Automated method of measuring the temperature dependences of the dielectric parameters of ferroelectrics with second kind phase transition

D V Ryabov¹, E A Pecherskaya², J V Shepeleva³ and R M Pecherskaya⁴
¹ Postgraduate, Penza State University, 40 Krasnaya Street, 440026, Penza, Russia
² Professor, Penza State University, 40 Krasnaya Street, 440026, Penza, Russia
³ Teacher, Penza State University, 40 Krasnaya Street, 440026, Penza, Russia
⁴ Professor, Penza State University, 40 Krasnaya Street, 440026, Penza, Russia
E-mail: pea1@list.ru

Abstract. An automated method of indirect measurements of the temperature dependences of the dielectric parameters of ferroelectrics is proposed. The basic of its principle – linear dependences of the inverse dielectric susceptibility of the temperature in the ferroelectric and paraelectric phases. The method allows to optimize the research process by reducing the number of measurement procedures, measuring in a limited temperature range (not exceeding the phase transition temperature) and dependences modeling in the range which is characterized by the greatest instrumental components of the measurements errors.

The dielectric parameters changes of ferroelectrics in the ferroelectric phase under the influence of influencing factors make their use in small capacitors, various converters, including the resistors for temperature measurement and control. Study of the dependence of relative permittivity $\varepsilon$, polarized $P$, dielectric loss tangent $\tan \delta$ on temperature $T$ allows to set the Curie temperature, and consequently, to identify operating temperature range of functional elements of electronics based on these materials. Getting the listed functional dependences is possible either by indirect measurements or the basic of empirical and theoretical modeling. The phenomenological theory of Landau – Ginzburg – Devonshire explains the difference in the behavior of the temperature dependences of the dielectric parameters of ferroelectric with the phase transition of the first and the second kind indicating need of the development of various techniques and methods of their measurements.

This working paper proposes an automated method of the empirical and theoretical modeling of the dielectric parameters of ferroelectrics with a second kind phase transition, for which according to the phenomenological theory the Curie – Weiss, the following relations are made:
where $E$ – electric field tension, $T_c$ – Curie temperature, $\varepsilon_0$ – electric constant.

Accordance with the expressions (1), dependences $\chi(T)$ in ferroelectric and paraelectric phases can be approximated by straight lines, while the slope in the ferroelectric phase is twice higher than in the paraelectric phase (figure 1). The essence of the proposed method consists of the sufficiently of the inverse dielectric susceptibility measuring at least for these values of temperature $T$ and then calculating the inverse dielectric susceptibility $\chi$ in the whole temperature range.

Thus, in the dielectric phase the function $\chi_s(T)$ is described by

$$
\chi_s(T) = a_s + b_s T,
$$

where $a_s$ has a sense of the back dielectric susceptibility at $T = 0^\circ C$, it always takes positive values; the coefficient $b_s$ determines the slope of the line. As in the paraelectric phase the function $\chi_s(T)$ is decreasing, $b_s$ always takes negative values, its measure unit is $\frac{1}{^\circ C}$.

In the paraelectric phase the slope $\chi_p(T)$ of the line is twice less than the slope $\chi_s(T)$ in the ferroelectric phase, which is described by

$$
\chi_p(T) = a_p + b_p T = a_p - 0.5 \cdot b_s T,
$$

where the coefficient $a_p < 0$ is numerically defined as the ordinate of the point of intersection of the line continuation $\chi_p(T)$ with the vertical axis. Similarly, the coefficient $b_p$ represents the slope of the line $\chi_p(T)$. Both direct lines $\chi_s(T)$ and $\chi_p(T)$ cross the X - axis at point $(T_c, 0)$.

The basic steps of the methodology of function $\chi(T)$ measurement in both phases are below:

1. Values of temperature are set up at which the measurement of reciprocal dielectric susceptibility $\chi(T)$ is conducted.
2. Measurements of $\chi(T)$ at temperatures are specified in paragraph 1. To avoid accidental errors it is advisable to conduct multiple measurements with its subsequent processing (averaging of measurements).
3. Analysis of the measurements, i.e. their assignment to a particular phase. Thus the measurement results can satisfy one of the three situations:

   a) all measurement results correspond to the ferroelectric phase. This decision is made, if the function $\chi(T)$ is decreasing at a given temperature range ($T_{i+1} > T_i$), i.e. with increasing temperature $T$ the reciprocal dielectric susceptibility $\chi$ values are decreasing ($\chi_{i+1} < \chi_i$);
b) all measurement results correspond to the paraelectric phase. It means that the function \( \chi(T) \) at the determined temperature range is increasing, i.e. with increasing temperature \( T_{i+1} > T_i \) the reciprocal dielectric susceptibility \( \chi \) values are increasing \( (\chi_{i+1} > \chi_i) \);

c) all measurement results correspond to both phases and the Curie temperature \( T_c \) belongs to the determined temperature range.

In the beginning of the temperature range the function \( \chi(T) \) is decreasing, and then it is increasing. If dependence \( \chi(T) \) changes the values from decreasing to increasing more than once, it means there are errors at measurement results that must be eliminated by carrying out repeated multiple measurements or it indicates that the monitoring ferroelectric has blurred phase transition and, as a result, the method of indirect measurement of dependences of dielectric parameters of ferroelectrics is not applied to it.

The situation described above (after errors eliminating and in the condition that ferroelectric parameters obeys to the Curie-Weiss law) are formalized by the following system:

\[
\begin{align*}
\text{if } \chi_{i+1} < \chi_i, T_{i+1} > T_i, \text{ the phase is ferroelectric}, \\
\text{if } \chi_{i+1} > \chi_i, T_{i+1} > T_i, \text{ the phase is paraelectric}, \\
\text{if } \chi_{i+1} < \chi_i, T_{i+1} > T_i, T_i \leq T_c \text{ and } \chi_{i+1} > \chi_i, T_{i+1} > T_i, T_i > T_c, \\
\text{at both phases},
\end{align*}
\]

where the temperature corresponds to the minimum reciprocal dielectric susceptibility (respectively to maximum relative permittivity).

4. Approximation of the results of dependence measurements \( \chi(T) \). Approximation of given results by a straight line can be accomplished by any known method. In this paper, the method of least squares was used, which is applicable due to its accuracy in terms of the problem being solved. Approximation algorithm is different for the situations described in paragraphs 3a), 3b) and for 3c).

For example, in cases where all measurement results correspond to the same phase by the number of measured points approximating line parameters \( a_s \) (or \( a_p \)), as and \( b_s \) (or \( b_p \)) are determined by formulas:

\[
b = \frac{n \sum_{i=1}^{n} T_i \cdot \chi_i - \sum_{i=1}^{n} T_i \sum_{i=1}^{n} \chi_i}{n \sum_{i=1}^{n} T_i^2 - \left( \sum_{i=1}^{n} T_i \right)^2}, \quad a = \frac{\sum_{i=1}^{n} \chi_i - b \sum_{i=1}^{n} T_i}{n},
\]

where \( n \) - number of measurements.

5. The Curie temperature \( T_c \) determination for ferroelectrics with the second phase transition is possible by the following ways: abscissa of reciprocal dielectric susceptibility \( \chi \) function of the temperature \( T \), corresponding to the minimum \( \chi \) (see figure 1); as abscissa of lines intersection point, approximating the function \( \chi(T) \) in the ferroelectric and paraelectric phases.

Algorithm in the base of this methodology allows to automate the measuring and data processing. The measurements were conducted using an automated measuring system, its structure and main metrological characteristics were presented in [1]. The results of research temporal instability of the dielectric parameters of ferroelectrics were shown in [2].
1 (shown by the continuous line) the dependence for triglitcinsulfat made with the developed program in Delphi is presented.

Figure 1. Temperature dependences of inverse dielectric susceptibility for triglitcinsulfat.

In this example the measurements were performed in the ferroelectric phase and modeling was carried out in the paraelectric phase. In addition to instrumental error, there is a methodological error. It is due to the difference of adiabatic conditions of experimental determination of the temperature dependences of dielectric parameters on the sinusoidal signal from isothermal condition in which obtained formulas are made according to the thermodynamic theory.

In relative unities the methodical error $\delta \chi$ is given by:

$$\delta \chi = \frac{16 \pi^2}{C^2 C_p} \frac{P^2}{\varepsilon_0}$$

where $C_p$ – the heat capacity of volume unit at constant polarization $P$; $C$ – Curie constant.

Based on known interactions with inverse dielectric susceptibility dielectric material parameters can be calculated. It was found that in ferroelectrics with heterogeneous structure, for example, in films type $\text{Ba}_x \text{St}_{1-x} \text{TiO}_3$ (BSTO) diffuse phase transition is observed and consequently, the Curie – Weiss law is not applied to them. This fact limits the application of the proposed measurement method. In turn, for modeling of the dielectric response of these ferroelectrics the Monte Carlo method was used in [3]. The proposed simulation method of the temperature dependences of dielectric parameters of ferroelectrics with a second kind phase transition allows to improve the research efficiency in 1.4 times by reducing measuring time and also it does not require temperature measurements in a wide range.

References

[1] Pecherskaya E A 2007 Measurement Techniques. 50 (10) 1101 - 1107
[2] Pecherskaya E A, Solov’ev V A, Metal’nikov A M, Varenik Yu V, Gladkov I M and Ryabov D V 2013 Semiconductors. 47 (13) 1720 - 1722
[3] Yudin P N, Nikol’sky M A and Zubko S P 2003 Technical Physics. 48 (8) 995 - 1000