MODELING OF DIELECTRIC PROPERTIES OF POROUS PEROVSKITE CERAMICS

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Abstract
Porous ceramics is modeled as random set of overlapping cubic grains. It is a two–component system with percolated both grains and pores. Dielectric properties were analyzed using the spectral representation of permittivity. It was shown that the permittivity is well described by the semi-empirical Lichtenecker formula. The calculations were done using the finite element method.

1. Introduction

The material properties (dielectric, magnetic, mechanical) of the heterogeneous systems composed of two or more components can be tunned significantly by varying their structure, by changing volume fractions of the components, and modifying internal geometry. In particular, dielectric properties of non–homogeneous dielectrics [1] or conductors [2] are crucially influenced by internal depolarizing fields generated at the interfaces and other inhomogeneities. There are two basic demands in this context: calculation of the effective properties when the structure is exactly known, and inversely, estimation of the internal structure when the effective properties are known from experiment. Theoretical determination of the effective properties is in general difficult even in the case of the two-component composite and the exact mixing formulae are known for several special micro-geometries only. For particular structures the approximate mixing formulae are often constructed within the framework of the effective medium approach and additional heuristic assumptions [3]. Important supplement to the analytical approaches represent numerical methods, but the numerical results lack of free parameters desirable for fitting experiment. The effective dielectric properties can be obtained by solving Maxwells equations using the finite element method (FEM) [4]. Recently the several regular and random two-dimensional microstructures were numerically studied and compared with the various mixing formulae such as the Maxwell-Garnett, Bruggeman and Lichtenecker [5]. In this contribution the 3D model of perovskite ceramics (e. g., $PbMg_{1/3}Nb_{2/3}O_3$ (PMN) [6]) with main characteristics such as porosity and randomness corresponding to real samples is constructed. Using the spectral function analysis it is shown that the dielectric properties of porous random structures are well described by the Lichtenecker-like mixing formulae. In Section 2, description of the permittivity using the spectral representation is reviewed, in Section 3, the 3D model of ceramics is discussed.

2. Permittivity of 2-component dielectrics

2.1. Permittivity of heterogeneous sample

In the quasistatic regime, i. e. when the wave-length of the applied field is larger than any non-homogeneity, the electric field $\mathbf{E}(\mathbf{x})$ in the sample is described by the static Maxwell equations. Knowing $\mathbf{E}(\mathbf{x})$ the effective permittivity ε of the sample is derived as [3]:

$$\varepsilon \int_V \mathbf{E}(\mathbf{x})^2 \mathrm{d}V = \int_V \varepsilon(\mathbf{x}) \mathbf{E}(\mathbf{x})^2 \mathrm{d}V \tag{1}$$

where the local permittivty $\varepsilon(\mathbf{x})$ takes the values of composite components depending on the position $\mathbf{x}$. Due to the linearity of the Maxwell equations the effective permittivity is homogeneous function of the individual permittivities:

$$\varepsilon(\varepsilon_1, \varepsilon_2) = \varepsilon_2 \varepsilon(r, 1) = \varepsilon_2 F(r) \tag{2}$$

where $F(r) = \varepsilon(r, 1)$, and the ratio $r = \varepsilon_1/\varepsilon_2$ is complex quantity.

2.2. Spectral representation of permittvity

The permittivity of the two–component composite can be expressed in an integral form [3, 5]:

$$\varepsilon = V_1\varepsilon_1 + V_2\varepsilon_2 + \int_0^1 v_{12}(n) \frac{\varepsilon_1\varepsilon_2}{(1-n)\varepsilon_2 + n\varepsilon_1} dn \tag{3}$$

$$V_1 + V_2 + \int_0^1 v_{12}(n) dn = 1 \tag{4}$$

$$V_1 + \int_0^1 (1-n) v_{12}(n) dn = 1 - x \tag{5}$$

$$V_2 + \int_0^1 n v_{12}(n) dn = x \tag{6}$$

where the percolation strengths V_1 and V_2 are the relative volumes of percolated clusters '1' and '2' (more precisely, of the regions with zero depolarizing field), the expression $v_{12}(n)dn$ represents the clusters characterized by the depolarizing factor n. The function $v_{12}(n)$ does not contain δ-singularities at n and $1-n$, which are in fact fully encountered in coefficients V_1, V_2. Expression (3) is a combination of parallel and serial capacities. Using the ratio of permittivities, the expression (3) is rewritten in the form [5]:

$$F(r) = V_1 r + V_2 + \int_0^1 v_{12}(n) \frac{r}{(1-n) + nr} dn \tag{7}$$

The percolation strengths V_1, V_2 and the spectral function $v_{12}(n)$ are the structural parameters, which do not depend on the component permittivities. They fully determine the dielectric response of the sample. The function $F(r)$ are either known explicitly (various mixing formulae)

or calculated numerically using FEM. The structural parameters are then obtained from $F(r)$ introducing $\tilde{F}(n) \equiv F(r = \frac{n-1}{n})$ and using the relation [5]:

$$\lim_{\delta \to 0^+} \frac{1}{\pi} \mathrm{Im} \tilde{F}(n + \mathrm{i}\delta) = V_1 \delta(n) + (1 - n) v_{12}(n). \tag{8}$$

2.3. Method of calculation

In Section 3, the structural parameters V_1, V_2 and $v_{12}(n)$ are calculated numerically for the model of ceramics in the following way. First, the spatially varying electric field $\mathbf{E}(\mathbf{x})$ is obtained by solving the static Maxwell equations, and then the structural parameters are calculated using Eqs. (1), (2) and (8). The spectral function is determined for n running from 0 through 1 with the step 0.01, the limit in Eq. (8) is approximated by $\delta = 0.005$. The segmented 3D images of the model were meshed using CGAL library [7] and Maxwell equations were solved using the finite element method (FreeFem++ [4]).

3. Model of cubic ceramics

Porous samples of perovskite ceramics are composed of densely packed grains with random position and orientation, their shape is cubic-like though not always regular, and their size is distributed around the mean value. It can be considered as the two–component composite of perovskite and pores (air). For simplicity, the model encountering only the most important features was constructed. The grains were assumed of cubic shape with rounded edges as created by the equation $(x - x_0)^6 + (y - y_0)^6 + (z - z_0)^6 \leq r^6$, where (x_0, y_0, z_0) is the grain center. Inside the box of L x L x L voxels, N grains with random positions and orientations were generated. For simplicity, all grains had the same size r. Let us introduce three characteristic lengths Δ_{min}, Δ_0, and $\bar{\Delta}$. Δ_{min} is the shortest possible distance between grain centers, and it is a fraction of L defined as $\Delta_{min} = L\delta$, $\delta < 1$. Two grains with common body diagonal, which are at the distance $\Delta_0 = 2\sqrt[3]{3}r$, are touching only by their corners. The average distance $\bar{\Delta}$ between nearest neighbors in the uniformly distributed grain centers in the box can be estimated as $\bar{\Delta} \approx L N^{1/3}$. Parameters of the model are chosen such that the distance Δ of two nearest grain centers cannot become too small, i. e. $\Delta > \Delta_{min}$, but at the same time two grains may overlap. The grain overlapping is allowed by the condition $\Delta_{min} < \Delta_0$.

The parameter values further considered are: $L = 512$, $N = 100$, $\delta = 0.2$, $r = 57$, then the size of the grain is $2r = 114$ and the characteristic lengths $\Delta_{min} = 102$, $\Delta_0 = 164$, and $\bar{\Delta} = 110$. The intersection of two grains cannot exceed approximately 11%. The example of generated random structure is shown in Fig. 1. Due to the finite box size, fluctuations of various quantities are expected. Therefore 10 random sets of grains with the above parameters were generated in order to smooth out the fluctuations. The porosity x and percolation strengths V_1, V_2 of each set of grains together with mean values are shown in the Table 1. It is evident that all deviations from the mean are small. It can be attributed to the severe restrictions imposed on distribution of grains in the box, as indicated by the small value $(\bar{\Delta} - \Delta_{min})/\bar{\Delta} \approx 0.07$. The spectral function $v_{12}(n)$ calculated for 10 random sets of grains is plotted in Figure 2 (red points). The percolation strengths, V_1 of the grains and V_2 of the pores, are depicted as full lines at $n = 0$ and $n = 1$, respectively. The fluctuations of $v_{12}(n)$ are also small. In principle, fitting $v_{12}(n)$ with an explicit

No.	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**mean**
x	0.247	0.234	0.242	0.241	0.235	0.242	0.238	0.238	0.252	0.252	0.242
$\mathbf{V_1}$	0.541	0.554	0.536	0.519	0.558	0.517	0.549	0.544	0.526	0.528	0.537
$\mathbf{V_2}$	0.105	0.088	0.104	0.100	0.096	0.098	0.102	0.101	0.104	0.113	0.101

Table 1. Porosity x and percolation strengths in 10 random sets of grains. The mean values are shown in the last column. There are only small fluctuations about the mean values.

function and then putting it to Eq. (3), the effective permittivity (mixing formula) could be obtained. Instead, the numerical results are compared with known mixing formulae in this contribution.

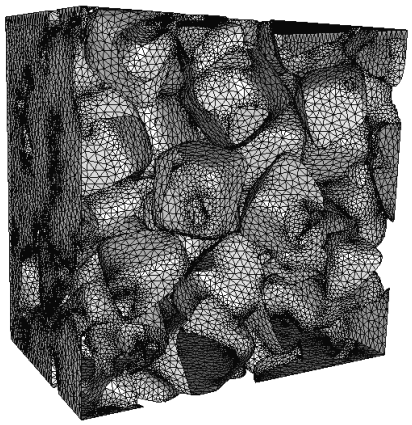

Figure 1. Cut of the 512x512x512 box with 100 grains. Grains are randomly distributed and can intersect. The volume fraction of air (pores) is about 0.24

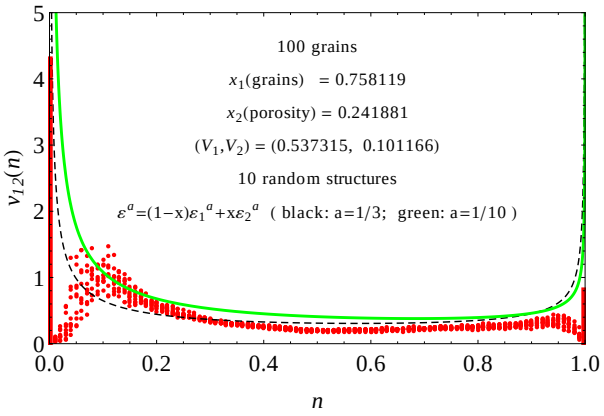

Figure 2. Spectral function of 10 random sets of 100 grains: numerical data (dots). The Lichtenecker model with $a = 1/3$ (dashed line) and $a = 1/10$ (full line). Notation inside the figure: $x_1 = 1 - x$, $x_2 = x$.

The spectral function of the model (red points in Fig. 2) is nonzero in the whole interval (0, 1). Among various types of mixing formulae similar to the Maxwell-Garnett, Bruggeman and Lichtenecker models [8, 5], only the last one exhibits the above feature. The Lichtenecker

formula:

$$\varepsilon^a = (1-x)\varepsilon_1^a + x\varepsilon_2^a, \tag{9}$$

where $-1 \leq a \leq 1$ is briefly discussed in [8, 9]. The grains in our model are percolated, therefore only $a > 0$ is further considered. The spectral function of the expression (9) can be calculated analytically, but it is not worthwhile to present it here due to its long and complicated form. The percolation strengths are obtained easily as: $V_1 = (1-x)^{1/a}$, $V_2 = x^{1/a}$. Varying the exponent a and comparing with numerical data the best agreement was obtained for $a = 1/10$, corresponding percolation strengths are very small, $V_1 \approx 0.06$, $V_2 \approx 0$. For comparison, the spectral function for two values, $a = 1/3$ and $a = 1/10$, is plotted in Fig. 2. Discrepancy between Lichtenecker $a = 1/10$ and numerical model is observed near $n = 0$ and $n = 1$, where primarily extended clusters contribute. This can be explained by the finite size of the box, where the maximal size of the clusters is restricted by the box size. In the infinite sample the large clusters (bigger than the box) contribute to the spectral function at n close to 0, while in the finite-size box such clusters become percolated and their contribution is shifted to $n = 0$, i. e. to the percolation strength.

4. Summary

The perovskite ceramics was modeled as the random set of the cubic grains. Dielectric properties, in particular structural parameters occurring in the spectral representation, were calculated using finite element method. The calculated percolation strengths indicate that both grains and pores are percolated. Comparison of numerically obtained spectral function with various mixing formula lead to the conclusion, that the permittivity of ceramic model is reliably described by the Lichtenecker formula.

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