Journal of the European Ceramic Society 21 (2001) 1345–1348

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Electrocaloric effect as a cause of dielectric loss

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Received 4 September 2000; received in revised form 23 October 2000; accepted 15 December 2000

Abstract

The difference between adiabatic and isothermal susceptibilities is caused by electrocaloric effect. Here we show how this effect contributes to dielectric dispersion in a sample of finite dimensions or in a non-homogeneous material. Maximum contribution to dielectric losses occurs at a frequency that is inversely proportional to the square of characteristic dimension. The first Fourier components of susceptibility in a non-pyroelectric material are proportional to the square of the amplitude of ac field. In a pyroelectric material with temperature dependent susceptibility a contribution to static polarisation arises due to alternating electric field. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Dielectric properties; Electrocaloric effect; Ferroelectric properties; Pyroelectric effect; Thermal properties

1. Introduction

Dielectric losses arise from different causes[1] and their frequency spectra are very different. Many studies have been devoted to relaxation processes connected with molecular motion or transport of free electric charge. The principal purpose of the present paper is to draw attention to dielectric losses that are connected with conduction of heat.

When periodically changing electric field in the sample, heat is periodically released or absorbed, for example due to electrocaloric effect[2–4] (ECE). If the sample is homogeneous and infinite (without any boundary), and the electric field is homogeneous as well, then in all points of the sample the temperature is the same and no heat flows from one point to another. In this case the process is adiabatic and no energy dissipation is present. However, if the sample is finite, then temperature at a given time and at a given point within the sample is generally different from the temperature outside of the sample. Similarly, temperature gradients arise in non-homogeneous materials, like polycrystals. In both last cases the heat flow is present and we can expect non-zero dielectric losses. From the above consideration it is obvious that dielectric dispersion properties depend on the sample thickness in the first case mentioned above and, in the second case, on characteristic dimensions of homogeneous regions in a non-homogeneous sample. We remark that the homogeneous regions can be domains, homogeneous crystallites in ceramics or microdomains connected with glassy dynamic properties of relaxors.

Although it is well known that difference between the adiabatic and isothermal values of susceptibility is caused by ECE,[2–4] little attention (as far as we know) has been paid in literature to the frequency law of dielectric dispersion due to this mechanisms. In the monograph[4] we can find formula (5.2.4) but it seems to us that it is little justifiable. One of the aims of this contribution is to derive this dispersion law.

In previous papers[5,6] the considered ECE is coupled only with the pyroelectric coefficient of spontaneous polarisation. In the present work we will discuss also the pyroelectric effect (PE) connected with temperature dependence of induced polarisation. It is clear that the electric polarisation induced by a biasing electric field plays a similar role as spontaneous polarisation in the discussed problem. The ECE coupled with induced polarisation is quadratic in the amplitude of ac electric field, nevertheless its contribution to polarisation is not only in the second harmonic but also in the first and zero harmonic. We do not consider dielectric hysteresis. It means that only reversible ECE is taken into account.[7]

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PII: S0955-2219(01)00015-2

All the results described in the present work depend on the thickness of a homogeneous sample or on the dimensions of homogeneous regions in a non-homogeneous sample.

The ECE is only one of the possible heat sources. Heat can be produced in the sample also in other ways, for example by means of mechanical oscillations induced by electromechanical effect. However, these effects will not be considered in the present treatment.

2. Theory

The relation between total polarisation P and electric field E in pyroelectric materials in linear approach has the form:

$$P = P_s(T) + \varepsilon_0 \chi(T) E \tag{1}$$

where P_s is spontaneous polarisation, ε_0 is vacuum permittivity and χ is isothermal susceptibility. The relation (1) describes a quasistatic isothermal process at constant temperature. When the process is not isothermal then the possible change of temperature $T = T_0 + \delta T$ has to be taken in account:

$$\chi(T) = \chi(T_0) + \frac{\partial \chi}{\partial T}\delta T \quad P_s(T) = P_s(T_0) + \frac{\partial P_s}{\partial T}\delta T. \tag{2}$$

We suppose that aside from the alternating electric field a biasing electric field is also present:

$$E = E_0 + E_1 \cos\omega t. \tag{3}$$

We insert Eqs. (2), (3) into Eq. (1) and obtain

$$\begin{aligned} P(T) = {} & P_s(T_0) + \varepsilon_0 \chi E_0 + \varepsilon_0 \chi E_1 \cos\omega t \\ & + (\Pi_s + \Pi_i E_1 \cos\omega t)\delta T \end{aligned} \tag{4}$$

where

$$\Pi_s = \left[\varepsilon_0 \left(\frac{\partial \chi}{\partial T}\right) E_0 + \frac{\partial P_s}{\partial T}\right], \quad \Pi_i = \varepsilon_0 \left(\frac{\partial \chi}{\partial T}\right). \tag{5}$$

The change of temperature is described by the equation for heat conduction, in which the ECE is the source of heat power:

$$\rho c_E \frac{\mathrm{d}T}{\mathrm{d}t} = \lambda \Delta T - T\left(\frac{\partial P}{\partial T}\right)_E \frac{\mathrm{d}E}{\mathrm{d}t}. \tag{6}$$

In the last equation, ρ is the mass density, c_E the heat capacity per unit of mass measured at constant electric field E, λ denotes the thermal conductivity of the material and Δ is the Laplacian. The quantity $\left(\frac{\partial P}{\partial T}\right)_E$ has the meaning of pyroelectric coefficient; pyroeffect (PE) is the inverse of ECE. It follows from the Eqs. (4)–(6) that

$$\begin{aligned} \frac{\mathrm{d}T}{\mathrm{d}t} = {} & a^2 \Delta T + \frac{T}{\rho c_E} \Pi_s E_1 \omega \sin\omega t \\ & + \frac{T}{\rho c_E} \Pi_i \frac{E_1^2}{2} \omega \sin 2\omega t \end{aligned} \tag{7}$$

where $a^2 = \lambda / \rho c_E$.

For simplicity we will consider the linear geometric case with the boundary condition

$$\delta T\left(\pm \frac{L}{2}\right) = 0. \tag{8}$$

The solution of the heat conduction equation with a periodic alternating source can be found in many monographs.[8] It has the form

$$\begin{aligned} \delta T = {} & f_1(x)\sin\omega t + g_1(x)\cos\omega t + f_2(x)\sin 2\omega t \\ & + g_2(x)\cos 2\omega t + \ldots \end{aligned} \tag{9}$$

where f, g are combinations of trigonometric and hyperbolic functions of coordinate x. If we inserted Eq. (9) into Eq. (4) we would obtain an expression for a local dielectric response in various points of the sample. Measured harmonic contribution to susceptibility is the value of this expression averaged over space coordinate. In the case of a homogeneous electric field it is sufficient to average the temperature. The space averaging gives

$$P = P_s + \varepsilon_0 \chi E_0 + P_{\mathrm{dyn}} + \varepsilon_0 E_1 (\chi' \cos\omega t + \chi'' \sin\omega t) + \ldots \tag{10}$$

In the above expression, the polarisation P_{dyn} is the dynamic contribution to "static" (zero harmonic) polarisation and χ', χ'' are real and imaginary part of the first-harmonic susceptibility. The explicit dependences of P_{dyn} and of the susceptibilities on material constants, electric field and dimensionless frequency $\Omega = \omega/\omega_0$ (with $\omega_0 = 2a^2/L^2$) are given by

$$P_{\mathrm{dyn}} = \frac{T}{2\rho c_E} \Pi_i \Pi_s (\beta_1(\Omega) - 1) E_1^2 \tag{11}$$

$$\chi' = \chi_s + \frac{T}{\varepsilon_0 \rho c_E}\left[\Pi_s^2 \beta_1(\Omega) + \Pi_i^2 \frac{E_1^2}{2} \beta_1(2\Omega)\right] \tag{12}$$

$$\chi'' = \frac{T}{\varepsilon_0 \rho c_E}\left[\Pi_s^2 \beta_2(\Omega) + \Pi_i^2 \frac{E_1^2}{2} \beta_2(2\Omega)\right]. \tag{13}$$

The functions $\beta_1(\Omega)$, $\beta_2(\Omega)$ introduced in the last equations are given by

$$\beta_1(\Omega) = \frac{\mathrm{sh}\sqrt{\Omega} + \sin\sqrt{\Omega}}{\left(\mathrm{ch}\sqrt{\Omega} + \cos\sqrt{\Omega}\right)\sqrt{\Omega}},$$
$$\beta_2(\Omega) = \frac{\mathrm{sh}\sqrt{\Omega} - \sin\sqrt{\Omega}}{\left(\mathrm{ch}\sqrt{\Omega} + \cos\sqrt{\Omega}\right)\sqrt{\Omega}}. \quad (14)$$

The term (11) shows that the dynamic process contributes to static (zero Fourier component) polarisation. It cannot be observed at ac permittivity measurements, but the evidence of this effect can be obtained by measuring the electric current induced by a change of temperature. We find an effect similar to dynamic PE measured on compositionally graded films.[9]

For the discussion of dielectric dispersion, it is useful to draw the graphs of $\beta_1(\Omega)$, $\beta_2(\Omega)$ (see Fig. 1) or to expand these functions in power series. For the case of low ω ($\Omega << 1$) we obtain

$$\beta_1 = 1 - \frac{\Omega^2}{30} + ..., \quad \beta_2 = \frac{\Omega}{6} + ... \quad (15)$$

In the case of high frequency the functions can be expanded as

$$\beta_1 = \frac{1}{\sqrt{\Omega}} + ..., \quad \beta_2 = \frac{1}{\sqrt{\Omega}} + ... \quad (16)$$

We remark that the function $\beta_2(\Omega)$ has a maximum at $\Omega_m \approx 5.08$ (i.e. $\omega_m \approx 10.16 \times a^2/L^2$) which corresponds to the maximum of χ'' when only quasi-spontaneous polarisation is present. The frequency $\omega_m/2$ corresponds to the maximum of χ'' if only the induced polarisation plays an important role. In the low frequency limit we have $\beta_1 \rightarrow 1$, $\beta_2 \rightarrow 0$ and, in agreement with expectation, $\chi' \rightarrow \chi$ (isothermal susceptibility) and $\chi'' \rightarrow 0$. In the region of very high frequencies the expression for χ' converges to adiabatic susceptibility χ_{ad} known in classical thermodynamics and χ'' approaches zero. If, for example, $\Pi_i = 0$, then it follows from the above discussion that

$$\frac{\chi'(\omega) - \chi_{ad}}{\chi - \chi_{ad}} = \beta_1, \quad \frac{\chi''(\omega)}{\chi - \chi_{ad}} = \beta_2. \quad (17)$$

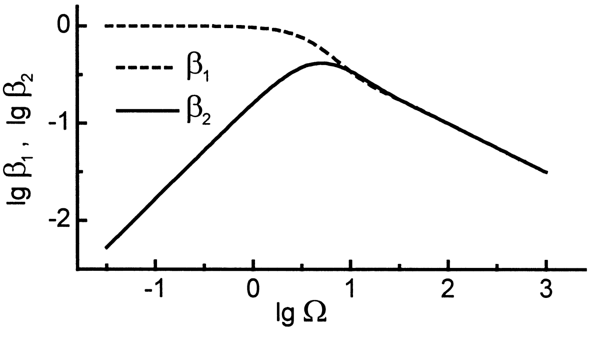

Fig. 1. Reduced real and imaginary parts of susceptibility due to ECE [β_1, β_2, see (17)] as functions of dimensionless frequency Ω.

This means that the graphs in Fig. 1 describe the frequency dependences of real and imaginary part of reduced susceptibility. Similar relations hold for $\Pi_s = 0$, but with the replacement $\Omega \rightarrow 2\Omega$.

3. Examples

At the beginning, we choose some frequently studied ferroelectric materials: TGS [$(NH_2\ CH_2\ COOH)_3\ H_2\ SO_4$], KDP [$KH_2\ PO_4$] and $BaTiO_3$ for which we will discuss the magnitudes of quantities studied in the previous section. Material constants we will use here are summarised in Table 1.

The dynamic contribution to static polarisation has not yet been studied. In the non-pyroelectric phase, the limit value of P_{dyn} for high frequencies is given by the relation [see (5), (11)]:

$$\frac{P_{dyn}}{E_0 E_1^2} \cong \frac{T\varepsilon_0^2}{2\rho c_E}\left(\frac{\partial\chi}{\partial T}\right)^2. \quad (18)$$

First, we find the value of the right-hand side of Eq. (18) in the case that temperature of the sample is one degree above the Curie temperature. Supposing the Curie–Weiss law for susceptibility and using numerical values of Table 1 we obtain the value of the order of 10^{-19} for TGS and for KDP and the value of the order of 10^{-16} for $BaTiO_3$. We can also compare the values of P_{dyn} and P_{ind} induced by the same static field E_0. For example, if we chose the amplitude $E_1 \cong 10^3$ V/m we obtain $P_{dyn}/P_{ind} \cong 10^{-4}$ for $BaTiO_3$. If we wanted to choose the magnitude of the field in such a way that $P_{dyn}(T = T_C + 1\ K) \cong P_s\ (T = T_C - 1\ K)$ we would have to choose $E_0\ E_1^2 \cong 10^{15}$ V/m for $BaTiO_3$, since P_s is about 10^{-1} C/m^2.

Table 1
Material constants[a]

Material	T_c (°C)	Curie constant C(K)	Specific heat (J/kg/K)	Molar heat (J/mol/K)	Molar mass (kg/mol)	Density (kg/m^3)	dP_s/dT (C/m^2/K)
TGS	49	3.2×10^3		313	3.067×10^{-1}	1695	3×10^{-3}
KDP	−150	3.3×10^5		63	1.349×10^{-1}	2338	1.15×10^{-1}
$BaTiO_3$	120	1.5×10^5	~500			6100	1.2×10^{-3}

[a] Values taken from Refs. 3 and 4, dP_s/dT has been determined from a graph.[3]

The maximum contribution to susceptibility due to PE induced by bias field E_0 (in the paraelectric phase) can be estimated from the formula [see (5), (13)]

$$\chi'' \cong \frac{T}{\rho c_{\mathrm{E}}}\left(\frac{\partial\chi}{\partial T}\right)^2 \varepsilon_0 E_0^2. \tag{19}$$

If the dispersion of dielectric susceptibility is measured for example at a biasing field of the order of 10^6 V/m then the contribution of ECE to susceptibility is about of 10^7 for $BaTiO_3$ and 10^3 for TGS, KDP. If the bias field E_0 is zero, then the PE is induced only by alternating electric field characterised by amplitude E_1. In this case an equation similar to the Eq. (19) holds but in this formula E_0 is replaced by E_1.

In the above part of this section we have been dealing with ferroelectrics in the paraelectric phase. Now, we will pay attention to the ferroelectric phase and the contribution of induced *PE* will be not taken in account. The magnitude of the true *PE* contribution can be estimated from the following equation

$$\chi'' \cong \frac{T}{\varepsilon_0 \rho c_E}\left(\frac{\partial P_{\mathrm{s}}}{\partial T}\right)^2. \tag{20}$$

This formula gives the dielectric losses χ'' of the order of 10^2 for TGS, 10^5 for KDP and 10 for $BaTiO_3$ in the vicinity of T_C.

At the end we determine a typical numerical value of frequency $\omega_{\mathrm{m}} \cong 10 \times a^2/L^2$ at which the dielectric losses reach maximum. Typical values $\rho c_E \cong 10^6$ J/(m$^3\times$K) and $\lambda \cong 10$ W/(m$\times$K) provide $a^2 \cong 10^{-5}$ m^2/s. If the sample has a thickness of 1 mm then the frequency at maximum losses is about 100 Hz. If, for example, crystallites in a polycrystal have linear size of 1μm then the dielectric dispersion connected with heat conductivity is in the region of 10^8 Hz.

The studied effect in materials mentioned above is small, due to relatively high coefficient $\rho c_E/T$. A more pronounced effect could be expected at low temperatures in materials with a low phase-transition temperature. As an example of such materials lithium–thallium tartrate (LTT) may be chosen which has a phase transition temperature of about 12 K. An essential difference between adiabatic and isothermal susceptibility observed even in paraelectric phase[10] suggests that this material could have good properties for testing the effect discussed. However, the absence of data on heat capacity of this material prevented us from calculating the numerical values of the expressions considered.

4. Conclusion

The electrocaloric effect manifests itself in the dielectric dispersion measured for a sample of finite dimensions or for a sample of a non-homogeneous material. The dispersion law of the above mentioned contribution to dielectric dispersion was determined for the case of simple geometry (Fig. 1). The frequency region where dielectric loss attains its maximum depends on the thickness of the sample or on the characteristic size of non-homogeneities ($\omega_{\mathrm{m}} \cong 10 \times a^2/L^2$). The value of the maximum of dielectric losses is about one half of the difference between the isothermal and adiabatic values of susceptibility for our simplified model.

We have taken into account three types of pyroelectric effect: the true effect connected with spontaneous polarisation, the effect induced by external bias field and the effect induced by an ac field. The last contribution to susceptibility is quadratic in amplitude of ac field and can become observable at very low temperatures on materials with low-temperature phase transitions. Interesting may be the conclusion that the alternating electric field contributes also to the "static" polarisation.

Our calculations are based on the assumption of linear dielectric properties. Therefore the non-linear dependences on the field in the resulting formulae are of purely dynamic origin.

Acknowledgements

Financial support of the Grant Agency of the Czech Republic (project Nos. 202/98/1282 and 202/00/1187) is gratefully acknowledged.

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