Study on the Electrothermal Effect of Dielectric Materials under Electric Field

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Abstract. Ferroelectric ceramic dielectrics have electrothermal effects, which usually show some changes in the thermodynamic quantities such as heat capacity and temperature under the action of electrostatic field. In the past few decades, it has only been found that there is a small electrothermal effect in polar ferroelectric ceramic dielectric materials. Recently, some ferroelectric materials have been found to have a large electrothermal effect, so the design of a refrigerator by using the electric method can be used as a research hotspot. In this work, we firstly introduced the electrothermal effects of polar ferroelectric ceramic dielectric materials, and then intensively discussed the refrigerating materials and their refrigeration capacities. Finally, it is hoped that it can be used as a reference for other refrigerating materials in the future.

Keywords: ferroelectric ceramic dielectric; electrothermal effect; refrigeration material; entropy.

1. Introduction
Polar ferroelectric ceramic dielectric materials [1] can generally change the temperature and entropy [2] under the action of electric field. For a long time, polar ferroelectric ceramic dielectric materials have only been found to have a very small thermal effect [3] and cannot be used in practice. Recently, researchers have pointed out that some ferroelectric materials have large electric heating effect [4]. How to use ferroelectric ceramic dielectric to design the refrigerator has become a hot spot [5]. At the same time, this refrigeration technology is pollution-free and has high refrigeration efficiency, so it has a huge prospect in the refrigeration industry [6]. If an electric field is applied to polar ferroelectric ceramic dielectric media, the dipole between the materials [7] changes from disorder to order instantaneously due to the polarization effect of the materials themselves. This will induce significant changes in voltage and charge, a phenomenon known as pyroelectric effect [8]. The pyroelectric effect and electrothermal effect are reversible, thus we can design and manufacture energy collection devices using ferroelectric ceramic dielectric materials with polarity [9], and hope to use this kind of materials as a reference for other refrigerating materials in the future.
2. Refrigeration principle

Working principle of ferroelectric ceramic dielectric material refrigeration: if we introduce a reverse electric field on the exterior of polar ferroelectric ceramic dielectric material, its polarity will disappear, thus further increasing the layer of material. So in an adiabatic condition, the system temperature will go down. From the thermodynamic analysis, we can further prove from the point of view of crystal. When a change occurs from ferroelectric to electrophilic, the dipole in this material can transition from the low energy to the high energy. The material absorbs heat in order to increase its internal energy and achieve the purpose of refrigeration.

Under current conditions, a large proportion of ferroelectric and antiferroelectric materials will undergo a phase transition when the temperature drops to a particularly low level, especially when the temperature reaches the Curie temperature. In general, the applied electric field makes the dipole change. The formula for the change of policy is:

\[ TdS = c_E dT + \left( \frac{\partial P}{\partial T} \right)_E dE \]  

(1)

In this case, \( dS \) represents the change of dilatation, \( P \) represents the intensity of polarization, \( c_E \) represents the specific heat, \( \left( \frac{\partial P}{\partial T} \right)_E \) represents the coefficient of pyroelectricity, and \( E \) represents the additional electricity.

When adiabatic, equation (1) can be changed into:

\[ dT = \left( \frac{T}{c_E} \right) \left( \frac{\partial P}{\partial T} \right)_E dE \]  

(2)

If it is polarized in an adiabatic manner, the coefficient will be less than zero, but cooling can be achieved only if equation (2) is less than zero. It can be changed into:

\[ \left( \frac{\partial T}{\partial E} \right)_S = \frac{TP_E}{c_E} \]  

(3)

At this point, \( T \) represents adiabatic temperature, \( cE \) represents specific heat, and \( PE \) represents the pyroelectric coefficient. If we ignore the influence of second thermoluminescence, we can derive its temperature change equation:

\[ dT = \left( \frac{T}{c_E} \right) P_E dE \]  

(4)

Its integral is:

\[ \nabla T = \frac{T}{c\rho} \rho E_1 \left( \frac{\partial P}{\partial T} \right) dE \]  

(5)

Where, \( E_1 \) represents the lowest electric field intensity, and \( E_2 \) represents the highest electric field intensity. In order to achieve the purpose of refrigeration, the material is required to have a large electric heat release coefficient and a large difference in electric field strength.
3. **Theoretical framework**

The polar ferroelectric ceramic dielectric material can be used as a thermodynamic system including electric displacement $D$ and temperature $T$ when subjected to electric field. The change process of its free energy is expressed as:

$$dW = EdD - SdT$$  \hspace{1cm} (6)

Since free energy can be expressed as $W = W(D, T)$, when minor changes occur, free energy can be expressed as:

$$dW = \frac{\partial W(D, T)}{\partial D} dD + \frac{\partial W(D, T)}{\partial T} dT$$  \hspace{1cm} (7)

According to (6) and (7):

$$\left( \frac{\partial W(D, T)}{\partial D} dD - E \right) dD + \left( \frac{\partial W(D, T)}{\partial T} dT + S \right) dT = 0$$  \hspace{1cm} (8)

Since this equation is true for any change in $D$ and $T$, the partial derivatives of $E$ and $S$ for electric field intensity are:

$$E = \frac{\partial W(D, T)}{\partial D}$$

$$S = \frac{\partial W(D, T)}{\partial T}$$ \hspace{1cm} (9)

And usually when we think about small deformation, we just think about the temperature. According to the definition of free energy, we can get $W_c(T) = U(T) - TS$, where $U(T)$ represents the internal energy of the system, and the expression can also be written as $U(T) = c(T - T_o)$.

When $c = T \frac{\partial S}{\partial T}$, we can simplify this formulation to $S = c \log(T/T_o)$, then its expression is

$$W = c \left[ (T - T_o) - T \log \left( \frac{T}{T_o} \right) \right].$$

In conclusion, $W(D, T) = c \left[ (T - T_o) - T \log \left( \frac{T}{T_o} \right) \right] + \frac{1}{2} \beta(T - T_c)D^2$ can be obtained, and (9) can be substituted into the formula:

$$E = \beta(T - T_c)D$$

$$S = c \log \left( \frac{T}{T_o} \right) - \frac{1}{2} \beta D^2,$$ \hspace{1cm} and $D = \frac{E}{\beta(T - T_c)}$ \hspace{1cm} (10)
4. Data analysis
According to the above equation, when the temperature increases, the entropy of the corresponding system will also increase, and the electric displacement will also increase with the increase of the electric field intensity. Figure 1 shows the relation between entropy $S$ and temperature $T$ when voltage is applied. When no electric field is applied, the dipole of its polarity is disordered. It has higher entropy. When the electric field is applied, the breakdown electric displacement can be reached along 2 paths, and the electric field can go through isothermal process and adiabatic process.

![Figure 1. temperature and entropy of polarity](image1)

Figure 2 shows the process of describing polar ferroelectric ceramic dielectric: isothermal process and adiabatic process. When the electric field is applied, the electric displacement can be gradually increased from 0 to the breakdown electric displacement $D_B$. One of the slopes is isothermal, while the other is adiabatic. In this figure, the slope of the curve can be determined by temperature. We can see that the higher the temperature, the higher the slope.

![Figure 2. displacement of polar ferroelectric ceramic dielectric](image2)
Through the above formula, table 1 can be calculated. Table 1 represents the parameter table that can be calculated by selecting six substances such as hydrogen peroxide and ether.

| Materials         | Entropy Change | Temperature Change | Cooling Capacity |
|-------------------|----------------|--------------------|------------------|
| Hydrogen peroxide | 112.5          | 12.3               | 1489             |
| Ether             | 1.08           | 0.15               | 0.3              |
| Amyl alcohol      | 6.01           | 0.51               | 3.6              |
| Carbon disulfide  | 0.42           | 0.12               | 0.12             |
| A phenylamine     | 135            | 35.12              | 4539             |
| Carbon tetrachloride | 1.73       | 0.42               | 0.5              |

It can be concluded from the table that the entropy changes and temperature change of hydrogen peroxide and A phenylamine are obvious, and the refrigeration effect is the best, while the relatively small change of carbon tetrachloride and carbon disulfide is relatively poor.

5. Conclusion
This paper introduces the polar ferroelectric ceramic dielectric material. Through the analysis and calculation, we find several polar ferroelectric ceramic dielectric materials. We also find that in the future, the electric heating effect can be used to study the refrigerator with promising application. The possibility of using this dielectric material as a refrigerating material was discussed and its refrigeration capacity was studied. Finally, we hope that these kinds of materials can be used as refrigeration materials to provide reference for other refrigeration materials.

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