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Dielectrics under Electric Field

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Abstract

The chapter first gives a brief introduction on conduction, polarization, dissipation, and breakdown of dielectrics under electric field. Then, two of electric field-related applications, dielectrics for electrical energy storage and electrocaloric (EC) effect for refrigeration are discussed. Conclusion and perspectives are given at last.

Keywords: dielectrics, electrical energy storage, electrocaloric refrigeration

1. Introduction

Dielectrics are materials that can be polarized by an applied electric field. Polarizability is the essential property for dielectrics. The term is closely related to insulator. In electrical phenomena, insulator is commonly used especially in electronic engineering and electrical engineering, that is, in electronic packaging printed circuit board, electrical wire, high voltage system, and so on. It has a longer history than "dielectrics." The main property of an insulator is to prevent the flow of current when it is not desired. This means that insulator must have low electrical conductivity and can resist breakdown under high electric field. Physically, insulator is a subgroup of dielectrics because of the existence of polarization. And dielectrics can include insulator, semiconductor, and other materials with polarizability. Nevertheless, poor insulation could screen the polarizability of dielectrics under electric field, which makes the polarization hard to be "seen" by electrical measurement. And in most cases, poor insulation makes dielectrics useless. Thus, insulating property is commonly expected for dielectrics. Although insulating dielectrics has been applied for long time, the study on the area is continually progressing, that is, using cold sintering processing [1], developing broadband dielectric spectroscopy [2, 3], optoelectrical effect [4, 5], and multiferroics [6].

The subgroups of insulating dielectric include piezoelectric, pyroelectric (electrocaloric), ferroelectric, and multiferroic. Electrocaloric is the reverse effect of pyroelectric. Because of interesting physics and technological importance, there are enormous books dedicated to these areas.

Thus, we only introduce the fundamental phenomena of dielectric under electric field in the chapter. Then, two state-of-the-art applications for dielectrics are included, which are electrical energy storage [7, 8] and electrocaloric refrigeration [9–11]. We show that electric field plays a critical role in both applications.

2. Dielectrics under electric field

2.1. Conductivity

The main properties for dielectric under electric field are conduction, polarization, dissipation, and breakdown. Although normally a dielectric material is a good insulator, there are still some charge carries flowing through the whole material under electric field, which is called leakage current. Under a direct current (dc) field, the current could be a constant for a material. If the detected current is I when a voltage U is applied to a material, the conduction G of the materials is I/U. If the material has a regular plate structure with surface A and thickness t, the conductivity σ of the material is:

$$\sigma_{DC} = \frac{I}{U}\frac{d}{A} \tag{1}$$

The property can also be expressed by bulk resistivity ρ, which is reciprocal of conductivity:

$$\rho = \frac{U}{I}\frac{A}{d} \tag{2}$$

Both conductivity and resistivity are electrical properties for all materials, that is, conductor, semiconductor, and insulator. Because of different mechanism of conduction, there is a huge gap between conductivities of dissimilar materials, which has been well understood by energy band theory. The conductivity of a conductor could be big as 10^9 S/m; the conductivity of good insulating dielectrics could be small as 10^{-18} S/m.

The DC conductivity in dielectrics is related to the hopping transition of defect charge carries, and thus, it is strongly temperature dependent:

$$\sigma_{DC} = \sigma_0 e^{-Ea/k_B T} \tag{3}$$

Here k_B is Boltzmann constant, T is temperature, and E_a is thermal activity energy. By fitting experimental date with Eq. 3, the fitted activation energy E_a gives information about current carriers.

The conductivity of dielectrics under alternative current (ac) field is related to the imaginary part of dielectric constant, which is introduced in Section 3. Since insulating is prerequired for dielectrics, the conductivity is less considered in the study of dielectrics. However, in some cases, it is crucial for dielectric properties [7].

2.2. Polarization

Polarization is the unique electrical properties for dielectrics, depending on which concept is defined. There are diverse types of polarization, that is, electronic polarization, ionic polarization, orientation polarization, interface polarization, spontaneous polarization, and so on.

In dielectrics, if one positive charge $+q$ and the corresponding negative charge $-q$ are separated by a distance d, an electric dipole is produced with magnitude $p = qd$. It is a vector with direction from negative charge toward positive charge. This dipole could be the one induced by electric field like in electronic polarization or ionic polarization, but it could also be one permanent like in polar molecules and ferroelectrics. After introducing electric dipole, the polarization in a material can be defined as the sum of individual dipole moments p divided by volume V of the material:

$$P = \frac{\sum p}{V} \tag{4}$$

From this definition, we can see that the magnitude of polarization equals to the surface charge density, in fact depending on which the spontaneous polarization of ferroelectrics is measured by Sawyer-Tower electrical bridge.

For all dielectrics under electric field, the mutual shifts of nuclei and electrons induce electronic polarization, which occur within very short time, that is, 10^{-14}–10^{-16} s. Electronic polarization exists for all materials. In ionic crystals, the relative separation of cation and anion is induced by electric field, which is called ionic polarization. The ionic polarization also builds at a very short time, that is, 10^{-12}–10^{-13} s.

In some molecules, the center of positive charge and negative charge does not coincide, which is called polar molecule. In polar molecules, permanent dipoles exist and can somehow rotate under electric field. In thermal equilibrium state, the dipoles randomly orient, and thus, there is no net polarization. When an external electric field applied, these dipoles align to it in some extent. Thus, orientation polarization is induced. The response time of these permanent dipoles changes from material to material, that is, 10^{-2}–10^{-12} s. For example, in water at 300 K, the response time is around 5×10^{-11} s.

Interface polarization, which is also called space charge polarization, builds at interface between two or more heterogeneous medium, i.e., between electrodes and dielectrics, between different dielectrics, between grain boundaries in ceramics, etc. The electrons, ions, and other defects trap at these sites, which have a slow response toward AC electric field. The response time varies from case to case, that is, 10^7–10^{-6} s.

In ferroelectrics, from high-temperature paraelectric phase to low-temperature ferroelectric phase, a permanent dipole is present because of symmetry break without electric field, which is called spontaneous polarization. The spontaneous polarization can be reversed by an external electric field, which makes ferroelectrics a smart material with lots of interesting properties.

In general, the relation between polarization P and electric field E follows [12]:

$$P = \varepsilon \chi E + \text{higher terms in E} \tag{5}$$

where ε_0 is the permittivity of free space, and χ is the susceptibility. The equation does not include spontaneous polarization of ferroelectrics. For most dielectrics, the first term is dominant. Higher terms are commonly omitted except for nonlinear dielectrics.

From Eq. (5), we can see that χ represents the polarizability. But the most widely used parameter is dielectric permittivity ε:

$$\varepsilon = \frac{D}{E} \tag{6}$$

Here D is electric displacement. And in engineering, the relative dielectric permittivity $\varepsilon_r = \varepsilon / \varepsilon_0$, or more generally called dielectric constant, is used because ε is too small in SI unit.

For a capacitor, electric displacement equals to the surface charge density. Assume a planar capacitor consisting of two parallel electrodes with surface S and distance d. When a voltage V is applied and there is no dielectric material between electrodes, the surface charge density $Q_0 = \varepsilon_0 V/t$ appears according to Gauss' law. If a dielectric material with susceptibility χ is filled in between two electrodes, it contributes surface charge density $Q_d = P = \varepsilon_0 \chi V/t$. As a result, the total surface charge equals the sum of two: $Q = \varepsilon_0 (1 + \chi) V/t$. As a result, combining Eqs. (5) and (6), we can get the relation between relative dielectric permittivity ε_r and susceptibility χ:

$$\varepsilon_r = (1 + \chi) \tag{7}$$

Both ε_r and χ are parameters describing the polarizable property of dielectrics under electric field.

2.3. Dielectric dissipation

Under AC electric field, there are two types of current flowing through a capacitor, the so-called polarization current I_P and conduction current I_R. In this case, dielectric constant is expressed by a complex number:

$$\varepsilon_r = \varepsilon_r^{'} - i\varepsilon_r^{''} \tag{8}$$

The first term is still called dielectric constant, while the second term is called the imaginary part of dielectric constant. When an AC electric field $E = E_0 e^{i\omega t}$ (E_0 is a constant, $\omega = 2\pi f$, and f is frequency) applied to a dielectric material, its equivalent circuit can be expressed as shown in **Figure 1**. The current I_P flows through capacitance saving energy, while the current I_R flows through resistance dissipating energy. If the surface of the capacitor is S and thickness of it is d, the polarization current is $I_P = i\omega \varepsilon_0 \varepsilon_r^{'} S E_0 e^{i\omega t}$, while conduction current is $I_C = \omega \varepsilon_0 \varepsilon_r^{''} S E_0 e^{i\omega t}$, which means that the phase of polarization current advances applied electric field by 90° while conduction current keeps the same phase as that of applied electric field. The ratio between the two defines dielectric dissipation, also called dielectric loss, or loss tangent $tan\delta$:
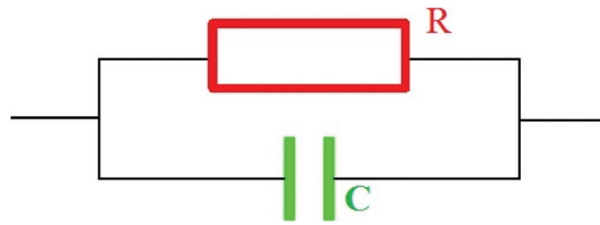
Figure 1. Equivalent circuit for a dielectric capacitor.

$$\tan\delta = \frac{I_C}{I_P} = \frac{\varepsilon_r''}{\varepsilon_r'} \tag{9}$$

The conduction current is normally harmful for applications. Thus, there are lots of work on how to decrease dielectric loss.

2.4. Breakdown

Under very high electric field, the conduction current increases significantly. Finally, a dielectric enters a high conduction nonequilibrium state, which is called breakdown. Mathematically, it can be expressed as:

$$\frac{dI}{dU} \to \infty \ \ \text{or} \ \ \frac{dU}{dI} \to 0 \tag{10}$$

If a material with thickness d and breakdown at voltage U_B, the breakdown field of the material is U_B/d, which changes for material to material, that is, ~MV/m for ceramics, ~10 MV/m for ceramic thin film, and ~100 MV/m for polymers. The breakdown field is also called dielectric strength. For most materials, the breakdown is normally induced by pores, impurities, and other defects because of electric inhomogeneities. Thus, processing control is critical for obtaining a high breakdown field. Covalent compounds commonly have larger breakdown field than ionic compounds. So far, 1.2 GV/m breakdown field gotten in SiO_2-BaO-B_2O_3-Al_2O_3 glass perhaps is the highest value for dielectrics [13].

Except electric field, heat also induces breakdown. Thermal breakdown occurs when a material cannot efficiently dissipate the produced heat. In many cases, a breakdown is companied by both electric and thermal breakdowns. Breakdown also has randomicity, which can be described by Weibull distribution.

3. Dielectric relaxation

One essential problem in dielectrics is the response time of a dielectric material toward to a periodic external electric field. When polarization delays with respect to an external oscillating electric field, so-called dielectric relaxation occurs. Dielectric relaxation may happen at an intrinsic time (so-called characteristic relaxation time) for a particular polarization, so it can help to identify the specific polarization mechanism. It also induces significant energy loss (or,

in some case, energy conversion like oscillator, and so on), which is very important for engineering applications. Because of mutual inverse between time t and frequency f ($f = 1/t$), the dielectric relaxation is more conventionally studied in frequency domain by dielectric spectroscopy technology. The typical impedance analyzer (or also called LCR meter) usually performs from few Hz to 10 MHz. From MHz to GHz, vector network analyzer can finish the job. For higher frequency, more sophisticated spectroscopy technologies may be applied, that is, waveguided system, THz time-domain spectroscopy, and so on. However, these methods in many cases are in-house and not commercialized.

For clarifying a relaxation mechanism, different electric parameters may be applied, that is, complex dielectric constant $\varepsilon^* = \varepsilon' - i\varepsilon''$, complex impedance $Z^* = Z' - iZ''$, complex admittance $Y^* = Y' - iY''$, and complex electric modulus $M^* = M' - iM''$. Electric modulus is the reciprocal of dielectric permittivity $M^* = 1/\varepsilon^*$, corresponding to the relaxation of electric field in a material when electric displacement remains constant.

3.1. Debye relaxation

Debye relaxation equation is the most simple and elegant mathematic equation so far used to describe relaxation phenomenon:

$$\varepsilon_r = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + i\omega\tau} \tag{11}$$

Here ε_s and ε_∞ are the static and high-frequency dielectric permittivity, respectively. τ is the characteristic relaxation time. This relaxation was first introduced by physicist Peter Debye for noninteracting dipoles in an alternating external electric field with unique relaxation time. In complex plane, ε'-ε'' plots an ideal semicircle for Debye relaxation. Because of the mutual interactions of dipoles in real materials, the semicircle changes to an ellipse, which is called Cole-Cole circle. The relaxation is called Cole-Cole relaxation, which is described by the following equation:

$$\varepsilon_r = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + (i\omega\tau)^{1-\alpha}} \tag{12}$$

Here exponent parameter α takes a value between 0 and 1. When $\alpha = 0$, the Cole-Cole equation reduces to Debye equation. Cole-Cole relaxation is seen in many polymers.

3.2. Maxwell-Wagner relaxation

Maxwell-Wagner relaxation is because of electric inhomogeneous of materials, that is, interface between dielectrics and electrodes, grain boundaries, and so on. It is usually represented by a two-layer equivalent electric circuit as shown in **Figure 2**.

The dielectric permittivity of Maxwell-Wagner relaxation can also be expressed as Debye relaxation style:
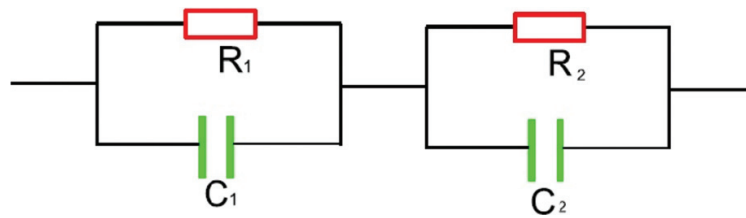
Figure 2. A two-layer equivalent electric circuit for Maxwell-Wagner relaxation.

$$\varepsilon_r = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + i\omega\tau} - i\frac{\sigma}{\omega} \qquad (13)$$

if we set the following parameters: $C_0 = \varepsilon_0 S/d$; $\varepsilon_\infty = C_1 C_2/[C_0(C_1+ C_2)]$; $\varepsilon_0 = [R^2_1C_1 + R^2_2C_2]/[C_0(R_1+ R_2)^2]$; $\delta = 1 /[C_0(R_1+ R_2)]$; $\tau = R_1R_2(C_1+ C_2)/(R_1 + R_2)$. It is obvious that the relaxation would be observed when there is a significant difference between two resistances. In **Figure 2**, each RC unit represents an ingredient in studied dielectrics, that is, grain, grain boundary, or electrode interface. To separate these different ingredient relaxations, plotting date in both impedance and electric modulus is commonly applied. The impedance of the circuit is as follows:

$$Z' = \frac{R_1}{1 + (\omega R_1 C_1)^2} + \frac{R_2}{1 + (\omega R_2 C_2)^2} \qquad (14)$$

$$Z'' = R_1 \frac{\omega R_1 C_1}{1 + (\omega R_1 C_1)^2} + R_2 \frac{\omega R_2 C_2}{1 + (\omega R_2 C_2)^2} \qquad (15)$$

The electric modulus of the circuit is as follows:

$$M' = \frac{C_0}{C_1}\frac{(\omega R_1 C_1)^2}{1 + (\omega R_1 C_1)^2} + \frac{C_0}{C_2}\frac{(\omega R_2 C_2)^2}{1 + (\omega R_2 C_2)^2} \qquad (16)$$

$$M'' = \frac{C_0}{C_1}\frac{\omega R_1 C_1}{1 + (\omega R_1 C_1)^2} + \frac{C_0}{C_2}\frac{\omega R_2 C_2}{1 + (\omega R_2 C_2)^2} \qquad (17)$$

From these equations, we can find that the impedance normalization highlights big resistance relaxation, while the electric modulus normalization highlights small capacitance relaxation. It should be noted that the equivalent electric circuit changes from case to case, and more complex circuit model may be applied for treating dielectric behavior of Maxwell-Wagner relaxation [7]. Here, we only give the simplest case in which there only exist two dielectric ingredients.

3.3. Universal dielectric relaxation

Universal dielectric relaxation is also called universal dielectric response. To have a better understanding of it, we first introduce complex conductivity σ.

$$\sigma = \sigma_0 + \sigma^{'} - i\sigma^{''} \qquad (18)$$

Here, σ_0 is the DC conductivity and σ' is the AC conductivity. The existence of σ_0 in the formula is an open question. The relationship between σ_0 and σ can be looked as: $\sigma_0 = \lim\sigma'$ as $f{\rightarrow}0$. Generally, from dielectric measurement, the AC conductivity is calculated by:

$$\sigma = \varepsilon_0\varepsilon^{''}\omega \qquad (19)$$

For many dielectrics, A. K. Jonscher found that the frequency-dependent AC conductivity satisfies the following exponent relation [14]:

$$\sigma = A\omega^n (0 < n < 1) \qquad (20)$$

which is called universal dielectric relaxation. If $n = 1$, it is called nearly constant loss. Universal dielectric response is understood as ion hopping effect. But, electric heterogeneity can also induce this behavior at high frequency. Nearly constant loss happens at sufficiently low temperature or high frequency, and the origin was understood as vibration relaxation or off-center relaxations swear out into a broad distribution [15].

So far, to identify a specific relaxation is still not easy. In most cases, the characteristic relaxation time constant τ is significantly influenced by temperature, which can be expressed as an exponent function of temperature:

$$\tau = \tau_0 e^{E_a/k_B T} \qquad (21)$$

Here E_a is activation energy, k_B is Boltzmann constant, and T is temperature. The activation energy reflects the energy needed to hop from one potential well to another for dipoles. Thus, it gives the information for possible relaxation mechanism.

4. Dielectrics for energy storage

Energy and environment protection are the challenges we are facing. Effective storing energy, reducing loss, and environment pollution are the hot topics for researchers. Electrical energy perhaps is the most convenient energy form to be applied. For applications in mobile electronic devices, stationary power systems, and hybrid electric vehicles, electric energy must be stored first.

There are many ways to storage electrical energy such as battery, supercapacitor, and dielectric capacitor. Battery has very high energy storage density (10–300 W·h/kg), but the power density is very low (<500 W/kg) and hazard for environment. Supercapacitor has average energy storage density (<30 W·h/kg) and power density (10–10^6 W/kg). But it has shortages such as complex configuration, low operating voltage, large leakage, and short recycling period. In comparison, dielectric capacitor has the highest power density (10^8 W/kg), broad operating temperature, fast charging and discharging, and long recycling period. The only disadvantage is low energy storage density (10^{-2}–10^{-1} W·h /kg). Thus, there is a crucial need for dielectric capacitor with improved energy storage density [7].
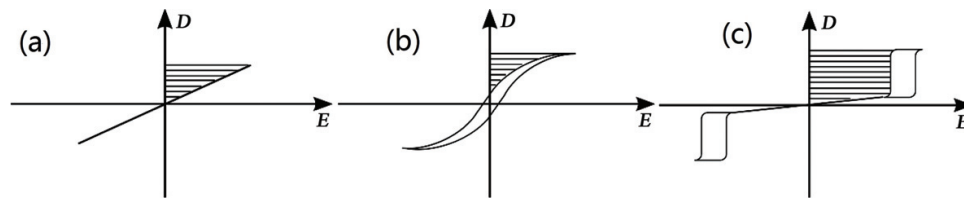
Figure 3. Electric displacement versus electric field for linear dielectrics (a), ferroelectrics (b), and antiferroelectrics (c).

The energy stored in a dielectric material under an electric field can be expressed by the shadow area in **Figure 3** in which different relationships between electric field E and electric displacement D are presented. The energy storage density J is defined as the stored energy per unit volume:

$$J = \int E \mathrm{d} D \tag{22}$$

According to Eq. (22), for linear dielectrics as shown in **Figure 3(a)**, energy storage density is proportional to the product of permittivity and the square of the applied electric field:

$$J = \frac{1}{2} \varepsilon_0 \varepsilon_r E^2 \tag{23}$$

Thus, high dielectric permittivity and high breakdown field are highly desirable for the dielectrics used in energy storage devices. For linear dielectrics, a very high electric field must be applied to obtain large J. As shown in **Figure 3(b)**, ferroelectrics have much higher polarization so more energy can be stored at low field. But because of quick saturation of polarization under high electric field, increasing electric field does not contribute much energy density. At the same time, ferroelectrics exhibit significant hysteresis which corresponds to energy loss. The antiferroelectrics, as shown in **Figure 3(c)**, have a very large area between D and E because of zero remnant polarization; thus, it can store much more energy than linear dielectrics and ferroelectrics. It is therefore indispensable for high-energy and high-power capacitive storage system [16]. However, few materials have antiferroelectric properties like $PbZrO_3$, $PbHfO_3$, and $NaNbO_3$. $PbZrO_3$ is probably the only choice, but it contains environmental hazard element lead.

4.1. Single-phase materials for energy storage

As we have stressed, ferroelectric and antiferroelectric materials have better energy storage density. However, lots of them are inorganic materials prepared by solid reaction method. Various defects, like pores, impurities, and vacancies are produced during sintering, deteriorating the dielectric strength. For instance, the theoretical antiferroelectric-ferroelectric phase transition happens at 2.2×10^7 V/m for $PbZrO_3$, but the breakdown field for $PbZrO_3$ ceramic is about 1×10^7 V/m. The typical energy storage density for ferroelectric ceramic is around 1 J/cm³. If materials are prepared in thin-film forms, the energy storage density could increase 10–50 times. However, reducing thickness also means reducing weight or volume, an impractical method for large energy storage application. The configuration of multilayer ceramic capacitor

may be employed in this case. On contrary to ceramics, polymers have high breakdown field (10^8 V/m), although the dielectric constant is very small (<10). The energy storage density of polymer is around 10 J/cm^3. In addition, polymers are flexible, which can be used in flexible electronics.

It is should be noted that many already developed dielectrics may have super electric energy storage density. For instance, BiFeO$_3$-SrTiO$_3$ is a multiferroic system [17]. Recently, it was shown that BiFeO$_3$-SrTiO$_3$ thin film can get an ultrahigh energy density of ~51 J cm^{-3}. The breakdown field of the film is 360 MV/m, which is comparable with polymer dielectrics [18].

4.2. Ceramic-polymer composites for energy storage

Combining high dielectric constant ceramic with high breakdown field polymer to prepare composites has been extensively studied for energy storage, which is usually called 0–3 composites because zero-dimensional ceramic particles embedded in three-dimensional polymer matrix.

By filling ceramic particles with dielectric constant ε_f with volume fraction φ in polymer matrix with dielectric constant ε_m, the effective dielectric constant ε_{eff} of 0–3 composite increases with the increase in φ. Its value is in between parallel and series connections of the two phases, which is well known as Wiener limits:

$$\left[\varphi\varepsilon_f^{-1} + (1-\varphi)\varepsilon_m^{-1}\right]^{-1} \leq \varepsilon_{eff} \leq \varphi\varepsilon_f + (1-\varphi)\varepsilon_m \tag{24}$$

There are enormous works of 0–3 composites. For example, in BaTiO$_3$-polymer composites, filling 40%, 70%, 70%, 40%, and 70% of BaTiO$_3$ in epoxy, PVDF, polystyrene, PVC, and polyamide, the corresponding dielectric constant is 44 [19], 152 [20], 100 [21], 18 [22], and 80 [23], respectively. It is obvious that dielectric constant limited increase although high volume of ceramic particle is filled in polymer. We propose that this is probably because polymer matrix normally has higher resistivity than ceramic filler [7]. By filling high-resistivity ceramic fillers in polymer matrix, a great increasing of dielectric constant may be achieved. As a result, the overall energy storage density can also be improved.

5. Dielectric for refrigeration

Electrocaloric (EC) effect is defined as the isothermal entropy or adiabatic temperature change of a dielectric material when an electric field is applied or removed. It could be used for efficient refrigeration and for the conversion of heat flows into electrical power. As the reverse effect of pyroelectric, EC effect has been explored before but the conclusion was that it was too small for practical applications. Recent interest on it is partly intrigued by the findings of 12 K temperature change in PbZr$_{0.95}$Ti$_{0.05}$O$_3$ [24] and more than 12 K temperature change in P(VDF-TrFE) (55/45 mol %) [25]. More importantly, EC refrigeration has been paid great attention for its environment-friendly and solid-state characters. Nowadays, because of highly integrated, a chip may be comprised of thousands of components, which results in large heat generation.

The future of IC may rely on the development of on-chip refrigeration technology, particularly with solid-state character. EC cooler is greatly expected for on-chip refrigeration.

5.1. Characterization of electrocaloric effect

At here, we first derive the equation for evaluating EC effect. The thermodynamic Gibbs free energy G of dielectrics under constant stress condition can be expressed as:

$$G = U - TS - EDV \tag{25}$$

where U is the internal energy of the system, T and S are temperature and entropy, E and D are electric field and electric displacement, and V is the volume of the system. The differential form of the Gibbs free energy is:

$$dG = -VDdE - SdT \tag{26}$$

According to Maxwell relation, we have

$$\left(\frac{\partial S}{\partial E}\right)_T = V\left(\frac{\partial D}{\partial T}\right)_E \tag{27}$$

Thus, the isothermal entropy change ΔS and adiabatic temperature change ΔT are as follows:

$$\Delta S = -V\int_{E_1}^{E_2} \left(\frac{\partial D}{\partial T}\right)_E dE \tag{28}$$

$$\Delta T = -\int_{E_1}^{E_2} \frac{T}{\rho C_P}\left(\frac{\partial D}{\partial T}\right)_E dE \tag{29}$$

in which ρ and c_p are density and specific heat capacity of material. These equations are applied to estimate ΔS and ΔT according to the experimental data of temperature dependency of dielectric displacement under constant electric field, which is commonly called indirect method.

It is obvious that the EC effect can also be directly measured by modified differential scanning calorimeter, which has not yet commercialized. Thus, the main method is still the indirect method.

Recently we find that in fact it is possible to evaluate EC temperature variation at paraelectric phase by a simple equation because of dielectric nonlinear behavior of ferroelectric at paraelectric phase [10]:

$$\Delta T = \frac{1}{2}\frac{\varepsilon_0}{\rho C_P}\frac{\beta^3}{\gamma}T(T - T_0)^2\left\{\frac{1}{\varepsilon_0\beta(T - T_0)} - \frac{1}{\left[\varepsilon_0{}^3\beta^3(T - T_0)^3 + 3\varepsilon_0{}^3\gamma E^2\right]^{1/3}}\right\} \tag{30}$$

where T_0 is Curie temperature, β is related to the Curie-Weiss law of $\varepsilon_r(T) = 1/[\varepsilon_0\beta(T-T_0)]$, γ is related to the dielectric nonlinearity under electric field:

$$\varepsilon_r(E) \approx \frac{\varepsilon_r(T,0)}{\left\{1 + 3\gamma[\varepsilon_0\varepsilon_r(T,0)]^3 E^2\right\}^{1/3}} \tag{31}$$

In fact, it is also the biquadratic coefficient in Landau-Devonshire Gibbs free energy density. Because dielectric constant of relaxor follows power law, we also can get corresponding EC temperature variation for relaxor [10]. Since EC effect normally gets maximum at phase transition point, our method is practical for fast evaluating EC effect for materials with available Landau-Devonshire Gibbs free energy density with biquadratic term. For materials, the free energy density is not available; measuring dielectric nonlinearity under electric field also can save time than measuring temperature-dependent dielectric displacement under different constant electric fields.

More generally, EC effect over broad temperature range can also be predicted if the complete Landau-Devonshire potential of a material is available. For example, in monodomain state, the potential of Landau-Devonshire including up to eighth-power term can be written as:

$$g = g_0 + \alpha_1(T - T_0)P^2 + \alpha_{11}P^4 + \alpha_{111}P^6 + \alpha_{1111}P^8 - EP \tag{32}$$

where α_1, α_{11}, α_{111}, and α_{1111} are the Landau coefficients and g_0 is the Gibbs free energy density without considering the contribution of polarization. The polarization in (T, E) field can be obtained by finding the minimum of the potential. Then, the EC ΔT can be calculated according to Eq. (29) since dielectric displacement D equals to polarization P for ferroelectrics.

5.2. The influence of electric field for electrocaloric effect

Enormous materials have been studied for their electrocaloric effect from inorganic to organic. Most of them are ferroelectrics. Using model ferroelectric $BaTiO_3$ as an example, we can see the influence of electric field for electrocaloric effect. In single crystal, the reported ΔT for $BaTiO_3$ changes from 0.9 K@1.2MV/m [26], ~1.2 K@1.2MV/m [27], 1.6 K@1MV/m [28], and 4.8 K@10 MV/m [29]. It is obvious that high electric field is the key factor to induce large electrocaloric effect.

Materials in thin film can withstand high electric field; thus, large EC ΔT can be measured. However, the overall thermal mass is low. This problem can be overcome by combining many films to form a multilayer capacitor, which is a well-developed commercial product. In multilayer, the ΔT of BaTiO3 varies from 1.8 K@17.6MV/m [30] to 7.1 K@80MV/m [31]. Again, improving breakdown field is essential for inducing large EC effect.

5.3. Device development

Figure 4 is a schematic diagram for EC cooling cycle. One cycle includes four steps. (1) By applied electric field under adiabatic condition, EC unit changes from state 1 (E_1, T_c, S_h) to state 2 (E_2, T_h, S_h). The temperature of the unit increases. (2) Continuing increasing electric field under isothermal condition, EC unit changes from state 2 (E_2, T_h, S_h) to state 3 (E_3, T_h, S_h). The
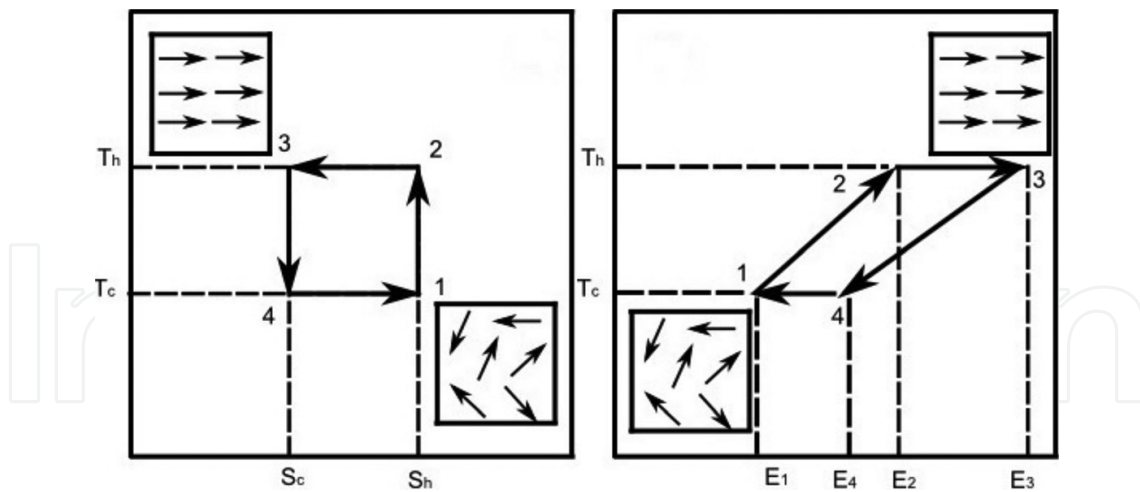
Figure 4. A schematic diagram of EC cooling cycle.

heat is expelled to a sink. (3) Decreasing electric field under adiabatic condition, EC unit changes from state 3 (E_3,T_h, S_c) to state 4 (E_4, T_c, S_c). The temperature of it decreases. (4) Continuing decreasing electric field under isothermal condition, EC unit changes from state 4 (E_4, T_c, S_c) to state 1 (E_1, T_c, S_h). The unit absorbs heat from a source. By one cycle, the heat of $T_C \Delta S$ is transferred from the source to the sink.

The critical point for an EC device is to achieve the unidirectional flow of entropy from a source to a sink. Some attempts to achieve it include: (1) shifting EC unit between the source and the sink [32, 33], (2) adding thermal switcher between EC unit with the sink and the source [34, 35], and (3) using liquid for heat transferring [36–38]. It is obvious that these designs increase the complexity of cooling device, which is not suitable for minimization and for chip-scale cooling. A new scheme is realized recently in which the cooler is composed of a flexible electrocaloric polymer film and an electrostatic actuation mechanism [9]. The device works for cooling battery of smartphone, although if it will work for chip cooling is still open. We stress here the sophisticated device development for chip-scale cooling based on EC effect is strongly expected, particularly adoptable for integrated fabrication.

6. Conclusion and perspectives

Conductivity, polarization, dissipation, and breakdown are the main electric responses of dielectrics under electric field. The weak electric field response of dielectrics is mainly studied by dielectric spectroscopy technology, particularly for dielectric relaxation. Equivalent electric circuit is the main technique to separate different relaxation mechanism by combining different normalization. The shortage of dielectric spectroscopy technology is that it is largely restricted by frequency limitation. Some relaxations may not enter the window of dielectric spectrum. Developing broadband dielectric spectroscopy is therefore strongly expected.

Dielectric for electrical energy storage is highly desired, but the energy storage density is still low. Theoretically, antiferroelectric can store more electric energy. The problem is we are shortage of practicable lead-free antiferroelectric materials. In 0–3 composite, we show that filling higher resistivity ceramics in polymer matrix has very potential to get higher energy storage density.

EC effect is very important for future cooling especially for microelectronic industry. The large EC effect normally happens around the phase transition. We have developed a practical and simple equation for predicting electrocaloric effect above the phase transition point, which can be applied for fast determining EC effect of a material. The future development in the area is to find new materials with high EC effect and practical device developments for chip-scale refrigeration.

In both applications, withstanding high electric field is essential. Both energy storage density and EC effect can be significantly improved if the breakdown field can be increased. Since breakdown field largely depends on processing, developing new preparation process for dielectric is also very important.

Lists of symbols

I current

U voltage

G conduction

E electric field

D electric displacement

P polarization

C capacitance

Z impedance

Y admittance

M electric modulus

σ conductivity

ρ resistivity

ε permittivity

ε_r relative dielectric permittivity or (relative) dielectric constant

χ susceptibility

A surface of capacitor

t thickness of capacitor

T temperature

U internal energy

S entropy

V volume

E_a thermal activation energy

τ characteristic relaxation time

ω angular frequency

ε_0 permittivity of free space

k_B Boltzmann constant

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