \times$ $\times (1 - v_c^{1/3})$	$1 - v_c^{2/3} - \bar{S}'_3$	$(\bar{S}'_1)^{1/2}$	$v_c^{1/3}$

$$*) \bar{S} = \begin{cases} [(v_c - v_c)/(1 - v_c)]^t, & \text{if } v_c > v_c, \\ 0, & \text{if } v_c \leq v_c; \end{cases}$$

$$\bar{S}_1^{(\sigma)} = \bar{S} + (\bar{S}' - \bar{S}) g(a_\sigma);$$

$$\bar{S}_1^{(\varepsilon)} = \bar{S} + (\bar{S}' - \bar{S}) g(a_\varepsilon);$$

$$g(a_c) = 5,53a_c - 8,3a_c^2 + 3,23a_c^3 + 0,54a_c^4;$$

$$g(b_c) = 5,53b_c - 8,3b_c^2 + 3,23b_c^3 + 0,54b_c^4;$$

$$\text{if } \sigma_e/\sigma_m < 1, \varepsilon_e/\varepsilon_m < 1, \text{ then } v_c = gv, a_c = \sigma_e/\sigma_m, b_c = \varepsilon_e/\varepsilon_m;$$

$$\text{if } \sigma_e/\sigma_m > 1, \varepsilon_e/\varepsilon_m > 1, \text{ then } v_c = 1 - gv, a_c = \sigma_e/\sigma_m, b_c = \varepsilon_e/\varepsilon_m;$$

$$v_c = 1 - v.$$

dielectric properties of the glass-ceramic ρ and ε , we assumed that $\rho_{IPL} = \rho_m$, and the value of ε_{IPL} was varied over the range $\varepsilon_{IPL} = 1$ to ε_m .

Figure 2 shows the concentration dependences of the resistivity of the glass-ceramic at $\omega = 0$. Curve 1 is the result of calculation at maximum filling $v^* = 0.75$ and curve 2, at $v^* = 0.6$, i.e., the volume concentration of interphase layer in the cluster of aggregated particles was assumed to be $(v_{IPL})_{max} = 0.25$ in the first case and $(v_{IPL})_{max} = 0.4$ in the second case. A comparison of the calculation and experimental data (see Fig. 2) indicates that $v_{IPL} = 0.15-0.3$ [$v_{IPL} = v_m - (1 - v_f/v^*)$]. These values of v_{IPL} are in good agreement with the results from studies of the structure.

The calculation and experiment also show (Fig. 2) that the percolation transition occurs in the given glass-ceramic at a glass (matrix) volume concentration $v_m \sim 0.4$, which is due to the conditions under which the structure is formed and the properties of the material.

Figure 3 compares the calculated dielectric constant of the glass ceramic and the experimental data at $\omega = 1$ MHz. This comparison suggests that rather good agreement between the experimental and calculated data is obtained when the dielectric constant of the interphase layer is assigned in the range $\varepsilon_{IPL} = (1 - 0.7)\varepsilon_m$. Calculation also indicates that the porosity (curve 1) of a cluster of aggregated filler particles has an influence on the effective dielectric constant of the glass-ceramic.

CONCLUSIONS

A method has been developed for calculating the dielectric properties of glass-ceramic materials. Comparison of calculation with experimental data revealed fairly good agreement.

NOTATION

Here N_{CN} is the average coordination number; R_3, R_4 , and H are the geometrical parameters of the averaged element; σ is the electrical conductivity; ε is the dielectric constant; ω is the frequency; S_1, S_2, S_3, l_1 , and l_2 are the geometrical parameters of the percolation model; v_f is the volume concentration of the filler; v_c is the volume concentration of a cluster of aggregated particles; v_{mc} is the volume concentration of the binder in a cluster of aggregated particles; and v^* is the maximum filling.

LITERATURE CITED

1. V. V. Novikov, M. V. Dmitriev, I. P. Shapolov, and L. N. Tartakovskaya, Tekhn. Sredstv Svyazi. Ser. TPO, No. 3, 48 (1987).
2. G. N. Dul'nev and V. V. Novikov, Inz.-Fiz. Zh., 45, No. 2, 136 (1983).
3. V. V. Novikov, Kompositsionnye Polymernye Mater., No. 3, 17 (1988), Kiev.