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INDIAN INSTITUTE OF TECHNOLOGY
BANARAS HINDU UNIVERSITY

$LiNbO_3$ based Environmental - friendly high T_c Ceramics for Electrical Energy Storage and Device Applications

Thesis Submitted in partial fulfillment for the Award of Degree

Doctor of Philosophy

By

Satyendra Kumar Satyarthi

SCHOOL OF MATERIALS SCIENCE & TECHNOLOGY
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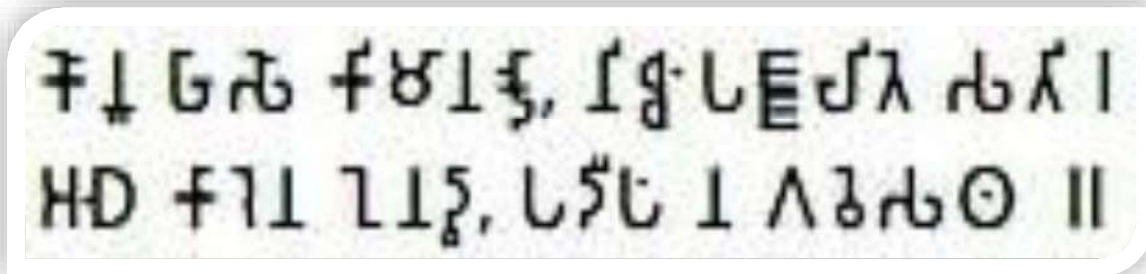

कोनू हासो कि मानन्दो, निच्चं पज्जलिते सति।

अंध कारेन ओनद्धा, पदीपं न गवेसथ॥

अर्थात्

जहाँ प्रतिक्षण सब कुछ जल (नष्ट हो रहा) रहा हो,

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This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

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Varanasi, Uttar Pradesh, India (Satyendra Kumar Satyarthi)

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LIST OF SYMBOLS & ABBREVIATIONS

η	Energy efficiency
α	Polarizability
$h\upsilon$	Photon energy
E_g	Band gap
υ	frequency
h	Plank constant
k	Boltzmann Constant
K	Kelvin
E_a	Activation Energy
U	Energy density
Å	Angstrom
ψ	Electric potential barrier
Hz	Hertz
T	Temperature
T_c	Curie temperature
χ	Susceptibility
σ	Conductivity
L_d	Debye length
V_{oc}	Open-circuit voltage
θ	Angle
eV	Electron Volt
λ	Wavelength
E_i	Applied electric field specific value
µm	Micrometer
ε	Dielectric Permittivity
τ	Dielectric Relaxation Time
ρ	Total charge per unit area in electrode
P	Ferroelectric polarization

E_c	Coercive field
P_{max}	Maximum polarization
P_s	Spontaneous polarization
Pr	Remnant polarization
E_b	Breakdown strength
XPS	X-ray spectroscopy
AFM	Atomic force microscopy
C.B.	Conduction band
V.B.	Valence band
DW	Domain wall
FESEM	Field emission scanning electron microscopy
HRTEM	High resolution transmission microscopy
FTIR	Fourier transform infrared
XRD	X-Ray diffraction
XPS	X-ray photoelectron spectroscopy
PL	Photoluminescence spectroscopy
UV-Vis.	Ultra Violet visible spectroscopy
AFM	Atomic force microscopy

PREFACE

The rapid increases in urbanization, high adaptability of portable electronic devices, daily increase in Internet on things, limitation of conventional energy sources, and rapid increases in pollution make the crisis of energy supply, and conventional fossil fuel energy sources cannot fulfill the demand energy supply. For a few decades, technologists, Researchers, and scientists have started thinking and developing new electrical energy sources in which energy materials always play a crucial role. As in this area of research developed, researchers started thinking about developing energy materials with various properties such as electrical energy materials should be highly useful in various kinds of applications, electrical energy materials exist with high energy-related properties, electrical energy materials should be environmentally friendly like it must be Lead (Pb) and Bismuth (Bi) free with nontoxic nature, materials should be applicable for a different kind of odd environmental condition like in the low temperature and high temperature that means highly thermally stable. In today, portable electronic devices have become a necessary part of everyone's life in many forms with different kinds of applications worldwide, therefore. The alternatives to fossil fuels are so much needed as batteries, sensors, optical displays, and sensing devices. Supply electrical energy in various kinds of electronic devices; dielectric-based batteries have played an important role for many decades in this kind of energy sector for portable devices, sensors, and home-made appliances. Dielectrics-based capacitors are the key components that make a great contribution to energy storage in energy applications. When we started studying this, it came to the knowledge that most of the energy materials are associated with non-ecologically unfriendly and also not very suitable for high-temperature applications in the form of batteries or other sensing and display devices. It has been proven that the energy density of dielectric-based capacitors is lower than conventional batteries, but the research scope in this area is very wide with positive results. The capacitors are associated with their unique importance as well as an important domain of applicability in the energy storage sectors because of their fast charging with fast discharging phenomenon, which is not found in batteries.

There are a lot of ceramic dielectric materials are generally in use, and those are also reported in various research papers, materials like $PbTiO_3$, $BiFeO_3$, $Bi_4Ti_3O_{12}$, $Bi_4Si_3O_{12}$, $BaTiO_3$, $BaZr_{1-x}Ti_xO_2$ (BZT), $Ba_{1-x}Sr_xTiO_3$ and many other solid solutions are used as energy storage dielectrics in the capacitors from the past many decades and are still very useful in various area of applications but when the environmentally friendly and high-temperature stability comes in the discussion, the alternatives of these materials are also a crucial need. Above all listed materials associated with good dielectric constant but they exist with below 500 ºC of curie temperature that's means high-temperature applications are very limited at but not at too high temperatures is observed at industries, mining's, space and other places. Rather than these materials, many solid solutions are also useful for dielectrics applications, but again, when high temperatures come into discussion, the same limitations come to the front. Several decades ago, Bellman synthesized $LiNbO_3$ in their laboratory with excellent Dielectric, Ferroelectric, Piezoelectric, and Photorefractive properties, and after that, they published an article in 1965 about the single crystal development of $LiNbO_3$ (LN) by using Czochralski method. Ashkin et al reported the photorefractive properties of $LiNbO_3$ (LN) in 1966. From the first development of $LiNbO_3$ to now, much research has been done for the synthesis of different kinds of LN, like ceramics, Nanofibers, thin films, and single crystals, for applications in various fields like sensor actuators, and energy storage, but many huge areas are still not filled and vacant for the extensive research work.

In this present work, we have selected LiNbO3 ceramic as a base material for the whole research work, and we used different additive and doping materials to enhance properties like sintering and related to electrical energy storage like Dielectric, ferroelectric, and optical properties. LN was reported as a Rhombohedral structure with R3c space group with a very high curie temperature of about 1210 ºC for the ceramic form. The addition and the doping in $LiNbO_3$ have been done using K_2O, Sm_2O_3, Dy_2O_3, and TiO_2, respectively. Where the K_2O is used as an additive in weight-by-weight percentage form, Sm^{3+} was doped at the Li site with different stoichiometric ratios, and Dy^{3+} and Ti^{4+} were co-doped in LN in different solid solutions. Our investigations on $LiNbO_3$ ceramics have obtained several important findings, which are as follows.

1. Enhanced Dielectrics, Ferroelectric and Optical properties of Lithium Niobate for High Temperature Applications Using Potassium Oxide (K_2O) Additive

Dielectrics, Ferroelectric, and Optical properties of Lithium Niobate have been examined using Potassium Oxide (K_2O) as an additive on the samples prepared by solid-state reaction using high-energy ball milling. The crystal structure analysis by Rietveld structure refinement confirms that the $LiNbO_3$ (LN) with K_2O additive also exhibits the rhombohedral structure with the R3c space group. The SEM characterization of the microstructure reveals that the samples sintered at a temperature of 1050 °C have regular and uniform grain morphology and better density. The average grain size decreases for the K_2O added compositions in the beginning and increases later for higher concentrations of additive. Thermal study with TGA suggests that as the activation energy decreases, the polarization is enhanced, and the LN composition with 2.72 wt% K_2O additive shows the best thermal stability. The frequency and temperature-dependent dielectric properties were investigated in a wide range of frequencies, and a substantial enhancement in the dielectric constant of LN was obtained by K_2O addition. A significant enhancement in permittivity is obtained with an increase in temperature. The band gap values for the various compositions' direct and indirect band gaps are also determined. The least direct band gap is discovered to be 2.36 eV for the composition with 2.72 wt% K_2O additive. The composition-dependent photoluminescence (PL) emission studies reveal that the emission spectra for both the pure $LiNbO_3$ and K_2O-added $LiNbO_3$ compositions lie in the UV-visible region. All the investigated compositions exhibit distinct green, yellow, and red emission peaks. The LN with 2.72 wt% K_2O additive shows the best dielectric, thermal stability, and polarization response with maximum polarization P_s ~1.16 μC/cm^2. The present investigations suggest that the properties of LN can be significantly improved by using K_2O additive for sustainable, low-cost, environmentally friendly energy storage material for high-temperature applications.

2. Electrical and Optical Properties of Environmental Friendly $Li_{(1-x)}Sm_{x/3}NbO_3$ Ceramics for High Temperature Energy Storage Applications

This research work delves into the synthesis and characterization of $Li_{(1-x)}Sm_{(x/3)}NbO_3$ ceramic, employing a high-energy ball milling process. The investigation explores the incorporation of Sm^{3+} at the Li^{+1} site across a range of compositions (x = 0, 0.01, 0.02, 0.03, 0.04, 0.05). Structural analysis, using X-ray diffraction (XRD) and Rietveld structural refinement, establishes that within the investigated composition range, no significant changes in the crystal structure are evident. The X-ray photoelectron spectroscopy revealed the presence of oxygen vacancies as well as the stable oxidation state of different elements like O^{2-}, Nb^{5+}, Sm^{3+}, Li^{1+}. At sintering temperature 1050°C, the average grain sizes vary approximately from 1.5 μm to 3.8 μm for different compositions with regular grain morphology. The UV-Vis analysis reveals a noteworthy reduction in the band gap to 3.09 ± 0.003 eV for the x = 0.01 composition. Photoluminescence studies exhibit distinct green, orange, and red bands, with the highest intensity observed for x = 0.01, showcasing promising optical properties. The dielectric permittivity of Sm-substituted compositions surpasses the response of pure $LiNbO_3$, demonstrating an increasing trend with temperature in the frequency range 100 Hz to 1 MHz intriguingly, no Curie temperature is observed up to 500º C for any composition. The polarization versus electric field hysteresis loop response highlights better polarization characteristics at the room temperature and maximum polarization is 0.66 μC/cm^2 for the composition x =0.05. The energy storage response of the developed compositions is investigated, which reveals a maximum efficiency of 46.64% for x = 0.04 in $Li_{(1-x)}Sm_{(x/3)}NbO_3$. The tunable optical properties, enhanced dielectric response, and notable energy efficiency of this high T_C ceramics suggest their utility across diverse applications. These findings not only contribute to the understanding of functional ceramic materials but also pave the way for their optimized utilization in advanced technological applications, particularly in energy storage devices under non ambient conditions at high temperatures.

3. Investigation of Multifaceted Properties for Environment friendly (1-x)$LiNbO_3$-x($Li_{0.5}Dy_{0.5}$)TiO_3 Solid Solutions

This research work presents experimental data on the development of environmentally friendly ceramics based on the solid solution (1-x)$LiNbO_3$-x($Li_{0.5}Dy_{0.5}$)TiO_3 prepared through high-energy ball milling with varying compositions. Structural analysis, employing Rietveld structure refinement, reveals a consistent presence of a mixed phase, encompassing cubic and Rhombohedral phases for compositions up to x = 0.1. Sintering at 1050 °C yields varied average grain sizes (3.46 μm to 1.09 μm) with distinct compositions, displaying regular and consistent grain morphology. X-ray photoelectron spectroscopy indicates the presence of oxygen vacancies and reveals the oxidation states of elements such as O^{1-}, O^{2-}, Nb^{5+}, Dy^{3+}, Ti^{4+}, and Ti^{3+}. Dielectric properties are investigated across a wide frequency range (1 kHz to 1 MHz) and temperatures up to 500 °C, revealing a frequency-dependent reduction in both dielectric constant and dielectric loss for all compositions. Ferroelectric properties show enhancement at room temperature, with the maximum polarization reaching approximately 0.8 μC/cm^2 for x = 0.1. A band gap reduction is observed in $LiNbO_3$ with increasing ($Li_{0.5}Dy_{0.5}TiO_3$) contents, and a minimum direct band gap of 2.95 ± 0.002 eV is obtained for x = 0.05 composition. Photoluminescence analysis demonstrates the presence of Yellow, Cyan, and Blue bands, which are valuable for Yellow laser and Light light-emitting diodes (LEDs) applications. The dielectric permittivity of (1-x)$LiNbO_3$-x($Li_{0.5}Dy_{0.5}$)TiO_3 ceramics shows a better response with an increase of temperature in the frequency range of 1 kHz to 1 MHz for all compositions than Pure $LiNbO_3$ and there is also no curie temperature observed up to 500ºC for any composition this makes it a candidate material for high-temperature applications. We achieved a maximum recoverable energy storage density of 17.96 mJ/cm^3 and a maximum energy efficiency of 34.00 %. Overall, these findings provide valuable insights into the structural, electrical, and optical properties of the studied ceramics, suggesting their potential for the development of high-temperature phosphor materials for white LEDs, yellow lasers, energy storage, and other diverse high-temperature technological applications.