INVESTIGATION ON VARIOUS METHODS TO ENHANCE THE PYROELECTRIC PERFORMANCE OF LEAD-FREE CERAMICS

A THESIS

Submitted by

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Dedicated to

my teachers

and

family

Indian Institute of Technology Mandi
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Declaration by the Research Scholar

This is to certify that the thesis titled **"Investigation on various methods to enhance the pyroelectric performance of lead-free ceramics"** submitted by me, to the Indian Institute of Technology Mandi for the award of the degree of **Master of Science (by research),** is a bonafide record of the research work carried out by me in the School of Engineering, Indian Institute of Technology Mandi, under the supervision of Dr. Rahul Vaish. 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.

In keeping with the general practice of reporting scientific observation, due acknowledgements have been made wherever the work described is based on the findings of other investigators.

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Preamble

The pyroelectric materials are well-known for their unique thermo-electric conversion ability as these materials have very high sensitivity towards temporal change in temperature and hence have huge market for sensors, detectors, thermal imaging and energy harvesting applications. In order to assess the performance of materials for pyroelectric applications, a variety of figure of merits (FOMs) have been developed to describe the ability of materials to generate energy for practical applications.These include FOMs for current responsivity (F_i), detectivity(F_d), voltage responsivity (F_v) and energy harvesting (F_e and F_e^*). These figures of merit depend mainly on factors like pyroelectric coefficient, dielectric constant, dielectric loss and specific heat which play a detrimental role in enhancing their figure of merits (FOMs). In this context, a plethora of ferroelectric oxides based on$LiNbO_3$, $BaTiO_3$, $Sr_{0.5}Ba_{0.5}Nb_2O_6$, $Na_{1/2}Bi_{1/2}TiO_3$ etc. in pure and modified forms are widely explored with renewed interest in last decade to match up with the lead-based counterparts. Although the pyroelectric effect has been studied for a long time and significant number of articles been already published, the thrust for looking advanced materials with ultra-high pyroelectric performance around room temperature is still of great interest considering their extensive applications. In this direction, the present study deals with investigation of performance of various lead-free ceramics for pyroelectric device applications. This advancement in pyroelectric performance is achieved by tuning the above mentioned parameters by various chemical and physical routes which is the main focus of the present work. Emphasis is also led on the potential of fabricated materials with the best lead-based and lead-free systems available in the market by comparing their performance for device applications.

The results obtained in the present investigations have been compiled as six chapters as follows:

Chapter 1 sheds light on introduction to pyroelectric materials and dwells on the importance of developing lead-free ceramics as a substitute for lead-based systems for many pyroelectric applications to date.

Chapter 2 begins with investigation of chemical modifications route (by doping) to improve their performance. In this context, the pyroelectric aspects of Sn doped $BaTiO_3$ ($BaTi_{1-x}Sn_xO_3$) were studied in detail. Description has also been provided with respect to measurement of various material parameters such as dielectric analysis and hysteresis measurement.

Chapter 3 expands on the previous study with exploring the physical modifications route which is established by inducing porosity by adding Poly(methyl methacrylate)(PMMA) as the pore former in $BaTi_{1-x}Sn_xO_3$(BTS) ceramics. Porosity was varied by adding PMMA 0,2,4,6 and 8 % by wt. to the base ceramic and was systematically characterized for microstructural, ferroelectric, dielectric and pyroelectric properties.

Chapter 4 explores the composite route by glass addition technique to improve the performance of pyroelectric ceramics. $3BaO$-$3TiO_2$-B_2O_3(BTBO) glass was added to $Ba_{0.85}Sr_{0.15}Zr_{0.1}Ti_{0.9}O_3$(BST-BZT) ceramics and the role of glass in ceramics microstructure has been investigated in detail. All the pyroelectric figure of merits was systematically estimated to present the effect of glass in enhancing pyroelectric performance of BST-BZT ceramics.

Chapter 5 investigates the effect of tuning phase transitions to improve the pyroelectric performance of $(1-x)(Ba_{0.9}Ca_{0.1})TiO_3$–$xBa(Sn_{0.2}Ti_{0.8})O_3$ (BCT-xBST) lead-free ceramics. All the FOMs were systematically obtained and confirmed by measuring electrical signal from pyroelectric set-up. All the FOMs were finally compared with best lead-based and best lead-free systems to highlight the significance of designing phase transitions for pyroelectric applications.

Chapter 6 concludes the thesis by summarizing the key findings of the investigation and highlights the best results obtained during individual studies.

The following publications are largely based on the studies conducted as a part of the research work reported over here.

1. **K.S.Srikanth**, Satyanarayan Patel, Sebastian Steiner and Rahul Vaish, "Engineered microstructure for tailoring the pyroelectric performance of $Ba_{0.85}Sr_{0.15}Zr_{0.1}Ti_{0.9}O_3$ ceramics by $3BaO$-$3TiO_2$-B_2O_3 glass addition", *Appl. Phys. Lett.***110** (23), 232901 (2017).

2. **K.S.Srikanth**,V.P.Singh and Rahul Vaish, "Enhanced pyroelectric figure of merits of porous $BaSn_{0.05}Ti_{0.95}O_3$ ceramics", *J. Eur. Ceram. Soc.***37** (13), 3943-3950 (2017).

3. **K.S.Srikanth**, Satyanarayan Patel, Sebastian Steiner and Rahul Vaish, "Pyroelectric signal in $(Ba,Ca)TiO_3$– $xBa(Sn,Ti)O_3$ ceramics: A viable alternative for lead based ceramics", *Scripta Materialia* **146***,* 146-149 (2017).

4. **K.S. Srikanth**, Satyanarayan Patel and Rahul Vaish, "Pyroelectric performance of $BaTi_{1-x}Sn_xO_3$ ceramics", *Int. J. Appl. Ceram. Tech.* **15** (2), 546-553 (2017).

Other articles include:

1. **K.S.Srikanth** and Rahul Vaish, "Enhanced electrocaloric, pyroelectric and energy storage performance of $BaCe_xTi_{1-x}O_3$ ceramics", *J. Eur. Ceram. Soc.***37** (13), 3927-3933 (2017).

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3. S. Patel, **K.S. Srikanth**and R. Vaish, “Effect of sintering parameters on the dynamic hysteresis scaling behavior of $Ba_{0.85}Sr_{0.15}Zr_{0.1}Ti_{0.9}O_3$ ceramics”, *Integrated Ferroelectrics* **176** (1),95-108: (2016).

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5. **K.S. Srikanth**, Sidhant Kumar, Satyanarayan Patel, Puneet Azad and Rahul Vaish, “Pyroelectric energy harvesting using $Ba_{0.85}Sr_{0.15}Zr_{0.1}Ti_{0.9}O_3$ ceramics and its cement based composites, *J. Intell. Mater. Syst. Struct.* (2017) (Under review).

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8. **K.S.Srikanth**, Satyanarayan Patel and Rahul Vaish, “Electrocaloric behavior and temperature dependent scaling of dynamic hysteresis of $Ba_xSr_{1-x}TiO_3$ (x=0.7, 0.8 and 0.9) bulk ceramics”, *J. Aust. Ceram. Soc.* ***54 (3),*** 439-450 (2017).

9.**K.S. Srikanth**, V.P.Singh, Satyanarayan Patel and Rahul Vaish, “Pyroelectric performance of $[Bi_{0.48}Na_{0.4032}K_{0.0768}]Sr_{0.04}(Ti_{0.975}Nb_{0.025})O_3$ ceramics”, *J. Aust. Ceram. Soc. (2017) (Under Review)*

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