ISSN 2347-3487

OPTICAL BAND GAP ANALYSIS OF NANO-CRYSTALLINE CERAMIC PbSrCaCuO

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ABSTRACT

Nano-crystalline Ceramic PbSrCaCuO have been prepared by a high-energy ball milling process through mechanically assisted synthesis. The prepared sample was then subjected to calcinations to acquire the desired homogeneity and phase formation. UV-VIS analysis of the sample was carried to study the optical properties of the sample. The band gap energy of the sample shows a marked variation in their value with the increase in temperature. The refractive index n was calculated and the results obtained is plotted with the wavelength. The refractive-index curves also show a systematic variation with temperature.

Indexing terms/Keywords

PbSrCaCuO, band gap energy, refractive index & Tauc plot.

Academic Discipline And Sub-Disciplines

Faculty of Science, Physics

SUBJECT CLASSIFICATION

Condensed matter Physics, nano ceramics composite

TYPE (METHOD/APPROACH)

Full research article - Experimental along with theory and analysis

Council for Innovative Research

Peer Review Research Publishing System

Journal: JOURNAL OF ADVANCES IN PHYSICS

Vol 5, No.3

japeditor@gmail.com

www.cirjap.com

ISSN 2347-3487

1.INTRODUCTION

Optical characterisation is considered to be a good quality check for nano crystalline ceramics. Nano crystalline materials have attracted considerable interest in recent years because of the possibility of improving macroscopic properties of materials by varying the crystallite sizes. For example, some nano crystalline ceramics that can be sintered at low temperatures and ductile ceramics were found that it can be shaped by pressing[1]. Nano crystalline materials contain a large fraction of grain boundaries, which can act as fast diffusion pathways. Therefore these materials are expected to be employed as solid electrolytes for battery systems, fuel cells, or sensors.

Nano composite materials are of 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 (and times) for photo induced holes and electrons in photochemical and photo catalytic systems, and increased sensitivity in thin film sensors[2].

Measuring the band gap is important in the semiconductor and nano material industries. The band gap energy of insulators is large (> 4eV), but lower for semiconductors (< 3eV). In solid state physics a band gap also called an energy gap, is an energy range in an ideal solid where no electron states can exist. As shown in Figure 1 for an insulator or semiconductor the band gap generally refers to the energy difference between the top of the valence band and the bottom

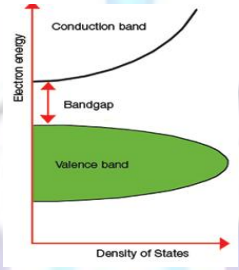


Fig.1.Energy gap determines the electrical conductivity.

of the conduction band. 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]. The band gap is a major factor determining the electrical conductivity of a solid. Substances with large band gaps are generally insulators (i.e., dielectric), those with smaller band gaps are semiconductors, while conductors either have very small band gaps or no band gap

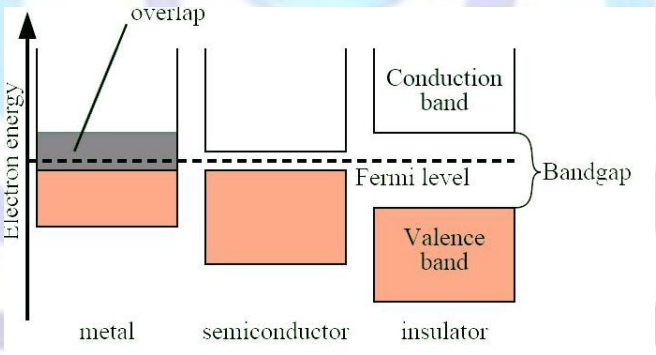


Figure 2. Band gap representation in different materials

(because the valence and conduction bands overlap as in Figure 2). It has been found that many of the nano material studies on these materials are being carried out using a small quantity of the sample.

The radiation from normal hot solids is made up of many wavelengths and the energy emitted at any particular wavelength depends largely on the temperature of the solid and is predictable from probability theory. Such radiation is known as 'black body radiation'. The energy of a photon absorbed or emitted during a transition from one molecular energy level to another is given by the equation, e=hv where h is known as Planck's constant and v is the frequency of the photon. The theory of bands in solids is one of the most important steps in the comprehension of the properties of solid matter [*4*]. For ultraviolet and visible wavelengths should show a few very sharp lines. Each line should occur at a wavelength where the energy of an incident photon exactly matches the energy required to excite an electronic transition. In practice it is found that the ultraviolet and visible spectrum of most molecules consists of a few humps rather than sharp lines. These humps show that the molecule is absorbing radiation over a band of wavelengths. One reason for this band, rather than line absorption is that an electronic level transition is usually accompanied by a simultaneous change between the more numerous vibrational levels.

In the present study, the temperature dependent band gap variation of the ceramic material PbSrCaCuO has been discussed and such optical study is rarely reported for this material. UV –VIS analysis of the sample at different

ISSN 2347-3487

temperatures are taken. The band gap energy values are in good confirmation with the theory. The refractive index variations with the wavelength are also plotted.

2.EXPERIMENTAL METHODS

2.1. Preparation of The Sample:

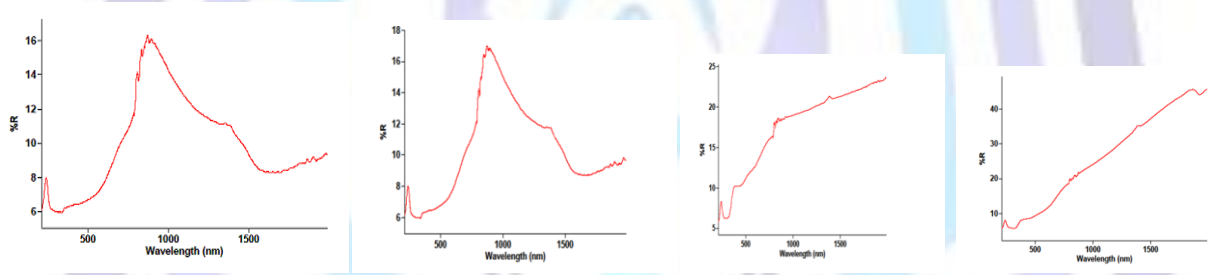
Ceramics with the chemical formula **PbSrCaCuO** were prepared by the conventional solid state reaction technique according to their molecular formula using a high-energy ball milling process through mechanically assisted synthesis. For preparing sample, the reagent grade chemicals of high purity Lead dioxide, Strontium Carbonate, Calcium Oxide and Cuprous oxide powders were used as the raw materials and weighed according to their molecular formula.

$$2PbO_2 + 2(SrCO_3) + CaO + 2CuO \rightarrow Pb_2Sr_2CaCu_2O_9(PbSrCaCuO) + 2CO_2$$

The required powders were mixed mechanically. Mechanical mixing is usually done by hand mixing in agate mortar for very long time. The sample was then 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. After each step the ceramics was grinded well before heating. On cooling oxygen flow was allowed immensely into the sample inside the furnace. High temperature is needed for metal oxide phase transformations.

2.2. UV-VIS. Analysis:

The sample **PbSrCaCuO** 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.). These type samples have high mechanical hardness, high thermal conductivity, large dielectric constant, and high resistance to harsh environment. For device applications improving the material quality and understanding of the fundamental properties are essential. Many properties of are unknown due to the increased difficulties to grow high quality materials. Among the basic properties and parameters the determination of the band gap and its variation with temperature and composition are fundamentally important to the design of practical devices based on these materials. Figure 3 shows the UV-VIS behaviour of the sample PbSrCaCuO at the different temperatures 30^{0}C, 550^{0}C, 850^{0}C & 950^{0}C**.**



(a) (b) (c) (d)

Fig.3. UV-VIS behaviour of PbSrCaCuO at different temperatures (a) 30^{0}C, (b) 550^{0}C, (c) 850^{0}C & (d) 950^{0}C

The diffuse reflectance spectra were translated into the absorption spectra by the Kubelka-Munk method.

Kubelka-Munk's equation is described as follows: α =(1-R)2/2R, α where is the absorption coefficient and R the reflectivity at particular wavelength[5].

2.3.Tauc's Plot.

The bandgap energy can be determined using the Tauc relation[6-10]. It is a convenient way of studying the optical absorption spectrum of a material. According to the Tauc relation, the absorption coefficient **α** for direct band gap material is given by **α = A(hν - Eg)n** , Where **Eg** the band gap, constant **A** is different for different transitions, (**hv)** 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.

For direct allowed transition…… n = 1/2

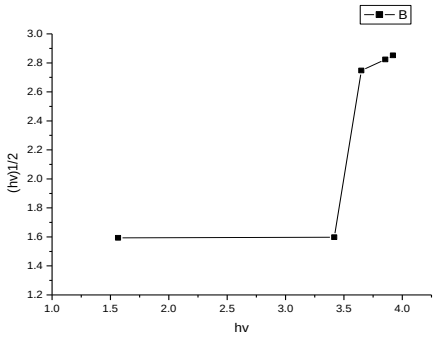
For direct forbidden transition…… n = 3/2

For indirect allowed transition…… n = 2

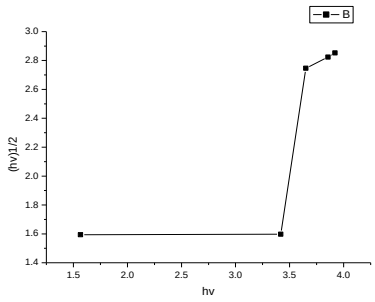
For indirect forbidden transition…… n = 3[5].

The Tauc plot for the sample PbSrCaCuO at temperatures 30˚C, 550˚C, 850˚C & 950˚C are presented in figure 4. Here we have taken the direct allowed transitions. The graph is plotted with **hv** along the Xaxis and **(hvα)** $^{1/2}$along the Yaxis. The band gap at a particular temperature is found by extrapolating the X axis.

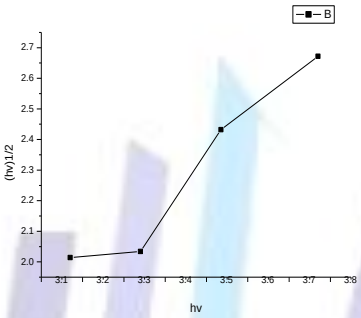
ISSN 2347-3487



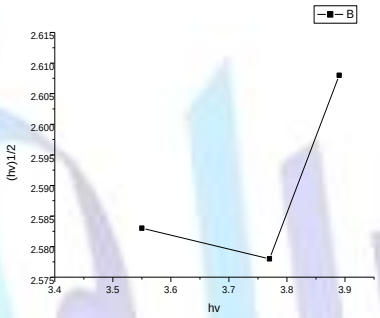
(a) at 30° C



(b) at 550° C



(c) at 850°C

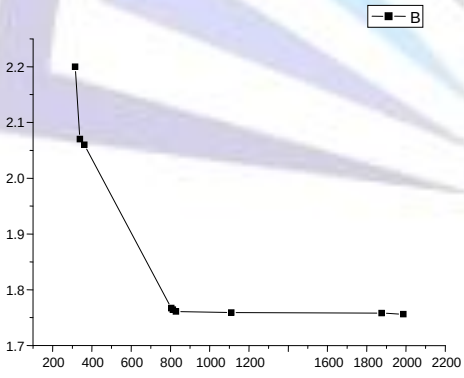


(d) at 950°C

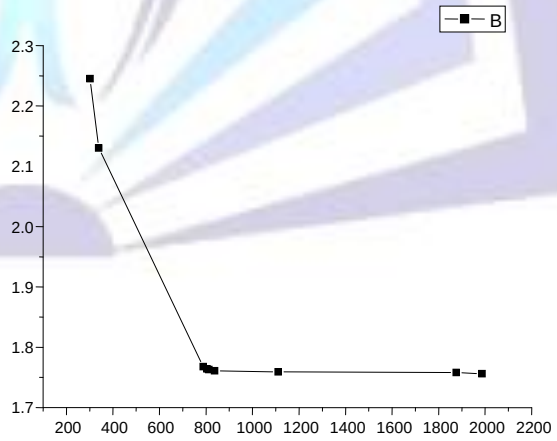
Fig.4. Tauc plot for the ceramics PbSrCaCuO at temperatures (a) 30°C, (b) 550°C, (c) 850°C & (d) 950°C

2.4.Refractive Index Study

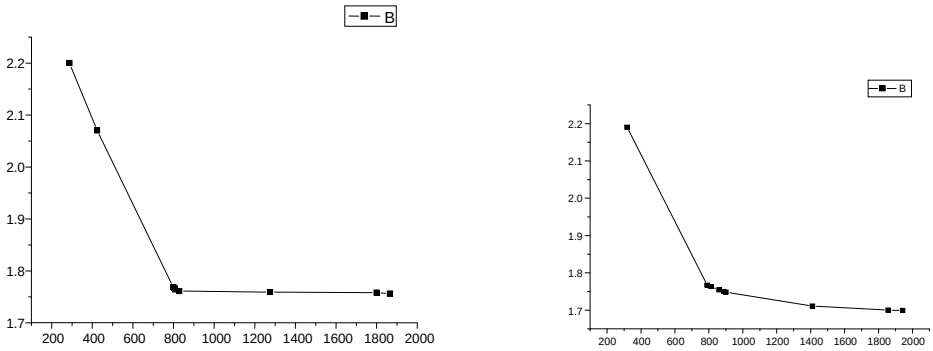
The variation of refractive index of the nano ceramic PbSrCaCuO with the wavelength was studied. The refractive index values showed a linear decrease with the increase in wavelength when plotted with refractive index along the Y-axis & wavelength along the X axis. The calculated values of the refractive index as a function of wavelength are shown in Fig.5.



(a) at 30^0C



(b) at550^0C



(c) at850^{0}C (d)at950^{0}C

Figure 5. refractive index Vs wavelength at different temperatures. (a) 30 ˚C, (b) 550˚C, (c) 850 ˚ C & (d) 950 ◦C

3. RESULTS AND DISCUSSION

The Ceramics **PbSrCaCuO** was prepared by solid state reaction technique in a special furnace with oxygen annealing in different temperatures in steps .Optical analysis of the same is done using UV-Vis Spectro photometer.

From UV-VIS. Analysis, The results very clearly confirms that band gap energy of a nano crystalline ceramic PbSrCaCuO 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.

$$\mathbf{e}^{\lambda\,\mathbf{max}} = \mathbf{0.0029km/T\ or\ \lambda\ inversely\ proportional\ to\ 1/T} \quad -(1)$$

The crystallite size of the sample PbSrCaCuO increases at d*ifferent treating temperatures[6*]. When the temperature reaches its sintering value, the bandgap energy tries to decrease. The crystallite size of the sample PbSrCaCuO at different temperatures are calculated [6] using the Debye Scherrer formula as $\boldsymbol{D = \frac{K\lambda}{\beta cos\theta}}$,

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 $\boldsymbol{\theta}$ *t*he diffracting angle in degrees .

The calculated values of the band gap energy of the sample of PbSrCaCuO at different values of temperature is given in the table -1 **.**

Table-1. Temperature Vs crystallite size and Band gap energy

Temperature	Crystallite size in nm	Band gap energy in e*V.*
30◦C	18.865	3.92
550◦C	21.44	4.09
850◦C	22.668	4.29
950◦C	24.449	3.89

From the Tauc plot data it is well confirmed that the band gap energy of the sample PbSrCaCuO increases when the temperature is raised. The increase in the crystallite size at different treating temperatures is already reported *[11].* But when the temperature reaches its sintering value, the crystallite size increases and hence the bandgap energy tries to decrease to the shorter wavelength regions.. A shift of band gap with a change in the size of nano scale materials is known as the quantum size effect. When the relation between the crystallite size and the energy gap is considered, it is observed that the band gap decreases with increase in the crystallite size. This is in agreement with the experimental results of Schuppler et al*[12].* Also with the theoretical calculations of Chang et al., Schuppler et al.*[12]* showed that with increase in crystallite size, the photoluminescence decreases i.e., band gap decreases. The theoretical calculations of Chang et al. through the surface bond contraction model showed that the width of the band gap grows as the dimensions of the crystallite size decreases [12] . The "quantum confinement" theory also showed the similar size induced band gap expansion. For thicker samples, the layer-layer interaction increases the dispersion of the electronic bands and tends to reduce the gap. From this, It can be concluded that the band gap is relative to the particle size of the materials, which is the most important feature of nano material.

In figure 5, it is observed that the refractive index of the sample decreases from **2.1 to 1.699** as the wavelength increases from **302nm to 901nm.**. The output of this fitting process gives us a relation between the refractive index and the wavelength. The full curve in Fig.5 represents the fitted data curve. The variation might be due to the eventual presence of the new phase formation in the sample*[13].*

4.CONCLUSION

The UV-VIS behaviour of the sample PbSrCaCuO at the different temperatures was successfully studied. Tauc plot data well confirms that the band gap energy of the sample increases when the temperature is increased. When the relation between the crystallite size and the energy gap is considered , it is observed that the band gap decreases with increase in the crystallite size which very well proves the quantum confinement.

The refractive index of the sample at different values of temperature were studied. Analysis clearly showed that refractive index of the sample decreases as the wavelength increases and attains a definite value for all the temperatures. This linear variation of the refractive index with the wavelength is due to dispersion of light energy at the different interstitial layers and the constant value attainment after a fixed wavelength is due to the new crystalline phase formation of PbSrCaCuO.This value of the refractive index is a constant for all the temperatures also.

ACKNOWLEDGMENTS

The authors are thankful to UGC and SAIF, Kochi for providing the data analysis and to the Principal, CMS College, Kottayam, Kerala for providing the facilities.

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ISSN 2347-3487

Author' biography with Photo

I, Ms. Reenu Jacob, Assistant Professor, Department of Physics, CMS College, Kottayam, Kerala, India, (wife of Er. Jacob Mathew, Kochukaleeckal, Rubber Board, Kottayam, Kerala,) was born on 23-04-1972. To fulfil my dream to learn Physics, I completed my PG course in MSc, Physics from University of Kerala Kariavattom,Trivandrum scoring 83%. I also cleared the eligibility test for Lectureship and joined as a faculty in Department of Physics at CMS College, Kottayam, Kerala. Presently I am concentrating with my research work in Material Science, Condensed Matter Physics under the Guideship of Dr. Jayakumari Isac, Professor (Rtd.), Research Guide in Mahatma Gandhi University, Kottayam, Kerala.