Investigation of Solid State Refrigeration Potential in $Ba_{0.85}Ca_{0.15}Zr_{0.1}Ti_{0.9}O_3$-based Ferroelectric Ceramics

A Thesis

Submitted

by

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Dedicated to

Lord Shri Krishna

Declaration by the Research Scholar

I hereby declare that the entire work embodied in this thesis entitled "**Investigation of Solid State Refrigeration Potential in $Ba_{0.85}Ca_{0.15}Zr_{0.1}Ti_{0.9}O_3$-based Ferroelectric Ceramics**" is the result of investigations carried out by me in the **School of Engineering**, Indian Institute of Technology Mandi, under the supervision of **Dr. Rahul Vaish** for the award of the degree of **Doctor of Philosophy** is a bona fide record of the research work carried out by me and that it has not been submitted elsewhere for any degree or diploma. In keeping with the general practice, due acknowledgements have been made wherever the work described is based on finding of other investigators.

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Thesis Certificate

I hereby certify that the entire work in this thesis titled "**Investigation of Solid State Refrigeration Potential in $Ba_{0.85}Ca_{0.15}Zr_{0.1}Ti_{0.9}O_3$-based Ferroelectric Ceramics**" has been carried out by **Satyanarayan Patel**, under my supervision in the **School of Engineering,** Indian Institute of Technology Mandi for the award of the degree **Doctor of Philosophy**. The contents of this thesis, in full or in parts, have not been submitted to any other Institute or University for the award of any degree or diploma.

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Preamble

Ferroelectrics are the second most important class of electronic materials after semiconductors and are slowly gaining momentum in various novel applications. This has allowed them to break free of the traditional applications of actuators and sensors to novel technologies like solar energy harvesting, catalytic effect and solid-state refrigeration. The most promising among them is the solid-state refrigeration which is on the cusp of commercial success pending a few minor drawbacks including low adiabatic temperature change, low volume specific entropy change, and temperature invariant performance. It is an established fact the ferroelectric behaviour is a function of the domain response/switching behaviour when subjected to external impetus. Thus, domain engineering is the key for inception of tuneable material attributes. Another successfully approach can be that of chemical modifications in the form of doping or solid-solutions. In this regards, this study attempts to shed light on the use of various physical and chemical routes towards systematic investigation of exploring and enhancing (electro) caloric effects in bulk lead-free $(Ba_{0.85}Ca_{0.15})(Zr_{0.1}Ti_{0.9})O_3$ (BCZT) ceramics. Caloric estimation have been made using Maxwell's relationship for entropy change in ferroic materials and its modified forms, as proposed for associated effects. Emphasis has been laid to discern the effect of various processing, physical and chemical parameters on the caloric performance of these ceramics.

Chapter 2 begins with detailed explanation of fabrication techniques for bulk BCZT ceramics and their characterization. Description has also been provided with respect to measurement of various material parameters such as dielectric analysis and ferroelectric hysteresis measurement.

Chapter 3 is followed by determination of dynamic hysteresis scaling behavior and measurement of electrocaloric effect in pristine BCZT and Fe-doped BCZT ceramics. The ameliorating effects of Fe doping have been explained in terms of switching energy and hysteresis scaling exponents have been determined.

Chapter 4 continues with investigating the effect of Sn and Sr addition on electrocaloric behavior in pristine BCZT system. The effect of doping concentration on the electrocaloric (EC) performance as well as ferroelectric behavior has been discussed.

Significant improvement was obtained in terms of maximum adiabatic temperature change. In this regards, the composition with the most temperature insensitive EC performance was selected and expanded upon. It was observed that relatively good performance can be obtained over a wide (60K) temperature range in the vicinity of room temperature.

In Chapter 5 analysis of processing parameters (sintering temperature/time) was conducted to obtain the best values for enhanced EC performance. This study investigates the effect of varying sintering time and temperature on maximum adiabatic temperature change, temperature change profile, grain size and its effect. This is expected to compliment the process of optimizing material chemistry as undertaken in earlier chapters.

Chapter 6 first attempts towards unification of two individual caloric effects (EC and elastocaloric (eC)) using bulk lead-free ferroelectric ceramics. We have investigated the multicaloric cooling potential in $(Ba_{0.85}Ca_{0.15})(Zr_{0.1}Ti_{0.9})O_3$ (BCZT) polycrystalline ceramic. Additionally, a novel cycle has been proposed for effective coupling of the two caloric effects to obtain enhanced coupled-caloric cooling capacity in bulk ferroelectric ceramics.

Chapter 7 discussed various modes of entropy change mechanisms with respect to bulk ferroelectric materials. Details have also been provided on how these can give rise to multiple caloric effects and how to suitably combine these using novel electro-thermo-mechanical cycles to obtain enhanced cooling.

Chapter 8 is followed by a discussion regarding other non-conventional caloric effects in ferroelectric materials and how to quantify these effects based on modified forms of Maxwell's relationship. Additional details have been provided regarding the origin and behavior of these caloric effects as explained in terms of various actuation mechanisms.

The thesis concludes by summarizing the key findings of the investigation and highlighting the best results obtained during individual studies. This research is expected to greatly benefit the field of ferroelectric solid-state refrigeration and to expedite the development of a practical cooling system. The following publications are largely based on the studies conducted as a part of the research work reported over here.

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