Broadening of PTC Signature with Augmented Uv-Vis Optical Absorption in Carbophobic SrBi$_{1.98}$La$_{0.02}$Nb-TaO$_9$ Material

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Abstract. Surface sensitive Aurivillius materials are investigated in present work for tailorable IR-activity, carbon contamination and supplemented UV-vis absorption besides having broad PTC signature. Introduction of tantalum onto niobium sites strengthens octahedron rigidity and checks oxygen leaving unit cell positions to occupy surface interstitials. High solid solubility between tantalum and niobium oxide compounds permits systematically increasing unit cell volume. Optical and electrical energy bandgaps are investigated on doping tantalum besides tailoring IR-activity of unit cell. Equal doped sample with $x=1.0$ offers broadened PTC region by nearly 400% compared to other samples. Energy states are estimated to overlap in diffused manner on doping tantalum to increase amount of UV-vis spectrum absorption in $x=1.0$ material. Differential thermal analysis (DTA) was used to confirm diffused phase transition behavior with release in lattice strain on doping tantalum in SrBi$_{1.98}$La$_{0.02}$Nb$_{1-x}$Ta$_x$O$_9$ (SBLNT) materials.

Keywords: Carbon contamination, Optical Energy Band gap, Electrical Energy Band gap, PTC, IR-Active

1 INTRODUCTION

In recent years a variety of technological applications has increased a surge in nontoxic, chemically stable, cost effective metal based perovskites owing to their flexible structure in terms of A- and B-site cation options [1,2] over rare earth metal based oxides involving complex manufacturing process. Many researchers have emphasized on potential of polarizable perovskites not only in conventional application areas of sensing and data storage but extended to photovoltaics, pyroelectric, solid state refrigeration, drop wise condensation [3,4]. In family of layered perovskites ABO$_3$, strontium based BLSF are obvious choice over lead as they are relatively in-expansive, eco-friendly and having almost similar ionic radii as lead, enormous literature has been reported for ferroelectric and piezoelectric applications of SBN, SBT solid solutions [1,5]. Now a days solar cells based on different phases of perovskites like oxy-nitride, oxides are considered superior to conventional solar cells by researchers [6,7] and attempts are ongoing to improve stability and durability along with strong absorption power by compositional variations. In layered metal oxides reaction sites are interlayer space also these perovskites are polarizable which inhibits electronhole recombination and high dielectric constant promotes defect states which provides enough scope for higher photovoltaic activity [8]. SBN, SBT ceramics, both have direct band gap highly desirable for efficient light absorption, it has been reported in literature, Sr based halide perovskites are moisture sensitive due to inherent hydrophilic nature and possess comparatively high energy band gaps while oxy-nitrvides has been studied to achieve relaxor like behavior to implicate narrow band gaps at cost of dielectric constant [2,8,9]. In more recent works Pritam et al, Hwang et al has reported enhanced visible region absorption in tin doped SBLN, vanadium doped SBN respectively [3,7,10]. Based on these motivations, current series SrBi$_{1.98}$La$_{0.02}$Nb$_{1-x}$Ta$_x$O$_9$ ($x=0$-2 in steps of 0.5) SBLNT was prepared. This work presents critical investigations on role of Ta doping at B-site to improve optical and electrical properties of studied SBLNT series.
2 EXPERIMENTAL

The target compositions $\text{SrBi}_{1.98}\text{La}_{0.02}\text{Nb}_2\text{Ta}_x\text{O}_9$ with $x=0.0-2.0$ were prepared by solid state reaction route assisted with microwave heating obtained from high purity grade (99.9%) powders of $\text{SrCO}_3$, $\text{Bi}_2\text{O}_3$, $\text{La}_2\text{O}_3$, $\text{Nb}_2\text{O}_5$, $\text{Ta}_2\text{O}_5$ (all from Aldrich) in stoichiometric proportions. The microstructure of fractured surfaces were determined by scanning electron microscopy. DTA thermograms were taken to study phase change and thermal stability of prepared compositions up to 500°C. For structural characterizations, powders and sintered pellets were examined by X-ray diffractometer with Cu Kα having $\lambda=1.5406$ Å radiations with $\theta$ varied between 10° to 80° (step increment-0.02° with a time duration of 2sec/step). FTIR spectra of powder samples was recorded in range (525-4500) cm$^{-1}$ on FTIR spectrophotometer of Thermo Fisher Scientific make and Model Nicolet iS5. Tauc plots were used to calculate optical energy band gap for SBLNT compositions. Uv-Vis diffuse absorption spectra were measured in an integral sphere mode using spectrophotometer SHIMADZU Uv-vis 3700. The Curie temperature measurements were taken from room temperature to 575°C at fixed frequency on computer interfaced impedance analyzer high frequency LCR meter ZM2376 (NF corporation, Japan). Dc conductivity of all samples was measured using electrometer based on conventional two probe setup.

3 RESULTS AND DISCUSSION

3.1 Crosssection Morphology

SEM micrograph of starting SBLN sample is shown in fig. 1, where grains have apparent non-uniform shapes and sizes because of microwave calcinations [3]. The sample shows significant porosity with grain size ~230 nm. The grain boundaries are observed to improve on doping tantalum besides improving grain connectivity at the expense of reduced porosity. Shiny boundaries of most grains are indicative of released oxygen interstitials in starting $x=0.0$ sample. These boundaries respond to atmospheric carbon via forming polar dangling bonds. On increase in tantalum doping, oxygen of flexible bismuth layer are attracted tightly towards octahedrons to result into low possibility of surface contamination. 

![FIGURE-1. SEM image of fractured surface of SBLN.](image)

3.2 Thermal Properties

Calcined SBLNT powders show negligible tendency to absorb moisture from environment. The first stage thermal decomposition widely reported for SBN-SBT compositions [11] associated with vaporization of free or bound water between 100-200°C, is feebly present in SBLT (2.0), fig-2(a).
Broad exothermic peak in all samples between 300-500°C can be fairly attributed to process of crystallization for SBLNT phase free from carbonaceous residues, as overall weight loss observed is less than 1-2 %, fig-2(b). Jalled et al [11] and Junior et al [12] have reported major weight loss around 40-60% in SBN, SBNT solid solutions respectively due to decomposition of carbonates, oxides and vaporable metal complexes of bismuth around 300-500°C. In present study, the crystallization peak gets broadened and shifts to lower temperature regularly with increase in tantalum doping. This is a clear evidence of diffused phase transition in these compositions on account of released lattice strain. This implicates resolution of a small exothermic peak in vicinity of Curie temperature around 295°C and 275°C in x=1.5 and 2.0 sample respectively, which was otherwise superimposed with crystallization peak in x=0.5 and 1.0 samples.

3.3 FTIR Spectroscopy

FTIR results for SBLNT calcined powders are shown in fig-3. Weak O-H stretching bands around 1640cm⁻¹ and 3400cm⁻¹ are primarily due to the presence of lanthanum onto bismuth sites in addition to rigidity induced in unit cells post tantalum doping [12, 13, 14]. Significant carbon contamination in the form of bridged CO/CO₂ on starting SBN sample is observed via high intensity peaks of bending and stretching modes of C-O and C=O (1740 -1210 cm⁻¹). Minor intensity peak corresponding to C-H stretching vibrations centered around 2970cm⁻¹ [15] is also observed. An optimum control of IR-activity is recorded in current work, on increasing tantalum, overall transmittance increases to nearly 100% for sample with x=1.5 and decreases thereafter. Hence, sample with x=1.5 is almost IR-inactive whereas all other samples are prominently IR-active (Inset fig-3). SBLNT materials exhibit close overlapping of Bi-O and Nb-O bond vibration frequencies [11]. This overlap gets resolved around 750cm⁻¹ (in M-O stretching bands ranging 580-700 cm⁻¹) for higher tantalum content (x>1.0). Tantalum induced octahedral distortions are also noticed through close band splitting for Ta-O (576cm⁻¹ and 581cm⁻¹) and Nb-O (601cm⁻¹) bonds [18]. The calculated values of M-O bond force constant (2.9053x10⁵ dyne/cm) remains constant on tantalum doping due to negligible lattice mismatch with niobium [18, 19, 20]. For final doped SBLT sample (x=2.0), the earlier mentioned overlap of M-O and Bi-O vibrations vanishes and hence transmission dip is observed slightly towards large wavenumber with increased force constant (3.20x10⁵ dynes/cm). This is presumably due to reduced displacement of tantalum ion in TaO₆ octahedron compared to niobium displacement in NbO₆ octahedron.
The UV-VIS diffuse reflectance spectroscopy is an important tool to investigate photocatalytic activity of materials. The diffuse reflectance spectra of SBLNT (x=0.0, 1.0, 2.0) powders is shown in fig 4(a). All SBLNT samples observed onset of absorption edge well with in visible region around 450nm, higher bind strength of La-O than Bi-O prevents bismuth evaporation thereby promoting the light absorption characteristics. In literature pure SBN has been reported with absorption edge in UV region around 386nm after that it shifts to longer wavelengths with doping [7]. Observed no variation in peak absorption coefficient of studied series may be attributed due to isostructural Nb, Ta compositions. SBLNT50/50 observed significant red shift of absorption edge towards longer wavelength, moreover absorbance is almost double than SBLN in entire visible region (400-700nm), Bathochromic shift (red shift) has been widely reported in semiconducting photocatalytic materials, by means of doping absorption shoulder/edge shifts towards longer wavelength indication of decrease in energy band gap, same has been observed too for SBLNT samples. Comparatively higher photo-absorption of SBLNT (x=1.0,2.0) than SBLN can be attributed to higher Ta-O-Ta bond angle than Nb-O-Nb agreement with reported studies large M-O-M angles favors easy separation of photo-generated electron –hole pairs [21],also supported by increasing volume of SBLNT compositions with Ta doping (table 1). In SBLN-SBLNT transition crystal structure changes to pseudo tetragonal to orthorhombic, difference in photocatalytic activity has been attributed to changes in crystal structure and modified electronic states by Li et al [8]. The optical band gaps is calculated by Tauc plots by plotting $(\alpha h\nu)^2$ versus $h\nu$ as shown in fig4(b). The observed band gap value of SBLN is significantly lower than reported values of pure SBN in literature, Hwang et al reported 3.02eV while Banerjee et al reported 3.05eV in bismuth excess SBN ceramics, SSBLN nanoparticles has been reported Eg value lower than 3eV by Pritam et al, Li et al reported SBT with band gap 3.64eV. Further observed band gap value of 2.5428eV for SBLNT50/50 is significantly lower than SBLN and SBLT samples which clearly indicates that Ta incorporation enhances photovoltaic activity and SBLNT compositions can be fairly attributed more absorptive than SBLN and SBLT. It has been widely reported in literature SBN behaves like donor ceramics while SBT is acceptor ceramic, hybridization of donor and acceptor energy levels in co-mixed SBLT50/50 fills energy states between energy band gap which confirms contribution of extended 5d orbital of Ta. It can be adopted from DoS theory in literature [20, 21] for SBN, SBT oxides Fermi level has mainly s, p character due to strong hybridization of Bi 6s and O2p orbitals while metal d orbital do not contribute to valance band maximum while bottom of conduction band has major contribution from metal d orbitals via overlapping with Bi 6s and O2p. It can be fairly interpreted for present studies that combined contribution of Nb 4d and Ta 5d along with overlapped orbitals of Bi 6p and O2p modify density of states distribution for enhanced photo-absorption in SBLNT solid solutions. This is in agreement with previous studies in literature reporting important role of orbital hybridization.
through metal d orbitals as an effective way to modify band structure [7]. In accordance with Burstein-Moss shift equation \( E_g = N^{2/3} \), where \( N \) is carrier concentration. The lower band gap of SBLNT50/50 can be fairly associated with comparatively lower carrier concentration and higher resistivity of this composition [22]. Thus, Ta doping provides a tool to control optical band gap and electron and hole concentration thereby transforms dielectric SBLN into photo-voltaic semiconducting SBLNT system. Pritam et al has well discussed electron/hole transport layers in tin doped SBLN where tin doping varies electron/hole concentration, reduces optical band gap and modify visible region absorption.

**FIGURE-4** Uv-Vis Diffuse absorption spectra (a) and Tauc plots (b) for SrBi\(_{1.98}\)La\(_{0.02}\)Nb\(_2\)-xTa\(_x\)O\(_9\) (x=0.0,1.0,2.0)

### 3.5 DC Conductivity

Fig. 5(a) shows the electrical conductivity versus temperature of SBLNT(x=0.0-2.0) using the relation \( \sigma = 1/\rho \), it is clear that studied compositions observed conventional PTCR (positive temperature coefficient of resistance) behavior of ceramics attributed to dominant n type conduction under the effect of external field at high temperature. Un-doped SBLN observed this PTCR transition in vicinity of Curie temperature, which is caused by grain boundaries effect[23,24]. With Ta substitution \( x=0.5 \), PTC region takes a 100OC shift at higher temperature as compared to SBLN, occurs much beyond ferroelectric – paraelectric transition temperature of this compositions. Observed length of PTCR behavior also decreases significantly compared to SBLN, get dissolved instantaneously in narrow temperature range, clearly indicating decrease in concentration of negative charge carriers, a clear evidence of formation of charge trap centers implicated by distributed potential barriers due to higher bond dissociation energies of Ta-O(805kJ/mol) than Nb-O(753kJ/mol). Further increasing Ta content, sample \( x=1.0 \) shows exceptional behavior, PTC effect extends over a broad temperature range, when B site is equally occupied by Ta and Nb, diffused traps holds charge carriers maximum, PTC region smeared over temperature range of about 100OC, which is 4 times higher than SBLN. This interpretation is in very well agreement with Uv-Vis studies which reveals perfect insulating properties of this composition \( E_g \) decreases due to electron and hole recombination in SBLNT50/50 [22]. It is interesting to observe here for \( x=1.5 \) sample, PTCR shifts back and behavior is almost identical for SBLNT25/75 and SBLNT75/25 which is a clear consequence of heterogeneous distribution of potential barriers (trapping centers) of equal concentration but of opposite kind. However corresponding to fixed La content, increasing Ta content at B-site further weakens insulating effect of bismuth layers thereby causing level of conductivity slightly higher in SBLNT25/75 than SBLNT75/25. The activation energies of these samples in intrinsic conduction region (3000C -7000C) calculated from Arrhenius relation are shown (table1), \( E_a=0.70eV \) is maximum for SBLN, decreases regularly with Ta content thereby easing out mobility of charge carriers through less strained lattice this interpretation get supports from regular decrease in tetragonal strain causing increase in volume of unit cell in SBLN-SBLT transition. Thus activation energy plays role of equalizer to reduction in charge carrier concentration thereby present SBLNT compositions shows speculated intermediate conductivity behavior of SBLN and SBLT, this observation is consistent with Kajewaski et al studies of SBNT 50/50 reporting mutually competing role of easy conducting paths due to cation place exchange between Bi-Sr sub lattice [25,26] and charge compensation due to simultaneous presence of Ta/Nb at B site, which is not
self-compensating in pristine SBN, SBT [26,27]. The activation energies less than 1ev corresponds to oxygen vacancy as the most mobile intrinsic defect in ceramics discussed by different researchers [28, 29], it also has been studied in ferroelectrics that conduction beyond Tc is not purely ionic but non-stoichiometry give rise to electron conduction[30].

![Graph showing Variation of dc electrical conductivity with temperature of different SrBi1.98La0.02Nb2- xTaxO9 (x=0.0, 0.50, 1.0, 1.5, 2.0) compositions.](image)

**TABLE 1.** Unit cell volume and DC activation energy of SrBi1.98La0.02Nb2-xTaxO9 (x=0.0, 0.5, 1.0, 1.5, 2.0) compositions.

<table>
<thead>
<tr>
<th>Composition (x)</th>
<th>Volume (Å)</th>
<th>Activation Energy E_a (eV)</th>
</tr>
</thead>
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<tr>
<td>0.0</td>
<td>761.7687</td>
<td>0.6962</td>
</tr>
<tr>
<td>0.5</td>
<td>761.7054</td>
<td>0.6447</td>
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**4. CONCLUSIONS**

In present studies tantalum doping improves microstructure properties by reducing oxygen concentration at grain surfaces. With increasing amount of tantalum doping crystallization peak shifts to lower temperature and phase transition becomes diffusive regularly with negligible mass loss (<2%). M-O stretching band observed no shift in SBLN-SBLNT transition, however tantalum doping at B-site provides a tool to tailor infra-red activity and to handle carbon contamination without involving high sintering temperatures. SBLN, SBLT compositions are more absorptive than pristine SBN, SBT reported in literature moreover hybrid orbitals of Nb, Ta further lowers down optical energy band gap in co-mixed SBLNT solutions. Among metal based oxide perovskite, investigated SBLNT compositions are potential candidates for photo-voltaic applications, they can withstand harsh environmental conditions as well and have high thermal stability. Extended PTCR over significant temperature range observed in SBLNT50/50 is crucial for high temperature thermistor applications.

**REFERENCES**