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Domestic Applicability of Solid-State Cooling

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Abstract - The global surge in energy consumption and the consequential environmental challenges have spurred an escalating demand for innovative, eco-friendly alternatives to current modern technology, and refrigeration systems are no different. With most households today owning a refrigerator amongst other appliances, there is a constant need for energy that is only growing by the year, in 2013 it was found that there was roughly 1.4 billion cold appliances in use within household globally, causing 450 million tons of CO_2, using approximately 650 TWh, which is 1.2 times the total electricity consumption of Germany that same year, with a 27% increase to the number of cold appliances [1]. Even with the efficiency of technology being improved over the years, there is still the ever-increasing demand for energy. Due to their complex crystal structures and the delicate balance required between their attributes, challenges do occur when attempting to identify suitable multiferroic materials, ongoing research aims to optimize their properties. Though harnessing the potential of these multiferroic materials and their intrinsic characteristics, may offer a sustainable solution for both industrial and residential refrigeration.

Keywords - Caloric cooling; Solid state caloric effect; Multicaloric effect.

1 Introduction

There has been a high demand in both industrial and household landscapes for refrigeration technology for a long time that has only been growing in recent years at a rapid pace, this being due to a similarly substantial increase in energy consumption across the globe. The traditional cooling methods that are currently in use today often rely on refrigerants which are normally hazardous chemicals and harmful greenhouse gases that are large contributors to global warming and climate change [2]. Solid-state cooling can be used to provide an eco-friendlier approach by eliminating the use of dangerous refrigerants, whilst also producing a more cost-effective method of refrigeration not only industrially, but also in civilian life.

2 The cooling cycle used for refrigeration

Currently, the most common technology being used for refrigeration today uses a cooling cycle based on the compression and expansion of vapour, this involves a refrigerant being circulated within a closed loop system. The cooling cycle is made up of four main mechanisms, these processes allow for the continuous removal of heat from the refrigerated space, allowing a low temperature to be maintained. Firstly, with the use of a compressor to pressurize the vaporized refrigerant, increasing its temperature and pressure, next the refrigerant is sent through to a condenser, where it releases heat to the surrounding environment, causing it to condense into a high-pressure liquid. After this, the liquid goes through an expansion valve, where it will suddenly drop in pressure, resulting in a portion of the liquid evaporating into a mixture of liquid and vapour with a low pressure, and lastly this mixture will go into an evaporator, where it will absorb heat from its surroundings, causing the remaining liquid to vaporize, where it will then continue the cooling cycle.

3 How does solid-state cooling work?

The reason that solid-state cooling can work is due to the multicaloric effect [3], which occurs due to the simultaneous or coupled responses of multiple caloric effects within a single material [4]. The caloric effects are a phenomenon linked to the reversible temperature changes that occur with materials due to external stimuli. An example of this could be stress, an electric field, or an applied magnetic field. The three primary caloric effects are the elastocaloric effect, the electrocaloric effect, and the magnetocaloric effect, respectively.

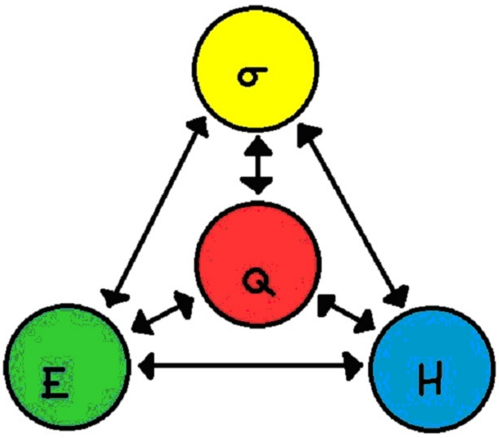

Figure 1: Diagram showing the relation of mechanical, electrical, magnetic, and thermal coupling within ferroic and multiferroic ordered solids.

The elastocaloric effect relates to the reversible temperature changes that occur when a material undergoes a mechanical deformation resulting from compression or tension for example. The material being used in this instance would be ferroelastic material, these are materials that exhibit a reversible deformation that can be induced by an external stress. When stress is applied to this type of material a phase transition occurs, where a temperature change is caused due to an absorption or release of heat. When the stress ceases, the material will return to how it originally was, similarly the temperature of the material will also return to its initial state.

Again, the electrocaloric effect is associated with a reversible temperature change, however this time it is in response to the application or withdrawal of an electric field. In the absence of an electric field, the direction of the polarization can be considered random, but when there is an electric field applied to materials such as ferroelectrics, the polarization of the material will cause the electric dipoles reorientate, causing a temperature change, the removal of this electric field reverses these effects.
Lastly, as with the others the magnetocaloric effect is also connected to a reversible temperature change, in this situation is in response to the implementation or elimination of a magnetic field. The materials used in this situation would likely be a ferromagnetic material, when these materials placed within an applied magnetic field, the magnetic dipoles within the material will align, this is an energetically favourable state for them, thus resulting in an increase in temperature through the absorption of heat from its surroundings, whilst the

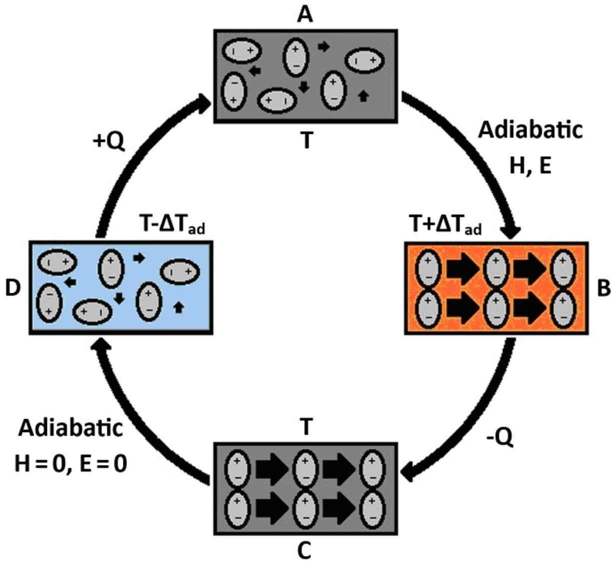

Figure 2: Labelled diagram showing the four cooling stages due to entropy change from the relaxation of the magnetic moments and electric dipoles.

removal of the field leads to the temperature of the material decreasing back to its initial value.

As stated before, the multicaloric effect occurs due to the exhibition of a combination of the effects stated, these effects are caused by a response in certain materials to external stimuli in the form of the three primary ferroic orders: ferroelastic order, ferroelectric order, and ferromagnetic order. There are materials that can exhibit at least two ferroic orders simultaneously, these are a type of compound called multiferroics. With the use of these multiferroic materials, it could be possible to induce a cooling effect usable within refrigeration technology as a more efficient, less energy consuming, as well as more environmentally friendly alternatives.

4 What materials would be applicable?

In the pursuit of environmentally friendly and efficient cooling solutions, materials have been identified as promising candidates, showing a unique interaction of ferromagnetic and ferroelectric properties, examples of these materials include, but are not limited to: Lead Iron Titanate $PbFeTiO_3$, Lead Magnesium Niobate-Lead Titanate (PMN-PT), and Bismuth Ferrite $BiFeO_3$. The appeal lies within the multiferroic nature of these substances, and presence of ferromagnetism and ferroelectricity simultaneously. This dual functionality enables the coupling of magnetic and electric fields allowing for inventive solid-state cooling mechanisms, offering a pathway to sustainable cooling without the reliance on traditional refrigerants [5].
The utility of multiferroic materials are further enhanced by their tailorable natures. Researchers can precisely tune transition temperatures and caloric responses, which is incredibly important as their viability for solid-state cooling is heavily influenced by transition temperatures. Transition temperatures mark points of phase transitions, the points of importance are Curie temperature (Tc) and the Neel temperature (Tn). The Curie Temperature, named after physicist Pierre Curie, is a critical temperature point at which certain materials undergo a phase transition, leading to a change in their magnetic or electrical properties. Ferromagnetic materials below this temperature will tend to exhibit spontaneous magnetization, aligning their magnetic moments in parallel.
As the temperature of the material increases, approaching the Curie temperature, thermal energy disrupts this alignment, and once it surpasses the Curie temperature, the material will

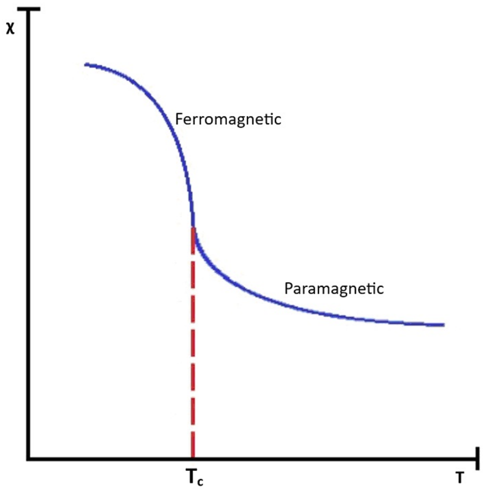

Figure 3: Labelled graph showing an example of the Curie temperature.

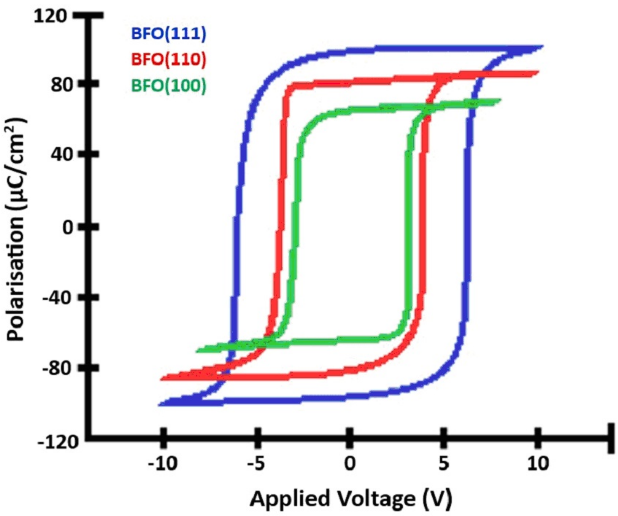

Figure 4: Ferroelectric polarization loops graph for Bismuth Ferrite,$BiFeO_3$ based on the data of [6] and [7].

become paramagnetic, with magnetic moments pointing in random directions. Similarly, within ferroelectric materials, the Curie temperature is used to represent the point at which the material goes through a transition from a ferroelectric phase, which is characterized by a spontaneous electric polarization, to a paraelectric phase where the polarization is lost.
The Neel temperature, named after French physicist Louis Néel, is a critical temperature point associated with particularly antiferromagnetic substances. The Neel temperature marks the temperature at which an antiferromagnetic material goes through a phase transition, with the occurrence of changes to its magnetic behavior. In antiferromagnetic materials, neighboring magnetic moments align antiparallel to each other, creating a canceling effect. When the temperature of the multiferroic material is below its Neel temperature, this antiferromagnetic order is preserved, with the magnetic moments pointing in opposite directions. However, as the temperature increases and approaches the Neel temperature, thermal energy disrupts this alignment. Once temperature overcomes the Neel temperature, the material transitions to a paramagnetic state where the magnetic moments become disordered.

A key benefit of using materials such as Lead Iron Titanate and Lead Magnesium Niobate-Lead Titanate is that their phase transitions often occur at temperatures close to or within the range of room temperature. Which is incredibly advantageous for practical applications, as it permits the material to exhibit its desirable properties without the need for extreme temperature conditions. Another benefit of using materials such as Bismuth Ferrite and

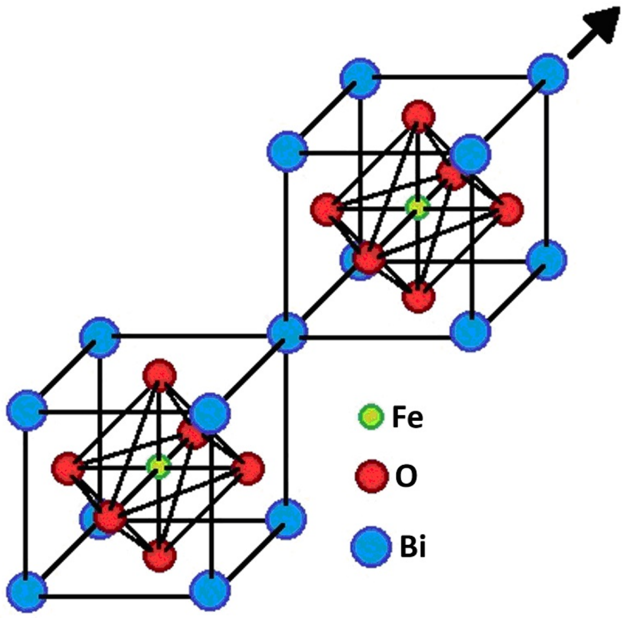

Figure 5: Diagram showing the crystal structure Bismuth Ferrite, $BiFeO_3$.

the others is the absence of moving parts, which are characteristic of traditional cooling systems, allowing for a more reliable system. The lack of compressors, pumps, and central components in conventional cooling would be eliminated, reducing the requirements for maintenance whilst also permitting more durable and sustainable cooling systems.

5 Material identification challenges

When it comes to multiferroic materials there is a complexity that comes with how they are made that affects whether they are usable within such systems. For example, for a multiferroic to display a strong magneto-electric coupling it needs to fulfill certain requirements, with these conditions met it would then be exhibiting direct magneto-electric coupling, one of two possible types with the other being indirect magneto-electric coupling which typically occurs due to the interaction between magnetic and electric domains from two different materials, or a composite multiferroic. The challenges for identifying these multiferroics do make it harder to find viable options for various roles as it creates a scarcity of these materials. Ongoing research aims to discover and optimize multiferroic materials for diverse applications, including solid-state cooling [8]. The identification of complex materials that exhibit multiple ferroic orders simultaneously can be quite a significant challenge, as these materials can require intricate crystal structures and specific arrangements of ions or atoms to necessitate the coexistence of these orders. Compounding these difficulties, the mutual exclusivity of ferroelectric and ferromagnetic orders in many materials makes it tough to find a material with a balance between them. This obstacle in material design impedes progression towards creating these innovative multiferroic technologies. Another issue is that these various materials behave in diverse ways at specific temperature ranges. This limitation poses a challenge for applications like refrigeration, which require effective cooling near room temperature. However, new materials are still being identified that exhibit robust multiferroic properties without requiring extreme temperature conditions. Some materials can undergo phase transitions or lose their cooling properties under certain conditions, affecting the stability and reliability of the cooling system. Ensuring the material has stable properties over a range of temperatures and environmental conditions is crucial. Identifying materials that exhibit multiferroic properties with reproducibility is difficult, whilst guaranteeing that the materials can be synthesized with consistently dependent properties is essential for the practical implementation of solid-state cooling technologies, and their commercial viability.

This requires extensive screening, a considerable amount of time, money, and research to develop practically. The materials cost and fabrication play a significant role when determining the feasibility of modern technologies. Identifying which materials are most cost-effective whilst meeting necessary performance criteria is a challenge.

6 Application in refrigeration technology

A solid-state cooling cycle would be functioning on the principles laid by the multicaloric effect within a magneto-electric multiferroic can be shown to be associated with the Brayton thermodynamic cooling cycle, it is a cyclic process used in gas turbine engines and refrigeration systems involving four main stages: compression, isobaric heating, expansion, and isobaric cooling. In this cycle, air is compressed, after isobarically heated via combustion. From here the gas then expands through a turbine, producing work, where the exhaust gas is cooled isobarically before the cycle repeats. This works due to electric dipoles and magnetic spins in multiferroic solids being capable of absorbing heat from the environment by the system returning to its equilibrium state, this is called the relaxation process. The multicaloric cooling cycle starts with the system in its initial state of thermal equilibrium, at temperature T. Whilst the temperature is at T, electric dipole moments and magnetic spins fluctuate randomly in a para-multiferroic state due to thermal activation, in this circumstance this is because the thermal energy allows the electric dipole moments and magnetic spins to overcome energy barriers and experience fluctuations disrupting their ordered arrangement. The application of a strong electric field, E or magnetic field, H to the refrigerant multiferroic system triggers a transition into an ordered multiferroic state, as represented by the transition from A to B in figure 6, there is no heat transfer here, so this is currently under adiabatic conditions.

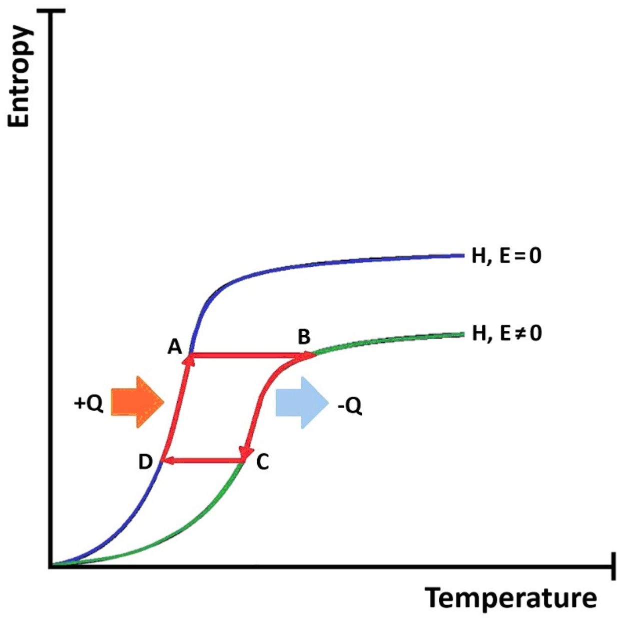

Figure 6: Labelled diagram showing a typical Brayton thermodynamic cooling cycle.

This is to signify a reduction in the system's entropy, and whilst under adiabatic conditions, results in the system warming up, leading to the new temperature being T+ ΔTad. The heat sink will then be able to eliminate this additional temperature. Throughout this procedure, maintaining a constant applied field is essential to prevent the re absorption of heat by the spins and electric dipoles. As determined by the heat sink, the system reverts to the equilibrium temperature T, as shown by the transition from B to C in figure 6. Thermal contact with the heat sink is severed using a thermal switch, insulating the system, and the total entropy is once again maintained at a constant level. The transition from points C to D found in figure 6 expresses how the applied field is turned off as well. This is essentially an adiabatic demagnetization and depolarization process, where the spins and electric dipoles absorb heat during their relaxation process, enabling the refrigerant's temperature to decrease below the heat sink's temperature, T- ΔTad. The refrigerant can now be in thermal contact with the environment undergoing refrigeration, this is exhibited by the transition from D to A in figure 6, and the cycle repeats. To ensure effectiveness, the cooling process demands significant temperature changes, ΔTad. This multicaloric cooling cycle would thus act in a similar fashion to the currently most common method of modern refrigeration systems, however instead of a refrigerant being pumped through a system of compressors and condensers, where it transitions between a liquid and gaseous form, the system would consist of a multiferroic material where an electric or magnetic field would be applied causing it to enter an ordered state. Whilst in this state, the temperature of the system will increase before a heat sink is then able to remove this additional heat, as the constant applied field prevents any heat being reabsorbed, the heat sink is cut off via a thermal switch, [9]. The field would then be turned off allowing the electric dipoles and spins to relax and absorb heat, thus the temperature of the refrigerant decreases, from here the refrigerant would be in thermal contact with, and conducting the thermal absorption to the refrigeration environment, after this the cycle would begin again.

7 Conclusion

In response to escalating demands for refrigeration technology and growing environmental concerns associated with conventional cooling methods, solid-state cooling emerges as a promising and eco-friendly alternative [10]. Utilization of multicaloric effects within magneto-electric multiferroics presents a viable solution for both industrial and residential refrigeration. This innovative approach employs ferroelastic, ferroelectric, and ferromagnetic orders in specific materials to induce reversible temperature changes when exposed to external stimuli. Materials with multiferroic properties, such as Lead Iron Titanate and Bismuth Ferrite, demonstrate dual ferromagnetic and ferroelectric functionalities. These materials exhibit tunable transition temperatures, often near room temperature, making them practical for various applications. Despite the significant challenges whilst identifying suitable multiferroic materials due to their complex crystal structures and the need for a delicate balance between ferroic orders, ongoing research strives to optimize their properties for solid-state cooling. The solid-state cooling cycle offers a cyclic process for heat absorption from the environment using the multicaloric effect in magneto-electric multiferroics, triggering transitions between ordered and disordered multiferroic states, which results in temperature changes suitable for refrigeration. While challenges persist when ensuring stability over temperature ranges, synthesizing reproducible materials, and addressing cost considerations, the integration of multiferroic materials into solid-state cooling has the potential for more reliable, energy-efficient, and environmentally friendly refrigeration technologies to be developed. While solid-state cooling research and development hold great promise for more energy-efficient and environmentally friendly refrigeration, its widespread replacement of current refrigeration systems is a complex process that requires further advancements in material science, engineering, and technology. Several challenges and considerations need to be addressed before solid-state cooling will be able to replace traditional refrigeration methods.

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