Temperature Green's function of the dielectric constant of a ferroelectric

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The application of the Green's temperature function method using the probabilistic Boltzmann factor to describe the temperature dependence of the dielectric constant of a ferroelectric is presented. Using the example of a ferroelectric solid solution of lead zirconate titanate, the Green's temperature function of the temperature dependence of the dielectric constant is calculated taking into account the presence of activation processes caused by the interaction of domain and defect structures of the ferroelectric. Using the method of activation-relaxation of dielectric constant, the activation energies of these processes were determined: disruption of domain walls from structural defects (oxygen vacancies); migration of defects (oxygen vacancies) and decay of the domain structure; dielectric response of a domainless paraelectric.

Keywords: dielectric constant, Green's function, activation energy, lead zirconate titanate.

1. Introduction

Examination of the response of functional materials to the variation of ambient conditions is a critical objective of fundamental and applied physics. Among a wide variety of approaches to mathematical description of time and amplitude dependences of properties of these materials, differential equations are most widely used. One of the methods of their solution is Green's function method that has several modifications: single-time, two-time, causal and temperature.

The study uses the analysis of experimental temperature dependence of ferroelectric permittivity $\varepsilon(T)$ measured with slow temperature variation to determine temperature Green's function G of permittivity. Possibility to use Green's functions in this case is based on the applicability of statistical mechanics methods to ferroelectric phase transitions [1,2], and on previous studies of general properties of Green's functions. Thus, as early as in 1960 Zubarev pointed out in [3] that two-time Green's functions (retarded and advanced) are be applicable to the study of processes with a minor deviation from the state of statistical equilibrium to determine temperature-dependent energy of elementary excitations of systems with interaction and low attenuation. Later, Bonch-Bruevich and Tyablikov in [4] correlated the thermodynamic potential of a statistical system with the simplest one-boson Green's function that allows calculation of the thermodynamic system response to external exposures. Following research has shown consistency of the Green's function method for description of ferroelectric phase transitions using order-disorder type ferroelectric materials, KH_2PO_4, with two-time fermionic Green's function [5] and $PbHPO_4$ [6]. Another application of the Green's function method is the simulation of dielectric response of thin-film variable-composition ferroelectric

$(Ba,Sr)TiO_3$ [7] and transition of multilayer ferroelectric thin film from the ferroelectric to paraelectric state [8], and the calculation of solid solution permittivity, including multiple phonon scattering on clusters consisting of impurities [9]. For the second-order ferroelectric phase transition described by the fluctuation approach formalism in a crystal with strong electron-phonon interaction, the Matsubara quantum Green's functions in a temperature dependence of thermodynamic potential near the phase transition temperature made it possible to consider the effect of thermal and quantum fluctuations on the phase transition [10]. In addition, the use of atomistic Green's function method in solid-state physics enables structural features of a test sample to be considered, in particular, grain boundaries in polycrystals and their influence on phonon distribution and heat transfer mechanisms through grain boundaries [11].

This was the fundamental nature of these issues that was behind the selection of this study.

2. Experiment procedure

For the experiment, a ceramic sample 10 mm in diameter and 1 mm in thickness $(Pb_{0.95}Sr_{0.05})(Zr_{0.53}Ti_{0.47})O_3$ — ferroelectric with perovskite crystal structure was prepared. This is a solid solution with tetragonal and rhombohedral symmetry phases and ferroelectric-paraelectric phase transition at a Curie temperature of $T_C = 550$ K. Phase composition was measured using DRON-3 (Cu-$K\alpha$) X-ray diffractometer. Such composition was selected due to high values of electrophysical properties [12], wide range of engineering applications [13], high processability of synthesis and sintering of ceramic samples [14], and by low Curie temperature due to the presence of Sr^{2+} that substitute Pb^{2+} in sites A of $A^{2+}B^{4+}O_3^{2-}$

perovskite compared with undoped $Pb(Zr_{0.53}Ti_{0.47})O_3$ ($T_C = 650\,K$).

Temperature dependence of permittivity of the sample was obtained at 1 kHz and electric field strength 1 V/mm on a setup connected to a personal computer. The setup consisted of a heating cell, RFT Trennstelltrafo LTS 002 automatic transformer, E7-28 broadband immitance analyzer, TPM251 programmable PID temperature gauge and control.

3. Findings and discussion

To find the temperature Green's function of ferroelectric permittivity, temperature dependence of ferroelectric permittivity $(Pb_{0.95}Sr_{0.05})(Zr_{0.53}Ti_{0.47})O_3$ was measured (Figure 1).

Mathematical analysis of description by the first-order linear differential equation was performed.

The Green's function method is applicable to a physical system in transit to a new state of equilibrium under external exposure, if this process can be described by a differential equation.

$$\frac{d\xi}{dq} + \gamma \cdot \xi = \varphi(q), \qquad (1)$$

where $\xi(q)$ is the parameter characterizing the system; q is the amplitude external exposure of the system; γ is the parameter characterizing the system capability to the state of equilibrium; $\varphi(q)$ is the external exposure that disturbs equilibrium.

When permittivity is assumed as a parameter characterizing a ferroelectric material and temperature variation is assumed as external exposure, then equation (1) will be written as

$$\frac{d\varepsilon}{dT} + A \cdot \varepsilon = B(T), \qquad (2)$$

where ε is the permittivity; T is the temperature; A is the coefficient (negative with increase of ε as T grows and positive with decrease of ε as T grows); $B(T)$ is function of temperature exposure of the sample. Such representation is justified by an experimental fact that ferroelectric permittivity varies nonlinearly when the ferroelectric temperature varies (Figure 1). As shown in [15] using ferroelectric $(Pb_{0.95}Sr_{0.05})(Zr_xTi_{1-x})O_3$ ($x = 0.45, 0.51, 0.60$), the temperature dependence of permittivity may be divided into segments or which equation specific to thermo-activation processes is valid

$$\varepsilon_i(T) = a_i \cdot \exp\left(\frac{\pm U_i}{kT}\right), \qquad (3)$$

where a_i is the coefficient equal to relative permittivity associated with physical process in the i-th segment when the temperature tends to a limit; U_i is the permittivity activation energy due to a physical process in the i-th segment of $\varepsilon(T)$, with preceding „$\pm$" that considers permittivity growth or reduction process as the temperature grows.
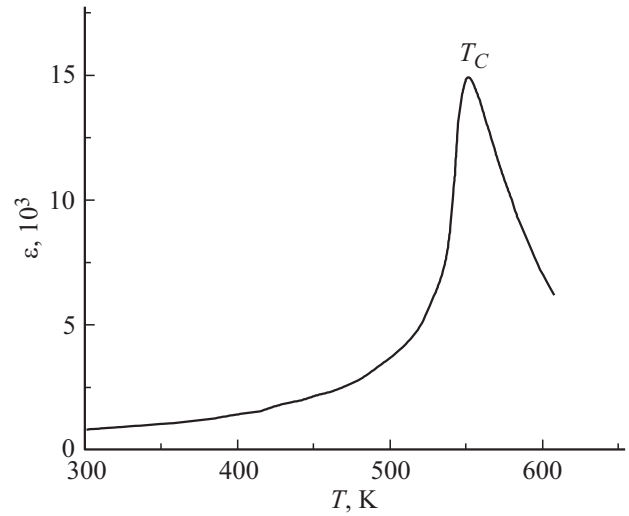
Figure 1. Temperature dependence of permittivity of ferroelectric $(Pb_{0.95}Sr_{0.05})(Zr_{0.53}Ti_{0.47})O_3$ on the Curie temperature T_C.

On the basis that equation (3) may be reduced to equation

$$\frac{d\varepsilon}{dT} = -\frac{U}{kT^2} \cdot \varepsilon, \qquad (4)$$

and equation (2) is written as:

$$\frac{d\varepsilon}{dT} = \left(\frac{B(T)}{\varepsilon} - A\right) \cdot \varepsilon, \qquad (5)$$

an expression for the temperature exposure function $B(T)$ introduced by us for the Green's function method applicability may be derived

$$B(T) = A + \frac{\varepsilon U}{kT^2}. \qquad (6)$$

However, in future calculations, $B(T)$ is an auxiliary function that does not need to be defined.

The required activation energies and corresponding temperature intervals of the given ferroelectric $(Pb_{0.95}Sr_{0.05})(Zr_{0.53}Ti_{0.47})O_3$ were determined by the permittivity activation/relaxation method described in [16] according to the temperature dependence of permittivity $\varepsilon_i(T)$ in a separate i-th segment of $\varepsilon(T)$:

$$\varepsilon_i(T) = a_0 \exp\left(\left(-\frac{U_i}{kT}\right) \cdot \left(1 - \left(\frac{kT}{U_0}\right)\right)\right), \qquad (7)$$

where U_i is the activation energy in the i-th segment; a_0 and U_0 are the experimental temperature dependence of permittivity of a particular sample; k is the Boltzmann constant; T is the temperature.

Therefore, four thermo-activation processes described by equation (3) with specific parameters are addressed and the corresponding activation energies were obtained: 0.08, 0.33, 1.68, 0.46 eV (Figure 2).

Coefficient a_i and activation energy U_i from equation (3) for $(Pb_{0.95}Sr_{0.05})(Zr_{0.53}Ti_{0.47})O_3$, and R-squared value R^2 of $\varepsilon(T)$ by equation (1) in segments 1−4 (Figure 2)

i	a_i	U_i, eV	R^2
1	$1.43 \cdot 10^4$	0.08	0.9406
2	$8.34 \cdot 10^6$	0.33	0.9749
3	$4.29 \cdot 10^{19}$	1.68	0.9951
4	$9.31 \cdot 10^{-1}$	0.46	0.9909

The obtained approximating dependences are close to the experimental points, which is proved by the fact that R^2 is close to 1 (Table).

The first three processes take place below the Curie temperature (in the ferroelectric state of the sample) and the fourth process takes place above the Curie temperature (in the paraelectric state of the sample). In view if this, the question now arises of whether the representation described herein agrees with the Curie−Weiss law for dielectric susceptibility above the Curie temperature

$$\chi(T) = \frac{C}{(T - T_0)}, \qquad (8)$$

that, considering permittivity ε and dielectric susceptibility χ ($\varepsilon = \chi + 1$), may be written as

$$\varepsilon(T) = 1 + \frac{C}{(T - T_0)}, \qquad (9)$$

where C is the Curie−Weiss constant, K; T is sample temperature, K; T_0 is the Curie−Weiss temperature (close to the Curie temperature T_C), K.

To reduce equation (3) (for $T > T_C$) to the Curie−Weiss law, it is necessary to expand the exponential function in the Taylor's series limited by the first two terms

$$\varepsilon(T) = 1 + \ln(a) + \frac{U}{kT}, \qquad (10)$$

and replace the variables by equating equations (9) and (10). Thus, an expression for the Curie−Weiss constant C may be derived in the paraelectric region with one activation process provided that C is independent on temperature
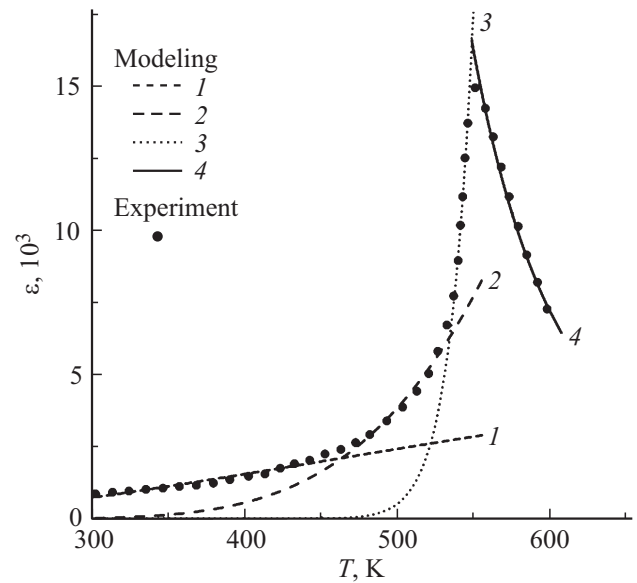
$$C = \frac{U - kT_0 \ln(a)}{k}. \qquad (11)$$

To implement this condition, the following equation shall be met

$$\frac{T}{T_0} \ln(a) = \frac{U}{kT}, \qquad (12)$$

that is possible in the paraelectric phase at $T > T_0$ and $U > kT$.

Calculation of the Curie−Weiss constant C using equation (11) reflects the dependence of this parameter of the

Figure 2. Comparison of experimental temperature dependence of ferroelectric permittivity $(Pb_{0.95}Sr_{0.05})(Zr_{0.53}Ti_{0.47})O_3$ with model dependences derived from equation (8) with activation energies U: *1* — 0.08 eV; *2* — 0.33 eV; *3* — 1.68 eV; *4* — 0.46 eV.

ferroelectric material on its internal structure: activation energy spectrum of dipole structural elements (U), dielectric properties ($\ln(a)$), ferroelectric phase transition (T_0). This may explain that the Curie−Weiss constant C calculated from experimental data may have several various values for the same ferroelectric material. Thus, the temperature dependence of permittivity written as (3) does not contradict the Curie−Weiss law in the paraelectric region and supplements it in the ferroelectric region (below the Curie temperature).

For each of the four activation processes addressed herein, physical processes that cause permittivity variation with temperature growth may be provided [15]. These processes are associated with the presence and interaction of domain and defect structures in the ferroelectric material. Thus, the first process corresponds to initial vibrations of domain walls; the second process corresponds to domain wall breakdown from the structure defects (oxygen vacancies); the third process corresponds to defect migration (oxygen vacancies) and domain structure disintegration; the fourth process corresponds to dielectric response of domain-free paraelectric material. The domain structure disintegration process as defined before in [17,18] for ferroelectric $(Pb_{0.95}Sr_{0.05})(Zr_xTi_{1-x})O_3$ ($x = 0.46, 0.48, 0.53, 0.58$) was in that heating of the sample at the critical temperature T_d below the Curie temperature T_C by $10-30\,K$ resulted in variation of the shape of diffraction lines corresponding to the polarization direction in the perovskite lattice cell that was maintained even in case of sample ageing to room temperature. Thus, redistribution took place in the intensities of doublet line (200) for the tetragonal symmetry samples and of doublet line (220) for rhombohedral symmetry samples.

Permittivity of the ferroelectric material is due to the presence of several subsystem components (electronic, ionic, dipolar, domain) and temperature dependence of permittivity in the simplest case is a sum of reactions of individual subsystems on temperature variation. This results in the presence of permittivity activation energy spectrum [15], that is exhibited as a ferroelectric response to temperature variation. The state of each of the subsystems is not equilibrium, but rather depends on the temperature, therefore the temperature activation energy of this subsystem U_i or the corresponding temperature T_i may be chosen as a parameter for each of the i-th subsystem.

According to [19], solution of equation (2) is written as a convolution with Green's function G:

$$\varepsilon(T) = \int G(T, T_i) B(T) dT, \qquad (13)$$

where $G(T, T_i)$ is Green's function of equation (13) that defines the dielectric response of the ferroelectric material to the temperature variation at T which took place at T_i. Then, considering the dependence of Green's function on T, T_i and $T - T_i$, G shall satisfy the following equation

$$\frac{dG}{dT} + A \cdot G = \delta(T - T_i), \qquad (14)$$

here, $\delta(T - T_i)$ is the delta Dirac function. Since at $T < T_i$ $G = 0$, in point $T = T_i$ it has a single jump $G = 1$, and at $T > T_i$ equation (14) is reduced to homogeneous $\partial_T G = -AG$ with initial condition $G = 1$ at $T = T_i$, then solution of equation (3) may be explicitly found as

$$G(T, T_i) = \Theta(T - T_i) \cdot \exp\left[-\int_{T_i}^{T} A(\tau) d\tau\right], \qquad (15)$$

where $\Theta(T - T_i)$ is the Heaviside function equal to zero at $T < T_i$ and equal to 1 at $T > T_i$.

Considering the case of one subsystem (electronic, ionic or domain) that undergoes temperature activation and has a constant temperature coefficient A, we obtain an expression for the temperature Green's function:

$$G(T, T_i) = \Theta(T - T_i) \cdot \exp(-A \cdot T). \qquad (16)$$

For the following analysis, physics of the addressed temperature process shall be considered. In particular, that the transition between the ferroelectric and paraelectric states of the ferroelectric material is the phase transition at which the perovskite lattice symmetry ABO_3 changes from the tetragonal (or rhombohedral) to cubic which is followed by displacement of A, B, O ions to new positions.

As Khon pointed out in [20], lattice behavior during phase transformations in solid bodies has two atomic displacement mechanisms: athermal and thermally activated. For the thermally activated mechanism addressed in the dielectric response model of the ferroelectric material, atomic displacements between the adjacent potential energy
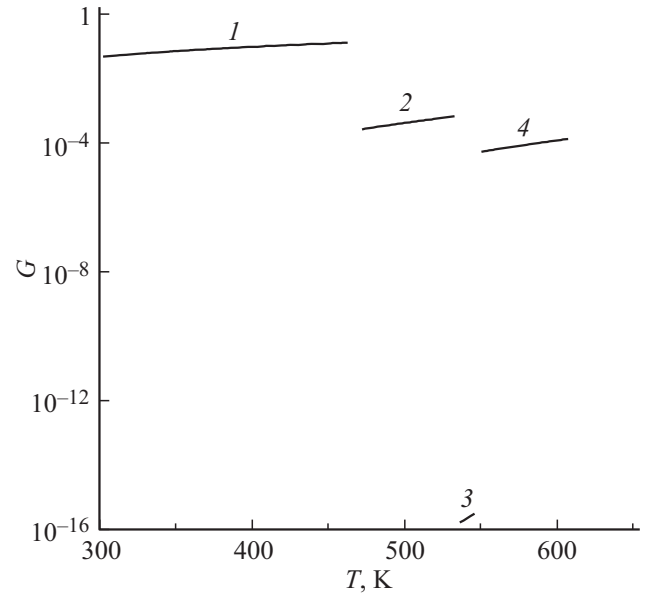
Figure 3. Temperature dependence of Green's function G of permittivity of ferroelectric $(Pb_{0.95}Sr_{0.05})(Zr_{0.53}Ti_{0.47})O_3$, calculated by equation (6) in temperature ranges *1−4* with corresponding activation energies $U = 0.08$, 0.33, 1.68 and 0.46 eV.

surfaces will be caused by thermal fluctuations. This results in the known temperature dependence of probability P of the ion transitions between potential energy surfaces with the transition activation energy ΔU:

$$P \propto \exp\left(-\frac{\Delta U}{kT}\right). \qquad (17)$$

Then, using the statistical approach described by Livshits and Pitaevky in [21] that is valid for thermo-activation processes and replacing the exponential factor by the Boltzmann constant, we get

$$G(T, T_i) = \Theta(T - T_i) \cdot \exp\left(-\frac{U_i}{kT}\right), \qquad (18)$$

where U_i are the energies of activation of the process flowing at. $T > T_i$.

It shall be noted that, like in our study, the Green's function method has been already used previously for simulation the dielectric response of ferroelectric material [22], and the Boltzmann probability factor was used to describe temperature and frequency dependence of dielectric susceptibility [23]. However, an explicit form of the temperature Green's function for a ferroelectric material, being a specific functional material, has not been defined before.

The calculated temperature Green's function for permittivity determined from the temperature dependence of permittivity using ceramic ferroelectric $(Pb_{0.95}Sr_{0.05})(Zr_{0.53}Ti_{0.47})O_3$ are shown in Figure 3.

As shown in Figure 3, in points whose temperatures correspond to the change in physical mechanism of permittivity activation process $(1 \rightarrow 2, 2 \rightarrow 3, 3 \rightarrow 4)$, Green's

function is broken. This occurs because the temperature distribution of activation energies is discrete herein. In case of continuous temperature distribution of the dielectric response activation energies, the temperature Green's function will presumably have another form. For processes in the ferroelectric phase, an attempt to find other physical mechanisms with other activation energies may be made to remove these break points because no lattice symmetry variation takes place here (rhombohedral or tetragonal for our samples). In the phase transition point, lattice symmetry changes to cubic and other physical mechanisms (dielectric response of a domain-free crystal) are responsible for thermo-activation processes. The model proposed herein addresses only the processes of some proximity on both sides of this point, rather than the direct thermo-activation mechanism of the phase transition point.

4. Conclusion

The study has established that introduction of Green's function into the temperature dependence of permittivity made it possible to describe this dependence by first-order differential equation at temperatures both below and above the ferroelectric phase transition temperature. Thus, an explicit form of the temperature Green's function for permittivity of the ferroelectric material was defined.

Statistical approach using the Boltzmann probability factor applied to the mathematical description of temperature dependence of permittivity of ferroelectric $(Pb_{0.95}Sr_{0.05})(Zr_{0.53}Ti_{0.47})O_3$ solid solution in the approximation of discrete temperature distribution of permittivity activation energies allowed the temperature Green's function of permittivity to be calculated and the temperature dependence to be plotted. The required permittivity temperature activation energies caused by the interaction between the domain and defect structures of the ferroelectric material were calculated by the permittivity activation/relaxation method.

Thus, the temperature Green's function method used for the permittivity of the ferroelectric material considering the experimental activation energies of its domain and defect structures gave an expression for the temperature dependence of permittivity in the form of the integral of convolution with the function of temperature exposure of the sample. The Green's function method may be used for the analysis and description of temperature dependences of permittivity of ferroelectric materials measured at various frequencies and amplitudes of an external electric field and in the presence of a shifting constant electric field. However, it is necessary to consider potential shift of phase transition temperature as well as variation of the activation energy spectrum of the domain and defect structures of ferroelectric materials.

Conflict of interest

The author declares that he has no conflict of interest.

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