



REVIEW OF LITERATURE ON THE ELECTROCALORIC EFFECT OF LEAD AND NON LEAD BASED SOLID SOLUTIONS

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Abstract: The electrocaloric effect (ECE) offers a pathway to environmentally sustainable and easily miniaturized refrigeration technology, positioning it as a front-runner for the next generation of solid-state cooling solutions. This research unveils a remarkable ECE in a finely tuned $(\text{Ba}_{0.86}\text{Ca}_{0.14})_{0.98}\text{La}_{0.02}\text{Ti}_{0.92}\text{Sn}_{0.08}\text{O}_3$ ceramic, exhibiting a temperature shift (ΔT) of 1.6 K across more than 85% of the maximum ΔT (ΔT_{max}) and spanning an exceptionally wide operational range of 92 K. Our investigation on dielectric responses and ferroelectric polarization-electric field (P - E) loops suggests that the broad operational scope results from the fragmentation of extended ferroelectric domains into smaller domains and polar nano-regions (PNRs) supported by PFM analysis. Furthermore, the introduction of La enhances spontaneous polarization by significantly extending the maximum electric field that can be applied, facilitating high-performance ECE at ambient temperature. This study positions BaTiO₃-based lead-free ceramic as a sustainable alternative for addressing the cooling demands of modern electronic components, marking a significant stride toward next-generation solid-state refrigeration

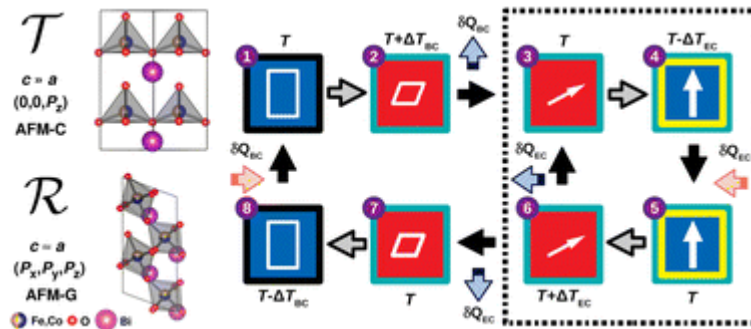
Keywords: REVIEW OF LITERATURE, ELECTROCALORIC EFFECT, LEAD AND NON LEAD BASED SOLID SOLUTIONS

Introduction: As electronic components advance towards higher integration and miniaturization, efficiently dissipating heat has become a paramount challenge. Traditional vapor-compression systems, hindered by their bulkiness and limited scalability, fail to meet the cooling demands of modern electronics [4,5]. Given these circumstances, electrocaloric effect (ECE) refrigeration technology stands out as an innovative solution, promising easy miniaturization to match the cooling requirements of compact electronic devices [[6], [7], [8]]. Furthermore, ECE cooling technologies are attracting attention for their high efficiency and absence of emissions, offering an eco-friendly approach to thermal management. The electrocaloric effect, a reversible adiabatic temperature change in polar materials induced by the application and removal of an electric field, results in entropy variations. Initially observed in Rochelle Salt by Kobeko and Kurtschatov in 1930, the ECE was not widely recognized until recent advancements [16]. The last two decades have made significant progress, particularly with the development of high ECE in PbZr_{0.95}Ti_{0.05}O₃ thin films and ferroelectric polymers, revitalizing interest in ECE as a key technology for future cooling applications [17,18].

Considerable efforts have been dedicated to advancing electrocaloric refrigeration technology, with the goal of securing significant ECE alongside wide temperature ranges near ambient conditions. Attention has largely centered on lead-based systems, renowned for their high dielectric permittivity and polarization, leading to impressive ECE performances. Notable achievements include Zdravko Kutnjak's realization of a $\Delta T = 3.0$ K ECE under a 90 kV/cm electric field around 150 °C [19], and Lovro Fulanović's attainment of a $\Delta T = 2.26$ K in 0.9 Pb(Mg_{1/3}Nb_{2/3})O₃-0.1PbTiO₃ multilayer ceramics capacitor at 100 kV/cm near 105 °C [20]. David Schwartz and N. D. Mathur have showcased significant temperature shifts of 5.2 °C and 5.5 K, respectively, in PbSc_{0.5}Ta_{0.5}O₃-based systems [21], while Emmanuel Defay introduced an electrocaloric cooler with a 4.2-W cooling capacity and a remarkable 20.9 K temperature span (T_{span}), attaining an unprecedented Carnot efficiency of 64% [22]. However, the environmental hazards associated with lead-based materials have spurred the search for lead-free alternatives, heightened by increasing environmental awareness. Against this backdrop, Bai et al. achieved a $\Delta T_{\text{max}} = 0.63$ K and a $T_{\text{span}} = 57$ °C in a laminated composite ceramic made of BaTi_{0.89}Sn_{0.11}O₃, BaTi_{0.85}Zr_{0.15}O₃, and BaTi_{0.89}Hf_{0.11}O₃ layers at low electric fields [23]. Qian et al. recorded a $\Delta T = 4.5$ K with a temperature span of 30 K in BaTi_{0.85}Zr_{0.15}O₃ ceramics under 150 kV/cm [24]. E. Venkata Ramana observed a $\Delta T = 1.479$ K and a temperature span of approximately 40 K in Ba(Ti_{0.8}Zr_{0.2})O₃-(Ba_{0.7}Ca_{0.3})TiO₃ lead-free ceramics at 60 kV/cm [25]. Wu et al. reported a $\Delta T = 1.14$ K

near 90 °C ($T_{span} \approx 52$ K) in 0.86NaNbO₃-0.1BaTiO₃-0.04BaZrO₃ lead-free ceramics [11]. Despite these advancements, achieving both a significant ECE and a broad operating temperature range in lead-free materials remains a challenge.

Solid-state cooling applications based on electrocaloric (EC) effects are particularly promising from a technological point of view due to their downsize scalability and natural implementation in circuitry. However, EC effects typically involve materials that contain toxic substances and require relatively large electric fields (~ 100 – 1000 kV cm⁻¹) that cause fateful leakage current and dielectric loss problems. Here, we propose a possible solution to these practical issues that consists of concertedly applying hydrostatic pressure and electric fields on lead-free multiferroic materials. We theoretically demonstrate this strategy by performing first-principles simulations on supertetragonal BiFe_{1-x}Co_xO₃ solid solutions (BFCO). It is shown that hydrostatic pressure, besides adjusting the occurrence of EC effects to near room temperature, can reduce enormously the intensity of driving electric fields. For pressurized BFCO, we estimate a colossal room-temperature EC strength, defined as the ratio of the adiabatic EC temperature change by an applied electric field, of ~ 1 K cm kV⁻¹, a value that is several orders of magnitude larger than those routinely measured in uncompressed ferroelectrics.



Review of Literature:

Piezoelectricity (pressure electricity) was discovered by Nobel laureates Pierre and Jacques Curie in 1880 [1] during their study of the effects of pressure on the generation of electrical charge by crystals such as quartz, tourmaline, and Rochelle salt. In fact, the development of an electrical charge under the application of mechanical pressure or vice versa is referred to as the piezoelectric effect. Low piezo-electricity is the main drawback of the natural piezoelectric materials. A major breakthrough came with the discovery of PZT and BaTiO₃ in the 1950s [2, 3] and the family of these materials exhibited very high dielectric and piezoelectric properties. To date, PZT is one of the most widely exploited and extensively used piezoelectric materials, having secured a permanent place in the field of material science and engineering. They are widely used as sensor and actuator devices [4–7], multilayered capacitors, as hydrophones, etc. with an estimated market of tens of billions of dollars worldwide. However, lead oxide, which is a component of PZT, is highly toxic and its toxicity is further enhanced due to its volatilization at high temperature particularly during calcination and sintering causing environmental pollution [8].

According to the recent developments, European Union (EU) is planning to restrict the use of hazardous substances such as lead as well as other heavy metals [9, 10]. However, there is no equivalent substitute for PZT; therefore, its use is still continued. This may be a temporary respite, but the legislation certainly impressed the researchers to develop alternative lead-free piezoelectric materials in order to replace lead-based materials [11, 12]. There had been many attempts by researchers in the past to develop alternative lead-free materials but the properties are nowhere near to the PZT system. Basically, the lead-free systems are (i) perovskites, i.e., BNT, BaTiO₃ (BT), KNbO₃, NaTaO₃, etc., (ii) non-perovskites, i.e., bismuth layer-structured ferroelectrics (BLSF), tungsten-bronze type ferroelectrics, etc. While the perovskites are suitable for actuator and high power application, BLSF seems to be a candidate for ceramic filter and resonator applications. Apart from polycrystalline lead-free materials, lead-free piezoelectric single crystals, e.g., langasite and ferroelectric ceramics with tungsten-bronze structure have been reported [10].



The important symptoms of lead poisoning are fatigue, aches in muscles and joints, abdominal discomfort, etc. Some of the symptoms and signs of lead poisoning are shown in Table 2. Patients with poor dental hygiene may exhibit a blue line at the dental margin of the gums due to deposition of lead sulfide. Lead poisoning has long been considered as an environmental health hazard, for its adverse effects on intellectual and neurological development [15–17]. The main route of absorption in adults is the respiratory tract where 30–70% of inhaled lead (mostly the inorganic form like oxides and salts) goes into the circulatory system. For a reasonably well-controlled occupational exposure, blood lead value ranges between 1.45 and 2.4 mol L⁻¹ (30–50 µg 100 mL⁻¹) with a provision that there is six monthly monitoring [18, 19].

The perovskite-type (ABO₃) ferroelectrics such as BaTiO₃ (BT), (Bi_{0.5}Na_{0.5})TiO₃ (BNT), KNbO₃, NaTaO₃, etc. are well-known lead-free piezoelectric materials. These ceramics show relatively large piezoelectric constant. However, the main drawbacks generally are low Curie temperatures (T_c), difficulties in poling treatments and/or low relative densities [10].

Many studies have been performed on NBT to determine how dopants affect the structural and electrical properties of the material. Some studies focus on dielectric properties, while others focus on piezoelectric properties. Both A-site and B-site dopants have been studied to determine how they affect the properties of NBT, some of these dopants include (Ba, Pb, Sr, Zr, La, K, Bi) [18–22]. Some of the main drawbacks of this material are that it has a high coercive field and high conductivity. Different dopants can be added to NBT to combat some of its drawbacks, such as to decrease coercive field or increase the piezoelectric constant. The effects of barium on the properties of NBT have been characterized by various groups over the years. Many studies that involve barium doping also include another A or B-site cation to evaluate the effects of multiplesite doping on the properties [23–26]. One of the advantages of doping with barium is that there is a morphotropic phase boundary (MPB) between the rhombohedral and tetragonal phases of the structure. Dielectric materials near an MPB are interesting because they exhibit anomalously large dielectric constant values compared to other compositions. Most of the papers cited in literature have shown that the system presents a MPB around 6 mol% BT, In the trigonal region, the dielectric behavior of the NBT–BT solid solutions is, as expected, very similar to the one observed for pure NBT or low-lead titanate.

The NBT–BT material system, like several other lead-free materials, was first reported in the 1960s by Smolenskii et al. but did not receive much attention until the recent surge in leadfree material development in the past two decades [27]. Some of the initial dielectric and optical property measurements of NBT were reported in the 1990s by various sources [28–30]. Preliminary structural studies of NBT did not provide a definitive structural understanding, but in 2002 Jones and Thomas found that it expresses the rhombohedral R3c space group at room temperature and changes to tetragonal and subsequently cubic during heating. NBT is a promising material due to its high Curie temperature and a piezoelectric constant similar to that of BT. But BT has very low curie temperature without addition of lead. Lead additions increase the Curie temperature up to about 150° C; however, lead also de-stabilizes the low temperature phase transitions. The commonly used materials are lead based eg-lead zirconate titanate (PZT), lead magnesium niobate (PMN), etc. However, the toxicity of lead oxide and its high vapor pressure during the sintering process results in serious environment problems. As a consequence, it becomes necessary to develop low-lead or lead-free piezoelectric materials with properties close to those of the PZT system. Because of environmental issues, new lead-free piezoelectric materials are the object of many studies. The Na_{0.5}Bi_{0.5}TiO₃ compound (NBT) is considered as a possible candidate for such applications. NBT has large polarization, high temperature dielectric constant and also no lead so it can be developed to be used as future replacement for all lead based compounds. But pure NBT has a drawback of high coercive field and the high conductivity causes problems during the poling process. To improve the properties some doping has to be done such as NBT–BaTiO₃, NBT–PbTiO₃, NBT–K_{0.5}Bi_{0.5}TiO₃, NBT–SrTiO₃ and NBT–BiFeO₃ [31–32].

The dielectric and ferroelectric properties were studied. Room temperature permittivity was found to decrease as Na_{0.5}Bi_{0.5}TiO₃ (NBT) content increases. Only the sample with 0.3 mol NBT was found to have relaxer behavior. The T_c shifted slightly only for NBT addition lower than 0.1 mol. The highest T_c (about 150 OC) was obtained for 0.2 mol NBT addition. The remnant (Pr) decreases whereas the coercive field, E_c, increases monotonously as the NBT content increases. Man-Soon Yoon et al [37] used pre-synthesized BaTiO₃ and pre-milled Bi₂O₃, Na₂CO₃, BaCO₃ powders and calcination powder milled with a high energy milling machine in order to obtain a nano-particle size. The second one is a conventional one to compare with the former process. The dielectric and the piezoelectric properties of sintered specimens fabricated by the two



different processes were evaluated. It was found that the properties of the nano-sized NBTBT ceramic increased by the modified mixing and milling method, showing superior characteristics in terms of the piezoelectric, dielectric constant and sintering density compared with those of the conventional process. It was found that the remnant polarization P_r for the nano-sized NBT-BT specimen has a higher value of 37.8 mC/cm² compared with that of 12 mC/cm² for conventional NBT-BT; whereas the coercive field (E_c) has a similar value

References:

- [1] a. A.J. Moulson, J.M. Herbert; Electroceramics 2nd Edition, John Wiley & Sons Ltd., 2003 b. B.Jaffe, W.R.Cook and H.Jaffe; Piezoelectric Ceramics, Academic Press, London, 1971
- [2]. Dielectric properties of some low-lead or lead-free perovskite-derived materials: Na_{0.5}Bi_{0.5}TiO₃-PbZrO₃, Na_{0.5}Bi_{0.5}TiO₃-BiScO₃ and Na_{0.5}Bi_{0.5}TiO₃-BiFeO₃ ceramics P. Marchet, E. Boucher, V. Dorcet, J.P. Mercurio.
- [3]. Structural and dielectric studies of the Na_{0.5}Bi_{0.5}TiO₃-BiFeO₃ system V. Dorcet, P. Marchet *, G. Trolliard.
- [4]. A. Herabut, A. Safari, J. Am. Ceram. Soc. 80 (11) (1997) 2954.
- [5] K. Yoshii, Y. Hiruma, H. Nagata, T. Takenaka, Jpn. J. Appl. Phys. 45 (5B) (2006) 4493.
- [6] S. Zhao, G. Li, A. Ding, T. Wang, Q. Rui, J. Phys. D: Appl. Phys. 39 (2006) 2277.
- [7] Y.M. Li, W. Chen, J. Zhou, Q. Xu, H.J. Sun, R.X. Xu, Mater. Sci. Eng., B 112 (2004) 5.
- [8] X.X. Wang, X.G. Tang, K.W. Kwok, H.L.W. Chan, C.L. Choy, Appl. Phys. A 80 (2005) 1071.
- [9] D. Lin, D. Xiao, J. Zhu, P. Yu, Appl. Phys. Lett. 88 (2006) 062901.
- [10] D. Lin, D. Xiao, J. Zhu, P. Yu, J. Eur. Ceram. Soc. 26 (2006) 3247.
- [11] Y.M. Li, W. Chen, Q. Xu, J. Zhou, X. Gu, S. Fang, Mater. Chem. Phys. 94 (2005) 328.
- [12] S. Zhang, T.R. Shrout, H. Nagata, Y. Hiruma, T. Takenaka, IEEE Trans. Ultrason., Ferroelectr., Freq. Control 54 (5) (2007) 910

