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Optical properties of ferroelectric lanthanum lithium niobate

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ABSTRACT

Fine structures (ferroelectric domains), ferroelectricity and Second Harmonic Generation results were found and studied as a function of laser linearly and circularly polarization dependent polarized excitations in ferroelectric stoichiometric $La_{0.05}Li_{0.85}NbO_3$ nanocrystals ceramic material. Scanning Electron Microscope images are taken as a comparison to Second Harmonic Generation intensity profiles revealed fine structures. By using laser polar measured response we are able to find the angle orientation from 0° to 90° angles of ferroelectric domains with highly good definition contrast obtained in blue/gray colors. It shows ferroelectric hysteresis loops at room temperature with a polarization saturation of (0.247 μC/cm^2), remnant polarization of (0.15 μC/cm^2) and coercitivity field of (1.31 kV/cm). X-ray Diffraction, Atomic Force Microscope, Raman spectroscopy and X-ray Photoelectron Spectroscopy, revealed well formed of ferroelectric ABO_3 perovskite crystal structure, piezo-electric image response indicate ferroelectric pattern domain structure, new vibrations modes on LaO_6, LiO_6 and NbO_6 octahedral sites and binding energies of electronic structure of La^{57}, Nb^{41}, O^8, Li^3 from the surface of the ferroelectric stoichiometric $La_{0.05}Li_{0.85}NbO_3$ nanocrystals ceramic material, respectively.

1. Introduction

Ferroelectric effect is a property of certain materials that may possess spontaneous ferroelectric polarization ($\mathbf{P_s}$) that can be reversed by applying an external electric field ($\mathbf{E_c}$) [1]. The ferroelectric oxides with ABO_3 perovskite crystal structures with high dielectric-κ constant have been attracting lots of attentions due to its combination of properties such as pyro-electric, piezo-electric, ferroelectric-magnetic and electro-optical in one single phase [2]. In ABO_3 Ferroelectric materials the $\mathbf{P_s}$, is achieved by cations from the transition metal group of the periodic table which are in the center of octahedron anions formed by oxygen atoms at the off-center position arising into a lattice distortion [3]. These kind of couplings between properties in one single phase materials make them suitable and useful candidates to develop new electronic devices, from a variety of applications such as in birefringence, sensors, micro-electro-mechanical systems, acoustic transducers, multiferroics, linear acoustic relays, beam deflectors, phase conjugators, dielectric wave guides, nonvolatile random access memories and holographic data processing, just to mention few [4]. On the other hand, ferroelectric domains in Ferroelectric ceramic nanomaterials, thin films and nanoparticles have electric polarization in absence of an external electric field. Furthermore, the vector polarization must have two stable states which can be irreversible by applying an external electric field. Ferroelectrical characterization with non-destructive methods are used as Atomic Force Microscope (AFM), Piezoresponse Force Microscope (PFM), hysteresis loop, just for mention a few [5]. K. Vasudevan *et al.*, reported ferroelectric properties at surface of nanomaterials by using Piezoresponse Force Microscopy (PFM) and AFM as complementary with macroscopic Polarization-Electric Field (P-E) method in lead based piezoelectric ceramics as $Pb(Zr_xTi_{1-x})O_3$ (PZT), bisthmut ferrite ($BiFeO_3$) thin films, barium titanate ($BaTiO_3$) and lanthanum aluminate ($LaAlO_3$) [6]. In addition, some of these ferroelectric materials may have a lack of symmetry or centrosymmetric, these types of crystalline structures may be twice as frequent from an optical laser source and may reveal spontaneous polarization (**Ps**) as part of ferroelectric domains in random positions. As a result, Second Harmonic Generation (SHG) turns out to be a powerful tool for detecting nanomaterial structures, phase transitions, lattice rotations and electromagnetic

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coupling in ferroelectric materials in a fast and noninvasive way. Therefore, SHG imaging provides high contrast in materials that have high polarization and noncentrosymmetric structures [7]. M. Fiebig *et al.*, have reported observation of coupled ferro-electric-magnetic domains in yttrium manganese oxide ($YMnO_3$) platelets around 100 μm by using polarized SHG light; their results confirmed that electronic excitations of Mn^{3+} ions lead to bulk second harmonic generation properties [8]. This crystal-symmetry breaking process produces a high resolution images for domain patterns with angle polarization dependence. Liu et al., reported ferroelectric phase transition by using Second Harmonic Generation microscope in ferroelectric lead strontium titanate ($Pb_{0.35}Sr_{0.65}TiO_3$) thin films synthesized by pulsed laser deposition with temperature dependence from 100 K to 400 K [9]. However, in the last decade an intensive research has been performed to substitute lead for some new ferroelectric materials; as alternative to this Lanthanide (La_2O_3) perovskites have been used with great potential in communication technologies devices, electro-optic, etc. [10]. It is well known that small changes in ABO_3 perovskite structures due to doping elements can result in new vibration modes. Thus Raman spectroscopy is very suitable in features such as disorder, interaction with excess carries and quantum confinement as investigating by Dobal et al. [11]. Cabrera et al., reported the synthesis of lanthanum ytterbium oxide ($LaYbO_3$) perovskite ceramic synthesized by a solid state reaction method, which exhibits exotic properties that can be changed by altering its structure or chemical composition rendered in a high distorted structure; this was confirmed by using X-ray Diffraction (XRD) and neutron diffraction characterization methods [12]. Che Bae et al., have reported ferroelectric properties on lanthanum doped bismuth titanate ($Bi_{3.25}La_{0.75}Ti_3O_{12}$) thin films synthesized by sol gel method; ferroelectric values were found at 650 °C, remanent polarization ($2P_r$), coercive field ($2E_c$) of 70 μC/cm^2 and 132 kV/cm using a 200 kV/cm electric field ($\mathbf{E_c}$), respectively. The characterization was done by using X-ray diffraction (XRD), Scanning Electron Microscopy (SEM) and ferroelectric hysteresis loop [13]. It is well know that certain solids can exhibit a level of conductivity, that can be determined by studying the electronic binding structure at the surface of solid systems by using X-ray Photoelectron Spectroscopy (XPS) which is a suitable for electrochromic windows, sensor technologies, fuel cells, solar batteries, just for mention few [14]. Kai Yang et al., reported a new synthesis of lithium (Li^+) doped on lanthanum niobium oxide ($La_{1/3}NbO_3$) perovskite system which is related with many order disordered atomic lattice spatial structure but with good electrical properties. Characterization methods was performed by using X-ray Diffraction (XRD) and SEM, results indicate a crystal structure of $La_{1/3}NbO_3$ synthesized by solid state solution and solubility of Li^+ of a 25% as a part of the compound. Electrical properties showed conduction of Li^+ with values in the order of 7.21×10^{-5} S cm^{-1} at $3x = 0.05$ according to AC impedance analysis [15].

In this work, we present the ferroelectric stoichiometric properties of lanthanum lithium niobate ($La_{0.05}Li_{0.85}NbO_3$) nanocrystals ceramic material synthesized by a solid state reaction analyzed under linearly/circularly polarization dependent by using Second Harmonic Generation microscope. Results indicate ferroelectric domain orientation in blue/gray contrast from 0° to 90° angle. Ferroelectric hysteresis loops obtained at room temperature reveal fine structures and structural characterization by using Atomic Force Microscopy (AFM), Scanning Electronic Microscope (SEM), Raman Spectroscopy and X-ray Photoelectron Spectroscopy (XPS).

2. Experimental details

2.1. Stoichiometric $La_{0.05}Li_{0.85}NbO_3$ nanocrystals ceramic material preparation

Previous investigations made by our group on synthesis on stoichiometric (equimolar quantity) of lanthanum lithium niobate ($La_{0.05}Li_{0.85}NbO_3$) nanoparticles used the mechanochemically method [16]. Here we synthesized stoichiometric lanthanum lithium niobate ($La_{0.05}Li_{0.85}NbO_3$) by mechanical milling by using lithium carbonate (Li_2CO_3), niobium oxide (Nb_2O_5) and lanthanum oxide (La_2O_3) as precursors. The sources of the materials were of high purity (99.99%), commercially available from Alfa Aesar, the time milling was 20 h to reduce the particle size. After alloying, the sample was calcined at 650 °C in order to remove carbonate residues and obtained the ferroelectrical crystalline phase according to the following solid-state reaction (2):

$$0.05La_2O_3 + Nb_2O_5 + 0.85Li_2CO_3 \rightarrow 2(La_{0.05}Li_{0.85})NbO_3(s) + 0.85CO_2\ (gas) \quad (1)$$

A second milling of 8 h was done in order to reduce the particle size. The particles were bounded with polyvinyl alcohol (PVA), were pressed at 105 kg/cm^2 and then sintered at 1000 °C, 1100 °C, 1120 °C, and 1150 °C for 5 h.

2.2. X-ray diffraction

X-ray diffraction (XRD) was confirmed from XRD patterns, using a Pananalytical X-Pert system with a source of *CuKα* radiation at 40 keV and 30 mA in the 2θ range between 20° and 80°, at 0.02° steps every 4 s.

2.3. Scanning Electron Microscopy

Scanning Electron Microscopy (SEM) images were taken with a Hitachi Tabletop Microscope, TM-1000. An accelerating voltage of 15kv was used with a working distance of 7.99 mm and an emission current of 48.4 mA. Magnification was set up to 5000x. Samples were mounted on an aluminum Hitachi stage with a conductive adhesive and then imaged.

2.4. Raman spectroscopy

Raman spectroscopy was made using a Micro Lab RAM HR model (Lexc = 632.8 nm), within a range from 100 to 1000 cm^{-1}, with a 14 mW laser excitation power by using a 100x objective and an aperture of ~ 1 μm.

2.5. X-ray Photoelectron Spectroscopy

The X-ray Photoelectron Spectroscopy (XPS) analyses were carried out with a PHI 5600 spectrometer with a hemispherical energy analyzer, using magnesium (MgK_α) source of 1253.6 eV at 100 W. The measurements were carried out on the sample after argon sputtering exposure of 5 min at 25 μA and 15×10^{-3} Pa. The pressure in the analysis chamber during XPS analysis was in the low range of 10^{-9} Torr. All spectra were recorded at 54° take-off angle, the analyzed area being currently about 1 mm^2. All spectra were recorded with 1.0 eV step, 10 cycles, 20 sweeps and corrected using carbon signal (C1s) at 284.5 eV. XPS spectra were analyzed using Casa-XPS software version 2.3.12. The Shirley method was used for extracting the background necessary for curve fitting.

2.6. Ferroelectric and atomic force microscope measurements

Ferroelectric measurement was carried out by using a RADIANT RT-66[a] at 300 K. The particles were bonded with PVA, pressed at 105 kg/cm^2 and then sintered at 1120 °C for 5 h, showing better densification; diameter (ϕ) was of 11.7 mm and height (h) of 1 mm. Domain imaging in XY was investigated by using piezoresponse force microscopy, in a commercial atomic force microscope Veeco with an internal lock-in amplifier. The PFM was operated with AC voltage amplitude of 4.0 Vp−p and frequency of 35 kHz, far below the resonance of the