BAND GAP ENERGY PROFILE OF BSFT $Ba_{0.6}Sr_{0.4}Fe_xTi_{(1-x)}O_{3-\delta}(x=0.1)$

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Abstract- A new nano ceramic material **BSFT** was prepared via a conventional solid state reaction technique and UV-VIS analysis of the sample was carried to study the optical properties. Tunable band gaps can be obtained by varying annealing temperatures. An exponentially varying absorption edge was observed and explained in terms of the Urbach's tail. The refractive index was calculated and the results obtained also showed a systematic variation with temperature. The EDX measurements confirmed the composition of the sample.

Index Terms- BSFT, TAUC plot, Urbach energy, band gap energy

I. INTRODUCTION

Nano composite materials are of great interest to researchers in the world over for various reasons. One drive for such research is the potential application in next-generation electronic and photonic devices. Particles of a nano meter size exhibit unique properties such as quantum effects, short interface migration distances for photo induced holes and electrons in photochemical and photo catalytic systems, and increased sensitivity in thin film sensors [1]. Nanoparticles have properties (optical, electrical, or magnetic) depending directly on their size.

The development of lead-free piezoelectric materials has gained good attention for the consideration of environmental protection. There has been a continuous succession of new materials and technology developments leading to a significant number of industrial and commercial applications after the discovery of ferroelectric ceramics in polycrystalline barium titanate [2]. BaTiO3 have been attracted considerable interest for a wide variety of applications. It has a perovskite structure that possesses a high dielectric constant [1] and widely used in multilayer ceramic capacitors (MLCCs), dynamic random-access ferroelectric memories (DRAMs) [4]

Measuring the band gap is an important factor determining the electrical conductivity in nano material industries. The band gap energy of insulators is large (> 4eV), but lower for semiconductors (< 3eV). In solid state physics a band gap, is an energy range in an ideal solid where no electron states can exist. This is equivalent to the energy required to free an outer shell electron from its orbit about the nucleus to become a mobile charge carrier, able to move freely within the solid material [3].

In the present work the authors describes the optical behaviour of **BSFT**, a lead free material since they are now at the top as ferroelectric and piezoelectric materials. Barium titanate compounds are well suited for optical applications because of its high optical transparency and its large linear and non-linear electro-optic coefficients. Since barium compounds have varied applications & properties, doping with other materials like Sr, Fe etc. will improve its characteristics. With that understanding a new nano material with the formula BSFT was synthesized. The energy band gap values of sample are analyzed for different temperatures and they are fundamentally important to the design of practical devices [2]. The band gap energy values obtained using TAUC plot shows a direct relation with temperature. The Urbach energy of the sample is also calculated. The refractive index dependence on wavelength of the radiation has been discussed and such optical behaviour is rarely reported.

2. Experimental Methods

2.1. Preparation of the Sample:

The new ceramic sample BSFT ($Ba_{0.6}Sr_{0.4}Fe_xTi_{(1-x)}O_{3-\delta}(x=0.1)$) is prepared by the solid-state reaction technique according to their molecular formula using a high-energy ball milling process through mechanically assisted synthesis. For preparing sample, the reagent grade chemicals of high purity Barium Carbonate, Strontium Carbonate, Ferric Oxide and Titanium dioxide powders were used as the raw materials and weighed according to their molecular formula.

The sample was ball milled for three weeks with suitable zirconium balls to insure homogeneity and milling. Then it was attrition milled for three hours. After milling the material was calcined at four different temperatures, 30˚C, 550˚C, 850˚C & 950˚C in a special furnace with oxygen flow arrangements. The temperature of the furnace was increased in steps. On cooling oxygen flow was allowed immensely into the sample inside the furnace. High temperature is needed for metal oxide phase transformation [5].

2.2. UV-VIS. Analysis:

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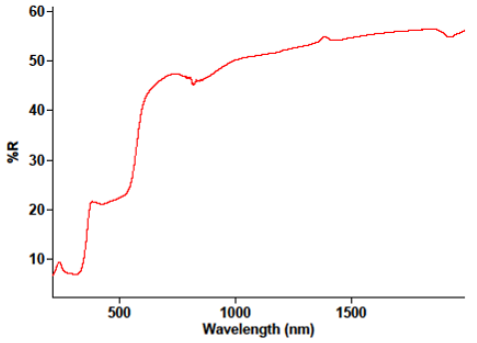
Understanding the fundamental properties is essential for improving the material quality. Many properties of are unknown due to the increased difficulties to grow high quality materials.
The UV analysis can be thought as a good quality check for the optical behaviour of the ceramic materials

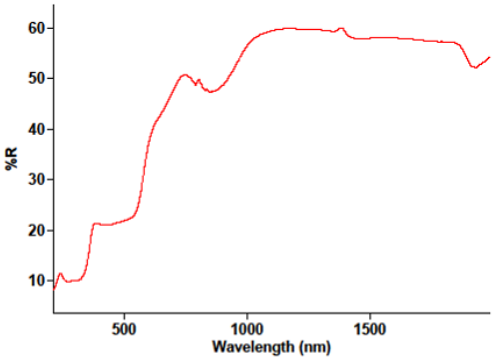
The sample obtained after calcination at different temperatures was subjected to UV-VIS-Near IR analysis using Varian, Cary 5000 Spectrophotometer over a spectral range of 175-3300nm with an accuracy of ±0.1nm (UV-Vis.). This type of sample has high mechanical hardness, high thermal conductivity, large dielectric constant, and high resistance to harsh environment.

Barium titanate compounds are one of the most attractive ferroelectric materials and show non-linear and electro optical properties because of the interaction between spontaneous polarization and polarized light. With regard to the optical band gap of nano scale, Matsuda et al. revealed that the band gap of barium titanate nano crystallites (10 nm) is approximately 0.1 eV larger than that of a single crystal by measuring the optical absorption of monolithic gels [6]. However, the above-mentioned report is the only available data on the size-driven band gap increment of barium compounds. This can be ascribed to a difficulty of the method for preparing ferroelectric nano particles.

UV-Visible spectrum gives information about the excitonic and inter transition of nano materials [7]. Figure.1 shows the UV-VIS behaviour of the sample BSFT at different temperatures 30^0C, 550^0C, 850^0C & 950^0C.



(a)



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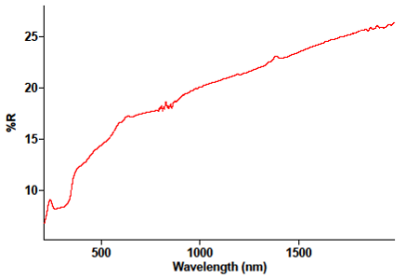

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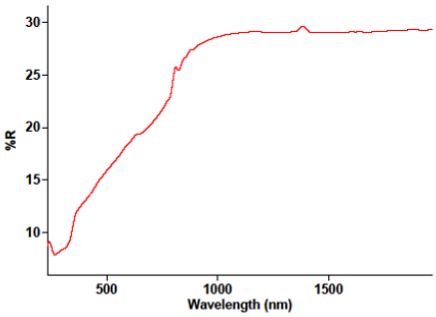

(d)

Figure.1(a)–(d)UV-VIS behaviour of BSFT at different temperatures 30^0C, 550^0C, 850^0C & 950^0C respectively.

The average transmittance in the visible part of the spectra (300-800nm) is about (80-90) %. The diffuse reflectance spectra were translated into the absorption spectra and absorption coefficient was calculated by the Kubelka-Munk equation [6].

2.2(1).TAUC PLOT

The band gap energy can be determined using the TAUC relation [8-13]. It is a convenient way of studying the optical absorption spectrum of a material. According to the TAUC relation, the absorption coefficient α for material is given by $\alpha h\nu = A(h\nu - Eg)n$, Where Eg the band gap, constant A is different for different transitions, $(h\nu)$ is energy of photon and n is an index which assumes the values ½, 3/2, 2 and 3 depending on the nature of electronic transition responsible for the reflection. The value of the exponent n denotes the nature of the sample transition [9].

Band gaps were then calculated from the TAUC plots by fitting a line through the linear portion of the band edge region. A sample having an indirect band gap shows a linear dependence where the Kubelka – Munk function first shows distinct increase if n = 2, while one having a direct gap will shows a linear dependence when n = 1 / 2 (Tauc et al., 1966) [14].

The TAUC plot of a sample defines the optical band gap as represented as the region A in fig.2

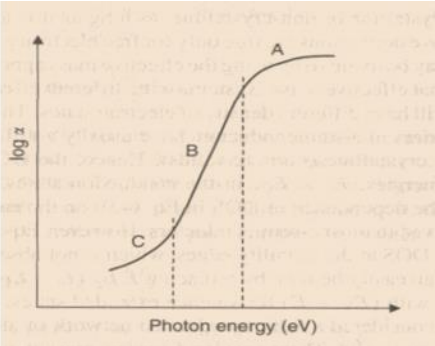

Fig.2 showing the variation of absorbance with photon energy.

The sample BSFT at temperatures 30˚C, 550˚C, 850˚C & 950˚C is analyzed and studied. Here we have taken the direct allowed transitions. The TAUC plot is plotted with $h\nu$ along the X-axis and $(h\nu\alpha)2$ along the Y-axis. The TAUC plot for different temperatures are given below in Fig 2.

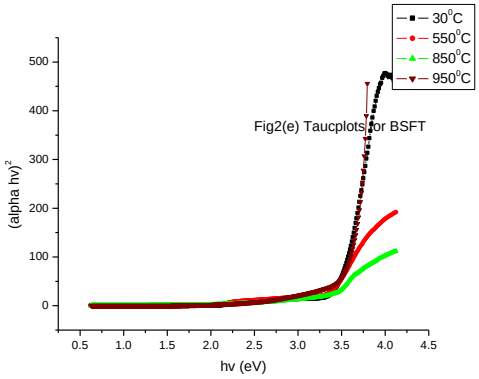

Fig2 TAUC plot of BSFT for temperatures 30◦C,550◦C,850◦C &950◦C.

The band gap energy values of BSFT calculated are listed in the table.1 given below

TABLE.1 band gap energy values of BSFT

. Temperature	Band gap energy in eV
30◦C	3.2
550◦C	3.25
850◦C	3.4
950◦C	3.49

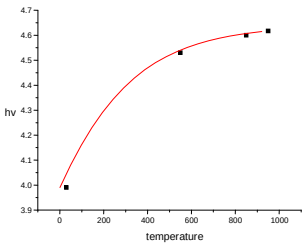

fig.3.1 photon energy with temperature

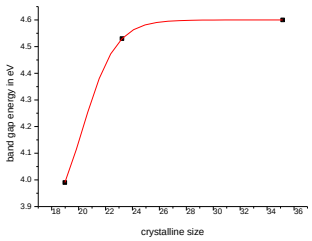

fig.3.2 photon energy with crystallite size.

From the results, it is confirmed that band gap energy increases with an increase in temperature(fig.3.1). The dependence of the crystallite size with the energy gap is also shown in fig3.2. The energy levels are dependent on the degree of structural order–disorder in the lattice. The band gap increases with the crystallite size but decreases as the perovskite phase is formed which proves the quantum confinement also decreasing the dislocation density.

2.2(2).URBACH ENERGY

The absorption coefficient at the photon energy below the optical gap (tail absorption) depends exponentially on the photon energy: $\alpha(\hbar\nu) \sim exp\ (\hbar\ \nu/E_u)$where E_u is called Urbach energy.The region B in the fig.2 represents the Urbach energy.
When the energy of the incident photon is lower than the band gap, absorption increases with an exponential decay of density of states of the localized band into the gap. The absorption edge here is called Urbach edge. The width of the Urbach tail is an indicator of defect levels in the forbidden gap. The exponential absorption tails, i.e. Urbach energy, depends on temperature, thermal vibrations in the lattice, induced disorder, static disorder, strong ionic bonds and on average photon energies [16].
Also it was deduced that the edge was most likely due to a radiative recombination between trapped electrons and trapped holes in tail and gap states as shown in Fig.2, and is dependent on the degree of structural and thermal disorder [14].

The natural logarithm of the absorption coefficient, α(ν), was plotted as a function of the photon energy, $h\nu$ (Fig.4). The value of E_u was calculated by taking the reciprocal of the slopes of the linear portion in the lower photon energy region of curves.
The Urbach Energy values decrease with temperature and the decrease is slightly more as the temperature increases. Sumi-Toyozawa (S-T model) explains the exponential shape of the absorption coefficient as the coexistence of free excitons and momentarily localized self-trapped excitons [16]. This theory can only be applied, however, to cases where the exciton radius is small and the effective mass of the hole is much larger than that of the electron. According to the S-T model, $\sigma_0 \sim 0$ .6(B/S) and E_0 ~Eg (0) − 0.8B, where S and B are the average exciton-phonon interaction energy and exciton binding energy. That is, the focal point E_0 must be located below the band gap energy. In

the present study, the focal point E_0 is in a lower energy region than the band gap energy. The value of Urbach energy for the sample under study is calculated. The Urbach energy is found to be 3.15eV. Accordingly, the S-T model can be readily applied to this study [17].

The measurement of temperature-dependent Urbach tails distinguishes a temperature-dependent tail and a temperature-independent part, which mainly are due to intrinsic defects. The latter can be controlled by improving the crystal growth and the purity of the ingredients. The temperature-dependent part of the Urbach tail, is purely of intrinsic reasons [18].

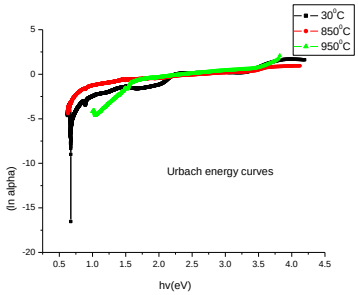

Fig.4.log of absorption coefficient plotted as a function of photon energy.

In addition, optical absorption by defects also appears at energy lower than optical gap region C of fig.2. This region is related to the structural properties of materials[15].

2.2(3) Refractive Index dependence

Refractive index with wavelength dependence is also studied. The refractive index values show a linear decrease with the increase in wavelength. Fig.5 shows the variation of the dispersion curve with annealing temperature. The refractive index values showed a linear decrease with the increase in wavelength. But refractive index value shows a slight increase with increasing annealing temperature when plotted with refractive index along the Y axis and photon energy along the X axis and attains a fixed value after a particular wavelength.

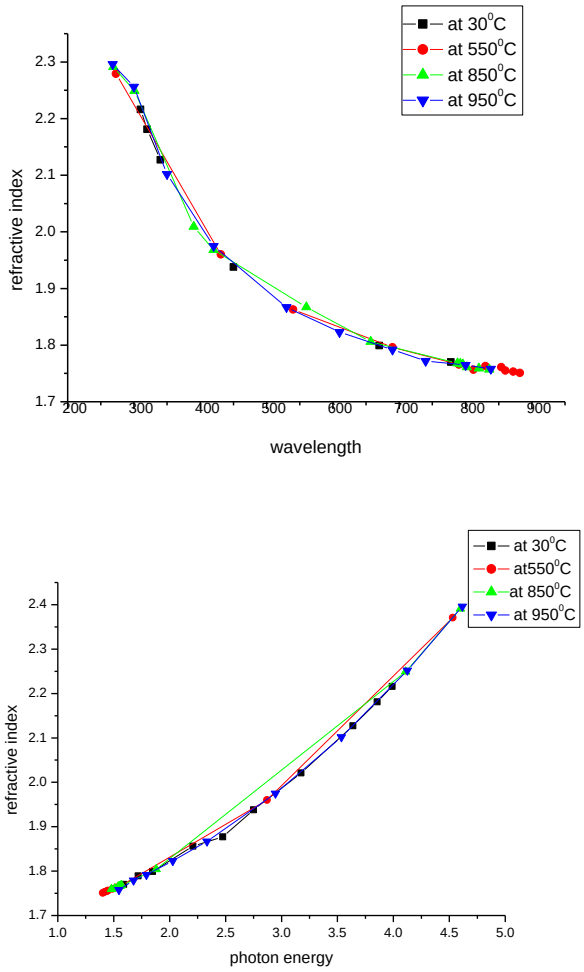

Fig.5. Refractive index variation with wavelength and photon energy for different temperatures.

3.Energy Dispersed X-Ray Spectrograph (EDX)

EDX shows the composition details of the prepared ceramic powders. The instrument used for this measurement is ISIS Link Oxford Instrument UK. This technique is generally associated with Scanning Electron Microscope (SEM). In this technique an electron beam of 10 - 20 KeV strikes the surface of a sample which causes X-ray to be emitted from point of incidence. The energy of the X-ray emitted depends on material under examination. When an X-ray strikes the detector, it will generate a photoelectron which in turn generates electron-hole pairs. A strong electric field attracts the electrons and holes towards the opposite ends of the detector. The size of the pulse thus generated depends on the number electron hole pairs created, which in turn depends on the energy of the incoming X-ray. In this method however elements with low atomic number are difficult to be detected. The detector which is lithium doped silicon is protected by a beryllium window and operated at liquid nitrogen temperatures. The absorption of the soft X-rays by the beryllium decreases the sensitivity below an atomic number 11.

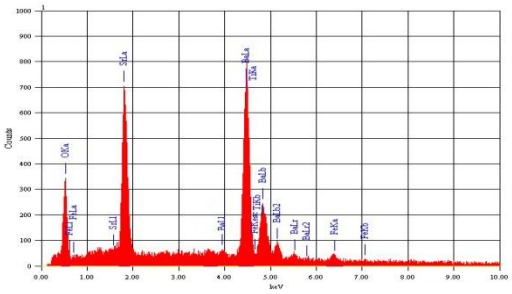

Figure.6. EDX of $BaSr._9Fe._1TiO_4$ The EDX spectrum obtained give the composition of the material under study.

Table.2 Material Content (EDX)

*M*aterial	content (%)
Ba	44
Sr	27
Fe	2.14
Ti	2.01
O	24.85

From the EDX spectrum, the four dominant peak positions at 4.465keV (Ba Lα), 5.1,.5,5.8keV (Ba Lβ, Lγ, Lγ2), 1.806keV (Sr Lα), 0.705, 6.398keV (Fe Lα, Kα), 0.452, 4.508keV (Ti Lα, Kα), 0.525keV (O Kα) correspond quite well to the energy pattern of the corresponding materials (Ba, Sr, Fe, Ti, and O) reported in the EDAX international chart [3].

4.Results

The Ceramic material prepared by solid state reaction technique in a special furnace with oxygen annealing in different temperatures in steps is successfully studied. .Optical analysis of the same is done using UV-Vis Spectro photometer. From UV-VIS. Analysis, the results very clearly confirm that band gap energy of the nano crystalline ceramic increases as the temperature is increased. This result is also a confirmation of the Wein's law which states that higher the temperature, smaller the wavelength of the maximum emission i e

λ max = 0.0029km/T or λ inversely proportional to 1/T – (1)

The crystallite size of the sample increases at different treating temperatures [*3*]. When the temperature reaches its sintering value, the band gap energy tries to decrease. The crystallite size of the sample at different temperatures are calculated [5] using the Debye Scherrer formula as $\boldsymbol{D=K\lambda/\beta}\cos\ \boldsymbol{\theta}$, where D represents the crystallite size in nm, K is a constant (=0.9), $\boldsymbol{\beta}$, the full width at half maximum in radians and $\boldsymbol{\theta}$,the diffracting angle in degrees.

The UV-VIS behaviour of the sample at the different temperatures was thoroughly analyzed. TAUC plot data well confirms that the band gap energy of the sample increases slightly when the temperature is increased. As the temperature is increased the crystallite size also increases which shows an increase in band gap energy too. The energy levels are dependent on the degree of structural order–disorder in the lattice. Therefore, the increase of structural organization in nano ceramic leads to a reduction of the intermediary energy levels and consequently increases the Eg values. But the band gap decreases slightly at high temperature with increase in the crystallite size which very well proves the quantum confinement.

Urbach energy is calculated by plotting the natural logarithm of the absorption coefficient with the energy in eV. This value is found to be lower than the band gap energy and hence Sumi-Toyozawa (ST) model theory can be well applied to this material.

The refractive index of the sample at different values of temperature is also studied. Analysis (Fig.5) clearly shows that refractive index of the sample decreases as the wavelength increases (varies from 2.27 to 1.76) and attains a definite value at all temperatures. Fig.5 also shows the dependence of the refractive index with the energy. This linear variation of the refractive index with the wavelength/energy is due to dispersion of light energy at the different interstitial layers. The refractive index of perovskites is known to be proportional to their electronic polarization per unit volume which is inversely proportional to distance between atomic planes. This result can be explained by an increase in crystallite size as already reported [3]. The increase in refractive index is due to crystallization of the perovskite phase.

The EDX analysis indicates that the elements exist in the sample and they agree with the chemical formula of the prepared compound. The mechano chemical process has an advantage due to low-costs and widely available materials, leading to a simplified process.

5.Conclusion

The optical properties of the new nano ceramic material BSFT can be taken as a better candidate for UV_VIS shielding applications. A sound understanding of the band gap variations of the sample with different temperatures are noted. It is confirmed that tunable band gaps are obtained by varying annealing temperatures. The increase in the band gap energy increases the dielectric properties of the material. The EDX measurements confirmed the composition of the sample. New generation capacitors are credited to the engineering and synthesis of new nano dielectric ceramic materials. Hence BSFT or Fe doped Barium Strontium titanate materials will definitely provide better future for power electronics.

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