Study on Electric Card Effect of Lead-free Piezoelectric Ceramics

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Abstract: The electrocaloric effect of ferroelectric materials can be used for refrigeration. This new method has the advantage of high efficiency, environmental protection and lower cost. Its variable size can satisfy the cooling requirements of different devices. However, it still exist some problems of lead-free ferroelectric ceramics refrigeration: its refrigeration temperature is less than 1 K; refrigeration temperature range is narrow; working temperature is either too high or too low. Sodium bismuth titanate ($Na_{0.5}Bi_{0.5}TiO_3$, NBT) material stands out and becomes the most promising candidate to replace lead-based materials. Properties of NBT almost meet the test requirements. Near depolarization temperature, this material shows ferroelectric/antiferroelectric phase transition, which brings a larger change in electric heating temperature. In this paper, electric card effect, lead-free piezoelectric ceramic materials and the BNT-xST ceramics were introduced in detail. Among these materials, BNT-xST is considered to be a promising material due to its excellent ferroelectric property and large electromechanical coupling coefficient.

Keywords: Electrocaloric effect, energy storage, Sodium bismuth titanate ceramics

1 Introduction

1.1 Development of refrigeration technology

Ferroelectric refrigeration uses the electric card effect of ferroelectric materials, that is, the temperature change of polar materials will be affected by the applied electric field and elimination [1]. Compared with the magnetic card effect, the advantage of the electric card effect is that it is easier to obtain the large electric field with large temperature variation than the large magnetic field, and the cost is lower. Although the thermoelectric refrigeration also has the advantages of environmental protection, quick reaction and control, but because of its low efficiency and high cost. Because the refrigerator made of ferroelectric materials does not need an external compressor and is very conducive to miniaturization, it can meet most of the cooling requirements under the new situation. Therefore, the development of ferroelectric cooling has positive significance [2].

Since entering the age of electrification, people's demand for electricity is increasing day by day. However, the traditional thermal power generation relies too much on fossil fuels. In addition to the non-renewable fuel and the serious shortage of reserves, the environmental damage brought by the combustion process is also in conflict with the call for environmental protection [3]. Therefore, people everywhere are trying new power generation methods. At present, the existing new energy sources such as solar photovoltaic power generation and thermoelectric power generation face the problem of energy storage in addition to power generation and efficiency. Energy storage capacitors play an irreplaceable role in electric power and electronic systems Has many advantages, such as high energy storage density advantage, large charge and discharge speed, high temperature and high-pressure resistance, and cyclic aging resistance. However, In today's materials technology, most capacitors cannot achieve high storage densities., the only way to obtain enough energy is to increase the volume of capacitors, so that the whole inverter equipment is too large. With the development of pulse power technology and the miniaturization of pulse forming lines, capacitors, as an important part, must not only store enough energy, but also increase the energy storage density, so as to reduce the volume of storage medium.

1.2 Research and development of the electric card effect

1.2.1 The working principle of the electric card effect

Electric card effect is polarity material because of the change of the external electric field leads to the change of its internal state, so as to make the polarity material adiabatic temperature changes, it is worth noting that the electricity card effect and neutralization, the process is reversible, that is to say, when an external electric field disappear, polar materials of adiabatic temperature will return to its original temperature (low temperature) [4]. At present, there is no universal theory about the electric card effect. The polarization intensity is usually expressed by thermodynamic formula (P), external electric field intensity (E) and temperature (T)[5]. The Gibbs free energy (G) of a dielectric can be expanded as a function of temperature (T), electric field (E), stress (X), and strain (X) [6].

$$G = U - TS - X_{\mathrm{i}} x_i - E_{\mathrm{i}} D_i \tag{1}$$

The cooling principle of the electric card is similar to the Carnot cycle of work done by compressed gas. The whole cycle is divided into four parts: (1) Stage 1: adiabatic polarization. Under the applied electric field, the electric dipole orientation in the dielectric is the same. If the temperature entropy is to remain constant, the temperature of the polar material must rise from T to δT. (2) Stage two: equipotential heat transfer. A constant electric field is applied so that the EC material no longer absorbs heat and then emits heat outwards, reducing the temperature. (3) Stage four, heat absorption. it absorbs heat from the outside[7]. Complete the loop. A refrigerator that uses the principle of electric card cooling works as follows: The material of the electric card is in contact with the load and absorbs heat from it. Then the external force separates the electric card material from the load. Contact the electric card material with the heat sink, the heat is released, and the temperature of the electric card material is restored to the working environment temperature (room temperature). Then disconnect the contact between the electric card material and the heat sink to make it contact with the load. At this time, the external electric field is removed to reduce the temperature of the electric card material, so as to absorb heat from the low-temperature load. By cycling the above process, heat can be continuously absorbed from the low-temperature load, thereby reducing the load temperature [8][9]. Because ferroelectric materials have large polarization strength, and the polarization is significantly flipped with the change of external electric field, the order degree of the system changes greatly, so there is a large adiabatic temperature difference [10].

1.2.2 Influencing factors of electric card effect

The cooling effect ΔT caused by the electric card effect is related to many factors, including working temperature T, applied electric field E, polarization strength P, dielectric constant, heat capacity C, etc., especially closely related to the electric field strength applied on the material. Moreover, ΔT is proportional to the magnitude of the electric field intensity, which means that to obtain a large temperature change, a larger electric field intensity must be applied [11]. At the same time, the temperature change response of thin film materials caused by electric card effect is very fast, almost synchronized with the electric field, which is also one of the advantages of thin film materials in the future applications. The non-polar capacitor is a capacitor without the positive and negative poles of the polar power supply. The two electrodes of the non-polar capacitor can be connected randomly in the circuit. Non-polar capacitors are used in pure AC circuits, and because of their relatively small capacitance, they can also be used in high-frequency filtering [12].

1.2.3 Measuring method of electric card effect

There are two ways to obtain the refrigeration effect: direct measurement method and indirect method. The so-called indirect method refers to the method of fitting the relationship between polarization intensity (P) and temperature (T) by measuring the hysteresis loop at different temperatures when the external electric field is constant, and substituting it into the formula below to calculate the temperature change and entropy change [13]. It should be noted that the stress in the test process mainly comes from the clamping of the polarization device, and the sample did not change its position during the measurement process, so the stress can be considered constant. Due to the high insulation level required by the direct method, the existing equipment of this experimental research group cannot meet its requirements, so the indirect method is adopted. Thacher first proposed the above indirect method in 1968. It can be seen from the formula that (ΔT) and (ΔS) are both integral of electric field intensity, so increasing the breakdown field intensity is one of the effective ways to obtain large electric card effect. the greater the variation of polarization intensity with temperature, the better the cooling effect [14]. Generally, ferroelectric materials have the largest pyroelectric coefficient at the phase transition temperature. At present, most electronic devices operate near room temperature, so it is very important to obtain a large ferroelectric cooling near room temperature.

$$\Delta T = \int_{E1}^{E2} -\frac{T}{PC_E}\left(\frac{\partial P}{\partial T}\right)_E dE \tag{2}$$

$$\Delta S = -\frac{1}{P}\int_{E1}^{E2}\left(\frac{\partial P}{\partial T}\right)_E dE \tag{3}$$

1.2.4 Research status of electronic card materials

The cooling cycle of electric card is based on the giant electric card effect, which uses the reversible enthalpy change in the process of dielectric polarization/depolarization to realize the thermodynamic cycle. Electric card refrigeration cycle using solid working medium, environmentally friendly, high energy conversion efficiency [15]. The solid working medium is directly driven by electric energy and has a simple structure, which has a potential technical advantage in the field of microsystem refrigeration. In the past decade, many international research institutions have observed the giant electric card effect in ferroelectric ceramics, single crystal, polymer, liquid crystal and other condensed matter materials. The research on thermodynamic cycle of electric card refrigeration has also made progress.

Cage compounds generally consist of atoms with four bonds forming a fullerene-like cage frame structure, forming many voids, which can enter some metal atoms, while the filled atoms are weak in binding with surrounding atoms, and are easy to vibrate in the cage voids, resulting in phonon scattering, and ultimately reducing the thermal conductivity[16]. At present, there have been a lot of experimental and theoretical studies on this kind of compounds, and many meaningful results have been achieved.

The figure-of-merit (ZT) value of superlattice film material is high, but its energy density is small, so it is difficult to realize high-power thermoelectric energy conversion. In the preparation of nanostructured bulk materials, the high thermoelectric properties generated by the nanomaterization effect are kept in the bulk materials, which is the direction of thermoelectric materials scientists' efforts in recent years. Bulk nanostructured materials can be divided into nanocrystalline materials and composite materials containing nanometer second phase.

Oxide thermoelectric material is a new thermoelectric material system, can work in oxidized atmosphere for a long time at high temperature, most of no toxicity, no environmental pollution, and simple preparation, sample preparation can be directly sintered in the air, without vacuum, low cost, in the field of thermoelectric power generation application potential is great. General oxide thermoelectric materials mainly have two categories: NA-Co-O thermoelectric materials and CA-Co-O thermoelectric materials. The $NaCo_2O_4$ composite oxide consists of the $Na_{0.5}$ layer and the CoO layer arranged alternately in a layered structure. The CoO layer is mainly conductive, while the $Na_{0.5}$ layer with half atomic vacancies is disordered and plays a good role in phonon scattering[17][18].

1.3 Research status at home and abroad

1.3.1 Comparative study of different measurement methods

Direct measurement refers to the direct measurement of the temperature change of the electric card and the heat absorbed or released when the external electric field is applied and removed. The so-called indirect method refers to the method of fitting the relationship between polarization intensity (P) and temperature (T) by measuring the hysteresis loop at different temperatures when the external electric field is constant, and substituting it into the formula to calculate the temperature change and entropy change[12].

1.3.2 Research on Enhancement of Electric Card Effect

Compared with magnetic cooling, ferroelectric cooling research is not deep enough, and most of the current research is mainly focused on the development of cooling working medium with large electric card effect, and there are few research reports on ferroelectric cooling prototype.

There was some work in this area in the 1990s. In 1992, Soviet scholars designed a prototype ferroelectric refrigerator device bucket with PST ceramics as the cooling working medium. When the applied electric field is 60 kV/cm, pentane is used as the refrigerant (the high insulation of pentane can significantly improve the strength of the applied electric field of the refrigerant working medium), and the maximum temperature change is 5 K[19]. Because of the low heat transfer efficiency of the refrigerant, the experimental value is less than the theoretical value. The experimental results show that the electric card effect of the refrigerant should be more than 2~3 K in order to prepare a practical ferroelectric cooler. So, to develop the material has larger electric card effect, and design a more effective cooling circulation structure device, is the key of the ferroelectric refrigeration towards commercialization in the design of the refrigeration cycle, Chinese scholars designed using ferroelectric crystal cooling regenerative cycle, optimization, and analysis the performance of the cycle, and proposes the corresponding refrigeration coefficient and cooling rate[20].

1.4. Research on lead-free piezoelectric ceramic materials

1.4.1 Research background of lead-free piezoelectric ceramic materials

In the 1930s, German scientists Kobeko and Kurchatov tested the electrothermal effect of Rointerest salt for the first time through experiments, and gave qualitative results because they did not give quantitative results, in 1963, two American scientists repeated their experiment, at 22.2ºC, The adiabatic temperature change of 0.0036ºC was measured under the electric field of 1.4kV/cm[21][22]. Subsequently, researchers studied the electric heating effect of other materials, but limited by the properties of materials, the measured adiabatic temperature variation is less than 1 K. Then the research fell silent. When the applied electric field is 776 kV/cm, the maximum adiabatic temperature difference δT =12 K is obtained, and the temperature is 226ºC. A new round of electric card cooling research upsurge. However, the main factor limiting the large-scale application of PZT is that the cooling temperature of PZT is too high. Since then, the research has focused on reducing the working temperature of refrigeration.

1.4.2 Development status of lead-free piezoelectric ceramic materials

X. q.liu studied the electrothermal effect of BST ceramics by SPS sintering process, and compared it with the same system ceramics prepared by traditional solid-phase sintering. The adiabatic temperature change δT = 2.1K at 30ºC for BST-35 ceramics prepared by discharge plasma sintering process[23]. Doped Mn reduces the leakage current and dielectric loss of BST-35 ceramics, and further increases the breakdown field strength. At room temperature, when the electric field is 130 kV·cm-1, the electric temperature variation δT =3.08 K, $\delta T/\delta E$ =0.0237 cm/KV. However, the cost is high, and the maximum temperature difference of ordinary solid-phase sintered ceramics is 1.29K.

1.5 The research content of this paper

ST doping can reduce the depolarization temperature of NBT ceramics and adjust the phase structure of ceramics. The phase structures of different ST-doped NBT ceramics were determined by XRD analysis, electro hysteresis loop and dielectric temperature spectrum at room temperature[6]. This paper introduces the development and research results of lead-free piezoceramics, as well as the related preparation technology and performance test.

2. Preparation process and performance test of lead-free piezoelectric ceramic materials

2.1 Preparation process of LiCe-doped $(NaBi)_{0.46}Bi_4Ti_4O_{15}$ lead-free piezoelectric ceramics

Ingredients: according to the reaction equation and proportion of accurate weighing of the required drugs.

The ball mill: after weighing the raw material, put it into the nylon ball grinding tank and add zirconia ball at the same time according to the ball to ball ratio of 5:1.

An appropriate amount of absolute ethanol was added as dispersion medium. The planetary ball mill is used, the rotation speed is 300R /min, when the ball is grinding. The slurry after ball milling is put into the oven and heated at 80°C for 12 hours to dry it.

Pre burn: the purpose of prefiring is to allow the raw material to react and presynthesize the main crystalline phase. Due to the volume of the powder after prefiring.In this way, deformation or cracks caused by excessive shrinkage in the sintering process can be reduced. The drying After grinding, the powder is placed in a corundum crucible and put into a box muffle furnace. The temperature is raised to 950ºC at 5ºC/min. Hold for two hours and let cool in the oven. [21]

Second ball milling, drying: due to the large particle size of the powder after the solid-phase synthesis reaction, it needs to pass through the second ball grinding refinement. Pour the pre-fired material into the nylon tank, add zirconium ball and an appropriate amount of absolute ethanol ball grinding. When the ball mill 10h, speed 300R /min. The powder required by the experiment can be obtained by drying the material after secondary ball milling and sifting it.[22] The powder will agglomerate after the drying process, and the purpose of sieving is to refine the powder.

2.2 $(NaBi)_{0.46}(LiCe)_{0.04}Bi_4Ti_4O_{15}$ lead-free piezoelectric ceramic performance test

(1-x) BNT-xST ceramics, Change the test voltage and measurement period according to the characteristics and requirements of the tested sample. Residual polarization strength and coercive field are important indicators of ferroelectric properties.[24]

3 Contents of the test

According to the hysteresis loop at different temperatures and electric fields, the relationship between polarization intensity and temperature was obtained by fitting and then substituted into Equation 1 and electric card effect. The larger δT and δS are, the better the cooling effect is. From the practical point of view still need wider working temperature area.[25] Because the breakdown field strength of different materials is different, in order to compare materials of different states, such as thin films and ceramics, a new factor is introduced, that is, the adiabatic temperature variation caused by the change of unit electric field. These are important factors to measure cooling efficiency.

According to the calculation formula of energy storage density: dielectric constant, breakdown field strength, and the difference between Pmax and Pr. The higher the energy storage density, the better the energy storage effect. At the same time, energy loss exists in the charging and discharging process of energy storage materials, so energy storage efficiency also needs to be considered. The use environment of energy storage materials requires high temperature stability of energy storage density.[26]

4. Conclusion

The direction of piezoceramics is still the hotspot of materials researches. Compared to the traditional piezoelectric ceramics contain Pb, lead-free piezoceramics are more environmentally friendly. As a kind of energy-saving and efficient green cooling technology, electric card effect of lead-free ceramic attracts people's attention, especially in recent years. It has become a hot topic in the field of electric card research to prepare materials with large electric card effect and explore its cooling characteristics. Lead-free ceramics can also be combined with other properties of ferroelectric materials (such as pyroelectric, piezoelectric, dielectric) to produce multifunctional, multipurpose devices. [27] Although lead-free ceramics have great development prospects. The research on the electric card effect is still not sufficient in terms of depth and breadth. More efforts should be put into it to realize the commercialization of lead-free ceramics refrigeration.

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