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Research Article

Growth and Characterization of Ferroelectric A Strategic Material for Commercialization and Usage

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Abstract

Ferroelectric means certain materials possessing spontaneous polarized domains and whose direction of polarization can be reversed by application of applied electric field. Ferroelectrics are in general insulators. Ferroelctricity is found in special group of compounds which synthesizes in structures having no centre of symmetry. It is never found in an element .They have permanent dipole moment and therefore they are referred as polar dielectrics .Some of the most common structures in which ferroelectric materials crystallize are tetragonal, orthorhombic, monoclinic, tungsten bronze, perovskite, pyrochlore. Ferroelectric materials discovered by Valasek in 1920 in the form of bulk crystals of Rochell salt. Since then the materials have been prepared primarily in the form of bulk crystals; ceramics; polymers and thin films-increasing their exploitability. Ferroelectric materials offer a wide range of useful properties namely ferroelectric hysteresis, high permittivity, high piezoelectric effects, high pyroelectric coefficient, strong electro-optic effects etc. The characteristics of ferroelectric materials enables to explore the drastic change in their properties if the material is synthesized in the Nano range. Physical and chemical methods are found to be of great significance for the various applications. In my work, have grown pure and rare-earth doped potassium niobate crystals, a perovskite characterised using XRD, DTA, SEM, and ICPA. The material has been explored by studying its dielectric, conductivity, pyroelectric study it is found that the rare earth doping is found to act as a growth habit modifier, dopant substitution influences the local polarisation in the crystals, its conductivity has been also due to polaron hopping responsible for the generation of vacancy site distribution. An attempt has been made to quantify the radius of polaron hopping due to rare-earth doping. Recently special focus has been given to ferroelectric nanostructures that represents better sensing properties than their bulk counterparts as well as thin films. To name the various applications of Nano ferroelectrics in different types gas sensors, piezoelectric and pyroelectric sensors of mechanothermal signals as photo detectors, ionising radiation detectors and biosensors. However, the future scope has been recently reported to be an overlapping of physical, chemical along with biological methods in exploring the ferroelectric materials namely $BaTiO_3$ nanoparticle to have great commercial potential.

Keywords: *Nano Ferroelectrics; Biosensors; Medical Sensors*

Introduction

Ferro electricity is a characteristic of certain materials that possess a spontaneous electric polarization that can be reversed by the application of an external electric field [1,2] All ferroelectrics are pyro electric, with the additional property that their natural electrical polarization is reversible. Ferro electricity was discovered in 1920 in Rochelle salt by Valasek [3] Some of the most common structures in which ferroelectric materials crystallize are tetragonal, orthorhombic, monoclinic, tungsten bronze, perovskite, pyrochlore. Ferroelectric materials have become potentially useful for device applications because of their high dielectric constant, non-linear behaviour, polarization reversal, and domain structure and pyro electric & piezoelectric behaviour in a temperature range where semiconducting materials fail.

The most prominent features of ferroelectric properties are hysteresis and nonlinearity in the relation between the polarization *P* and the applied electric field *E*. Ferroelectric materials exhibit ferroelectric properties only at temperatures below the curie temperature Tc because they are polar; For temperatures above the Curie temperature *Tc*, the crystal assumes a cubic structure and is in the para electric unpolarised state. At temperatures above it, they are not polar. Ferroelectric materials have a non-Centro symmetric crystalline structure, and are thus capable of generating a second harmonic of light [4] This distinctive feature of ferroelectrics is the basis for a growing number of applications of ferroelectric nanoparticles as imaging/diagnostic agents and Nano probes in optical imaging [5]. For example, second harmonic generation imaging has been successfully used for detection of osteogenesis imperfecta in biopsies of human skin [6] and lung cancer [7]. Nonlinear optical properties of ferroelectric nanomaterial's can be used for optical phase conjugation [8] and nonlinear microscopy [9,10] – these properties have allowed them to spread to the area of medical sensors.

Ferroelectric materials are classified as:

(i)Barium titanate ($BaTi0_3$)- [ABO_3], (ii) Potassium dihydrogen phosphate (abbreviated KDP, KH_2P0_4), (iii) Potassium-sodium tartrate tetra hydrate (Rochelle salt, $KNaC_4H_40_6$*$4H_20$), (iv) Triglycine sulphate (abbreviated TGS,(NH_2CH_2COOH)$3H_2S0_4$), (v) Alloys of lead, zirconium, & titanium oxide (abbreviated PZT, alloys of PbO,$Zr0_2$,&$Ti0_2$) and (vi) Polyvinylidene fluoride (abbreviated PVDF,-(CH_2-CF_2)-type ferroelectrics.

The most commonly used ferroelectrics have the Perovskite structure, with the chemical formula $AB0_3$. $BaTi0_3$ and $KNbO_3$belongs to the family of $AB0_3$. Perovskite mineral ($CaTi0_3$) structures, in which A and B are metals. The total charge of the A and B positive ions must be +6, and A and B must be of quite different sizes; the smaller ion, with a larger charge, must be a transition metal. There are now more than hundred materials that exhibit ferroelectric or anti ferroelectric properties. Now, ferroelectric materials can be modified so that certain values of the required properties can be achieved at room temperature. The control of properties is possible by varying the composition in solid solution or by incorporating suitable additives. [11]. All ferroelectrics possess piezoelectric and pyro electric character so their sensors can be fabricated or thought of. Potassium niobate, $KNbO_3$, single crystals have been thoroughly studied due to their applications in nonlinear optical, surface acoustic wave (SAW), and electromechanical transducer devices [12]. Ferroelectric $KNbO_3$ exhibits three successive phase transitions similar to that of $BaTiO_3$.[13]. Pyroelectricity, is one of the significant characteristics of polar materials and render these materials a significant solid state sensor for device application. It involves generation of pyroelectric current when the material is subjected to change in temperature. Pyroelectric effect has fundamental and applied interest. Pyroelectric detectors have lower sensitivity than photon detectors. However, they have useful features [14] of room temperature operation, simplicity of construction and operation and do not require an external bias. They can be used to detect any radiation (X-rays to microwaves) which causes change of temperature [15].

Pyroelectricity [16] is a necessary attribute for a ferroelectric crystal. Nowadays, the best industrial performance are given by ferroelectrics[17] i.e. substances with permanent electric dipoles even in the absence of an external electric field, such as the well- known perovskite materials $BaTiO_3$,$PbTiO_3$,$KNbO_3$ etc [18]. So far many new dielectric materials have been developed in recent years due to their interesting properties [19-22].

Recent advances in nanotechnologies, especially in nano instrumentation [23] and materials nanofabrication [24], allowed the direct probing of Ferro electricity at the nanoscale. This new world of nanoscale ferroelectrics raised fundamental questions and stimulated very active research in both academic and industrial sectors [25]. Almost all of the attention for the mentioned review [26] was devoted to the *thin film* nanoscale device structures (which can be easily integrated with a Si chip) with focus on ultrafast switching, electro caloric coolers for computers, phase-array radar, three-dimensional trenched capacitors for dynamic random access memories, room temperature magnetic field detectors, and miniature X-ray and neutron sources.

Experimental & Results

We have grown four compositions of potassium niobate single crystals with 0 wt% Sm (KN), 1 wt% Sm (KND-1), 2 wt% Sm (KND-2) and 1 wt% Sm + 1 wt% Sn (KND-3) by controlled cooling of the melt. In powder X-ray diffraction investigations, it is shown that doping has decreased lattice parameter b_0 values except for KND-1 retaining an orthorhombic nature and has increased tetragonality in the crystals. SEM study revealed that with increasing percentage doping, the grain size had increased. Growth habits are significantly influenced and modified due to doping. The layered growth of KN shows a needle-shaped growth habit with a rectangular cross section in KND-1. This change is more predominant in KND-3 and is insignificant in KND-2. It appears that impurities influence the kinetics of nucleation and growth [27].

Electrical conductivity as a function of temperature was studied from room temperature up to 500°C for these compositions. At room temperature the electrical conductivity has increased due to Sm as well as (Sm & Sn) doping. Crystals show increase in conductivity with temperature. Both pure and doped compositions show an anomalous behaviour with a small hump around their respective transition temperatures except KND-2. The conductivity in pure and doped potassium niobate is a complex phenomenon namely due to electronic contribution; extrinsic impurity; presence of impurity defects; vacancies created due to oxygen deficiency as well as doping and polaron hopping [28].The crystals were characterized for their pyroelectric behavior over a temperature range of 303 K to

773K. The pyroelectric coefficient shows an anomaly around expected transition temperature. The pyroelectric coefficient also show a change in polarity. The mechanism of pyroelectricity in these grown materials is discussed considering the pyroelectric figure of merit (PFM) [29].Dielectric properties were also studied using a LCR tester at varies temperatures, from 50 Hz to 100 KHz. Due to samarium doping change in the dielectric constant and dielectric losses are attributed to domain walls and Maxwell Wagner type respectively [30].Dielectric permittivity in the frequency range 01Hz-10MHz was studied using an impedance analyser at room temperature. Due to Sm doping the capacitance has increased about hundred times. Resistivity has not changed for lower frequency however it has increased ten times for higher frequency. It is also observed that Sm doping has marginally increased Tan δ for higher frequency, reduced the impedance, retaining value of permittivity of pure potassium niobate single crystals for the entire frequency range. The particular study has been undertaken to observe the effect of rare earth Sm on potassium niobate single crystals at room temperature to investigate it's potential to be used as a capacitor for device applications in the miniature circuits as resonators or filter applications [31].

In perovskites some intermediate region between large and small polarons is realized. An attempt has been made to quantify the polaron hopping distance &hopping energy associated with such mechanism. Using results of the DC conductivity measurements all four compositions, the values of the density of states at the Fermi level $N(E_F)$,the most probable Mott's hopping distance R & hopping energy W have been evaluated. A large value of hopping distance of (10^4) ^{0}A; much larger than the lattice parameters suggests large radius polaron observed in pure potassium niobate. However, it's value reduces due to rare earth Sm doping. Further reduction in hopping distance is observed due to higher percentage of Sm doping [32].

Conclusions of The Study Undertaken for Pure &Doped $Knbo_3$

Growth habits are significantly influenced and modified due to doping. The layered growth of KN shows a needle-shaped growth habit with a rectangular cross section in KND-1. This change is more predominant in KND-3 and is insignificant in KND-2. It appears that impurities influence the kinetics of nucleation and growth [27]. The conductivity in pure and doped potassium niobate is a complex phenomenon namely due to electronic contribution; extrinsic impurity; presence of impurity defects; vacancies created due to oxygen deficiency as well as doping and polaron hopping [28].The pyroelectric coefficient shows an anomaly around expected transition temperature. The pyroelectric coefficient also show a change in polarity. The mechanism of pyroelectricity in these grown materials is discussed considering the pyroelectric figure of merit (PFM) [29]. A high dielectric constant &high dielectric loss is attributed to Maxwell-Wagner type & dipolar relaxation respectively. Rare earth Sm reduces thickness of surface charge layers thus increasing loss factor. Heavy loss is attributed to dipolar relaxation [30]. The Dielectric permittivity frequencies from 01Hz to 10MHz has been carried out to study the effect of rare earth Sm on potassium niobate single crystals at room temperature to investigate it's potential to be used as a capacitor for device applications in the miniature circuits as resonators or filter applications [31]. A large value of hopping distance of (10^4) ^{0}A; much larger than the lattice parameters suggests large radius polaron observed in pure potassium niobate. However, it's value reduces due to rare earth Sm doping. Further reduction in hopping distance is observed due to higher percentage of Sm doping [32].

Future Scope

A century old ferroelectric material needs to be explored in the most significant way so as to be used not only as a strategic material but also a commercially realistic material of commercial usage .This is only possible if the methods to fabricate ferroelectric material particle involves a suitable combination of Chemical, Physical, Chemical-Physical, Biological in the Nano range [33] adopting a trans disciplinary approach in research instead of interdisciplinary one. Proposed method for the fabrication of ABO_3 type ferroelectric material in the nano range is the need of time .Later the various methods to characterize them can be effectively used. This paper highlights the need for material preparation, so that the grown ferroelectric is biocompatible, easy to fabricate, need of the time and can to be used as a medical sensor in medicine fraternity.

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