Determination of Basic Solid State Parameters and Characterization of Optical, Dielectric and Fluorescence Properties of Calcium Boro Lactate(CaBL)

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Summary: This paper describes the calculation of basic solid state parameters like penn gap, plasma energy, polarizability and fermi energy for calcium boro lactate single crystal. calcium boro lactate crystals were developed by solution growth method. Single crystal diffraction studies carried out and calculated basic solid state criterion for the CaBL compound. optical nature of these compound explained by using UV-Visible spectrum. Electro-optic behaviour of the crystal explained by dielectric studies. Light emitting properties explained by fluorescence studies.

Keywords: Solid state parameters; Optical properties; Dielectric studies; Fluorescence studies.

Introduction

Semiorganic materials having SHG property have an eminent role in fabrication of photonic devices [1, 2]. In recent years the synergy of optical signals with electrical materials has become an important part in the fields of solid-state and microwave electronics. This association, particularly through the areas of fibre-optic communications and optical computing, is ultimately resulting in the case whereby integrated optical and electronic systems have become vital as either one among them or its own. This SHG material shows wide variety of applications like mixing of frequency, electro-optic inflection, optical parametric oscillation, optical bistability, optical image refining, colour displays, underwater communication and medical diagnosis [3]. To alter optical signals to electrical signals and to exploit optical radiation [4] photoconductors, phototransistors, laser diodes, photodiodes, electro-optic modulators, and other components are frequently employed in optoelectronic telecommunications systems. Recently many experimenters have tried to seek out numerous sorts of novel SHG elements for doubling dye laser radiation [5]. In this paper we find out the basic solid state parameters like penn gap, plasma energy, polarizability and fermi energy for calcium boro lactate crystals. Optical, dielectric and fluorescence properties also explained for this title compound.

Experiment

Synthesis and Growth of Crystal

The method used to prepare the title compound(CaBL) is solution growth and slow evaporation method. Calcium boro lactate was prepared from the precursor materials of calcium carbonate, boric acid and lactic acid in 1:2:4 ratio. The calculated amount of lactic acid and boric acid were dissolved carefully in bidest water (ddH_2O). The required amount of calcium carbonate was then slowly added and stirred well for about 6 hours in a magnetic stirrer and evaporated to dryness. The temperature maintained for this reaction is 40^0C. Recrystallization of CaBL done by using 1:1 ethanol: water to get good quality of crystals. Fig. 1 and 2 shows the grown crystal and ortep diagram of calcium boro lactate.

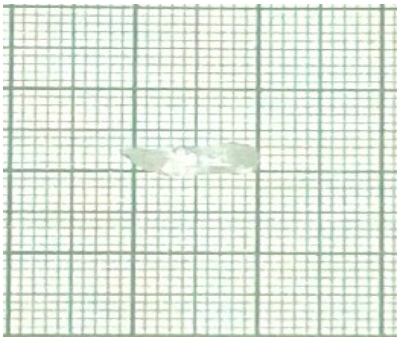

Fig. 1: Grown Crystal of CaBL.

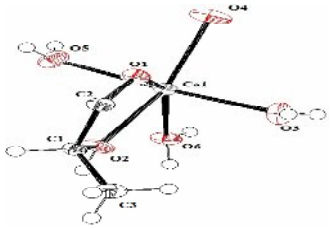

Fig. 2: Ortep diagram of CaBL.

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Results and Discussion

Single Crystal X-Ray Diffraction Analysis

Single crystal X-ray diffraction information was collected for CaBL at room temperature. An instrument named Bruker Kappa diffractometer with radiation of Mo Kα and using a scan mode of ω/2θ. In order to acquire exact unit cell parameters SMART APEX2 CCD area detector with radiation Mo Kα and scan mode ω. The x-ray diffraction studies disclose that the crystal corresponds to orthorhombic system a=8.49560(1)A^o b=10.0527(2) A^o c=21.3733(3) A^o v =1825.36(5) z = 4, 1.3469(1) mgm^{-3} R=0.03 and Mr = 1181.08. The CaBL crystal formed in the P_{212121} space group which was coincide with that of the disclosed values [6]. Molecular mass of CaBL crystal is M=370.13, and the total number of valance electron Z=144. The density comprises to be ρ=1.347 g.cm^{-3} for the developed crystal and relative permittivity at 1 MHz was evaluated as ε_∞ = 21.4. The valence electron plasma energy $\hbar\omega_p$ is termed as

$$\hbar\omega_p = 28.8\sqrt{\frac{Z\rho}{M}} \quad (1)$$

Total number of valence electrons is denoted by Z, density is denoted by ρ and M denotes the molecular weight of the CaBL single crystal. The Plasma energy in relation to Penn gap and Fermi energy [7] is termed as

$$E_p = \frac{\hbar\omega_p}{(\varepsilon_\infty - 1)^{1/2}} \quad (2)$$

where ε_∞ - relative permittivity at 1 MHz

and

$$E_F = 0.2948(\hbar\omega_p)^{4/3} \quad (3)$$

Polarizability, α is obtained using the relation

$$\alpha = \left[\frac{(\hbar\omega_p)^2 S_o}{(\hbar\omega_p)^2 S_o + 3E_F^2}\right] \times \frac{M}{\rho} \times 0.396 \times 10^{-24}\ \text{cm}^{-1} \quad (4)$$

S_o is denoted as constant for a specific substance and is termed as

$$S_o = 1 - \left[\frac{E_F}{4E_F}\right] + \frac{1}{3}\left[\frac{E_F}{4E_F}\right]^2$$

Clausius-Mossotti equation which is represented by the value of 'α' termed as

$$\alpha = \frac{3M}{4\pi N_{a\rho}}\left[\frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2}\right] \quad (5)$$

where N_a represents Avagadro number and the fundamental data on the developed crystal of CaBL are calculated and are tabulated in Index 1

Table-1: Some speculative data for CaBL single crystal.

S.No	Terms	values
1.	Fermi gap (eV)	20.47
2.	Plasma energy (eV)	20.84
3.	Penn gap (eV)	4.61
4.	Polarizability (cm^3) Penn analysis	9.14x10^{-23}
5.	Polarizability (cm^3) Clausius-Mossotti Equation	9.4x10^{-23}

Optical Transmission Studies

The absorption spectrum of UV-Vis for developed crystal was carried out between 190nm to 790nm with an instrument model lambda 25 spectrophotometer. The spectrum is taken in the speed 120nm/min with a data interval 1.0000nm. The graph shown in Fig. 3

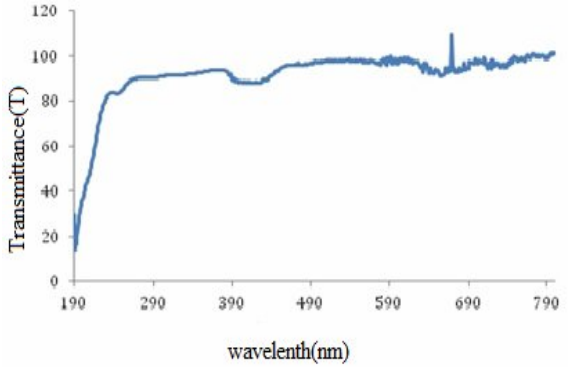

Fig. 3: UV-Visible spectrum of CaBL.

The significant elements for optical applications [8, 9] are optical transmittance translucence cut-off wavelength of the developed crystal. Appreciable transition of the developed CaBL in the whole region of visible wavelength suggests its propriety to frequency conversion [10, 11].The developed CaBL crystal was identified almost at 230nm for UV transmittance edge. Variety of transition of electrons [12] and electronic band structure were studied based on the optical absorbance coefficient depending on photon energy levels.

It is noticed that the spectrum in the total visible region shows low absorbance. So it has

sufficient transparancy of about 85% with lower cut-off wavelength 230 nm and the transmission extends neatly from 230 nm to 790 nm makes it helpful for those application need blue or green light. The label compound CaBL has good crystal quality with fabrication of non linear optical devices. As CaBL crystal shows wide transmission vary, ranging from 230 nm ahead, it is used for optical operation as well as frequency doubling of Nd:YAG (neodymium-doped yttrium aluminium garnet; $Nd:Y_3Al_5O_{12}$) laser of fundamental wavelength with λ=1064 nm. The evaluated transmittance (T) info was employed to determine the coefficient of absorption (α) belonging to subsequent relation,

$$\alpha = \frac{2.303 \log\left(\frac{1}{T}\right)}{t}$$

Thickness of the crystal is denoted as't'. To acquire accurate information regarding band gap of the crystal was determined by the coefficient of absorption depending on photon energy. The plot of coefficient (α) against operates of photon energy at ambient temperature as demonstrated in Fig. 4.

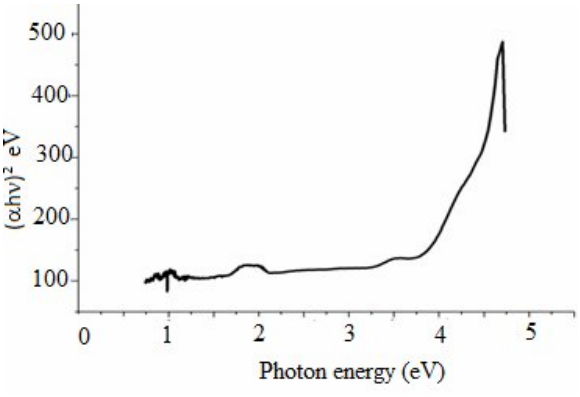

Fig. 4: Plot of $(\alpha h\nu)^2$ vs. photon energy of CaBL crystal.

By the graph it is evident that the absorption coefficient varies from 125 to 500 cm^{-1} with multiplying photon energy of 3.75 to 4.5 ev. By reason of ample band energy gap, the developed CaBL has broad transference in the wavelength of visible range [13]. Being a explicit band gap material, the crystal behind the test has coefficient of absorption (α) accepting the subsequent cognition for large photon energies (hυ)

$$\alpha = \frac{A\left(h\nu - E_g\right)^{1/2}}{h\nu}$$

Optical band gap is denoted as E_g for the crystal and 'A' is the arbitrary constant. Plank's constant is denoted by 'h' and frequency of incident photons is denoted by 'ν'.

Optical Constant Studies

Based on transmission (T) spectrum and Reflection (R) spectrum the optical constants (n,K) and the absorption coefficient(α) are defined.

$$T = \frac{(1-R)^2 \exp(-\alpha t)}{(1-R)^2 \exp(-2\alpha t)} \quad (1)$$

Thickness is denoted as 't'.

Relation of extinction coefficient K with α is given by

$$K = \frac{\alpha\lambda}{4\pi}$$

The reflectance (R) in terms of the absorption coefficient and refractive index (n) can be expressed

$$R = \frac{1 \pm \sqrt{1 - \exp(\alpha t + \exp(\alpha t))}}{1 + \exp(-\alpha t)} \quad (2)$$

$$n = \frac{(R+1) \pm \sqrt{3R^2 + 10R - 3}}{2(R-1)} \quad (3)$$

Fig 5 demonstrates the plot of absorption coefficient (vs) extinction coefficient.

Fig 6 demonstrates the plot of wavelength (vs) refractive index.

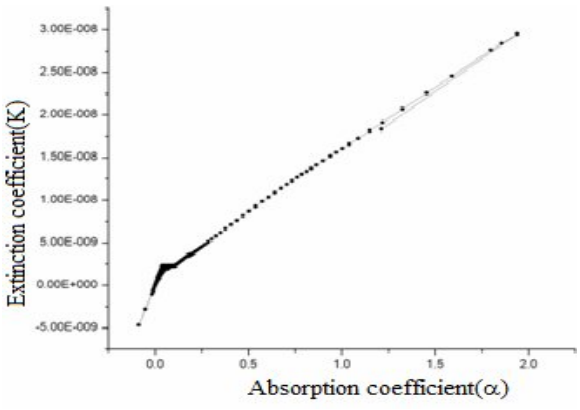

Fig. 5: Dependence of absorption coefficient (vs) extinction coefficient.

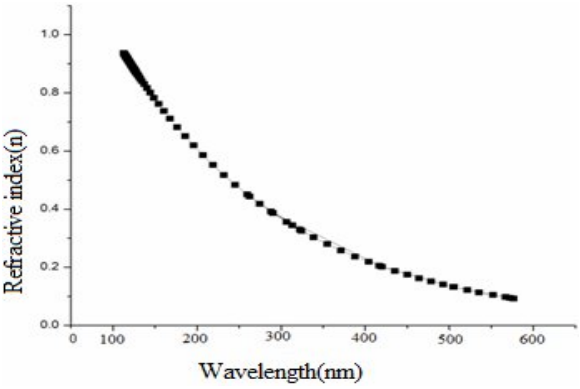

Fig. 6: Dependence of wavelength (vs) refractive index.

The reaction of electro-optical materials to an electric field is due to variation of their refractive indices. This reaction is employed towards the amendment of polarization state of light by employing voltage to an electro-optical crystal that acts as a voltage-dependant wave plate.

By graph, it is clear that both refractive index (n) and extinction coefficient (k) rely upon wavelength and coefficient of absorption. Internal potency of the device also relies upon wavelength. Therefore by tailoring absorption coefficient, one will conclude an apt material used for the fabrication of electro-optic and opto electronic devices.

Dielectric studies

Dielectric property of CaBL was studied as a function frequency crystal using a HIOKI-LCR HITESTER 3535 instrument. The temperature dependent dielectric property was observed for different temperatures (313 K and 323 K). The crystal sample was coated with silver paste on either side to form electrodes and the variation of dielectric permittivity and dielectric loss of CaBL at different temperatures is shown in Fig. 7 and 8.

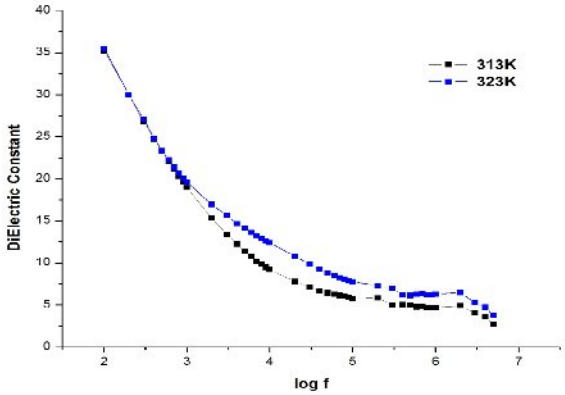

Fig. 7: Dielectric constant (Vs) log F graph.

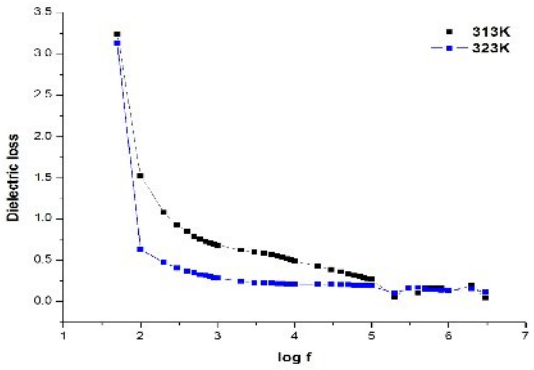

Fig. 8: Dielectric loss (Vs) log F graph.

The exchange of electrons between the ions in the material creates local displacement of electrons in the applied field direction and this causes polarization. The relative dielectric constant and dielectric loss of the crystal is due to the input of electronic, ionic, dipolar and space charge polarizations which depend on the frequencies. The dielectric constant and loss decreases very swiftly at low frequencies and slowly at higher frequencies. This is a common dielectric nature of the material [14, 15]. This is matched with the graphical representation of dielectric constant and loss of CaBL crystal. Higher the dielectric constant at lower frequencies is certified to space charge polarization. The distinctive low dielectric loss at a range of high frequency for a given sample concludes that the CaBL crystal possesses appreciable optical nature and this factor is play an important role in so many NLO applications[16]. After redistributing charges founds and the currents are triggered, so this crystal was focused with a separate electric field. By using the formula [17] $\sigma_{ac} = \varepsilon_0\varepsilon_r\omega\tan\delta$, the calculation was done for ac conductivity, in this ω is the angular frequency ($\omega = 2\pi\nu$). Fig. 9 demonstrates the variation of electrical conductivity of CaBL crystal with distinct frequencies.

Notable ac conductivity variation will be seen at greater frequencies. It proofs the well found relation $\sigma = n_d e\mu e$, that electrical conductivity is relative to carrier concentrations and mobility. In this n_d is the number solidity of electron and μe is the mobility of electron. This shows the CaBL crystals optical conductivity will grows by increase in the energy which applies.

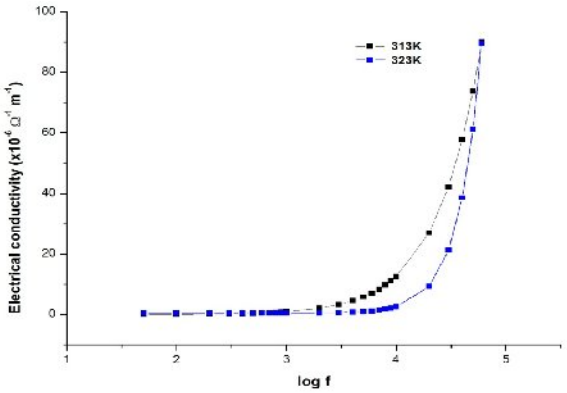

Fig. 9: Dependence of Electrical conductivity (vs) log F.

Fluorescence Studies

Fluorescence arises while atoms or molecules excited by collecting photons from absorption spectrum, and briskly exude photons as molecules drive back to ground state. Fluorimetry is a significant analytical method that describes resemblance between emitted and absorbed photons at specified wavelength which is economical and monitored easily. The occurrence of fluorescence in solids is of excitation of electronic states of solids by optical photons of particular energy. The fluorescence spectrum is observed in the range of 300-700nm with an excitation wavelength of 320nm as shown in Fig.10.

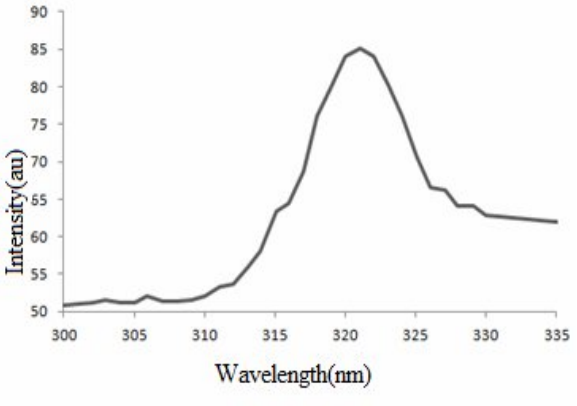

Fig. 10: Fluorescence Excitation plot of CaBL.

The first peak that corresponds to the wavelength is lower cut-off wavelength of~320nm. From this wavelength, optical energy gap is calculated. It is noticed to be 3.8ev.The optical energy gap obtained from the fluorescence spectrum is similar to that obtained from UV-VIS spectrum of the sample. The other peak observed at 550nm determines the green emission that may be due to the non-centro symmetric nature of the developed crystal and may be assigned as π-π* transition due to the interaction between the metal (Ca^{2+}) and the boro lactate [18]. The emission spectrum of CaBL shown in Fig. 11.

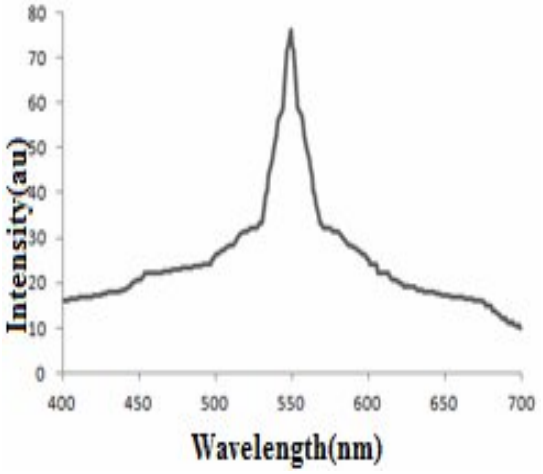

Fig. 11: Fluorescence Emission plot of CaBL.

Thus, the grown CaBL crystals possess the nonlinear optical properties and it is cross -checked by Kurtz Perry SHG test. Its efficiency is 1.5 better than that of KDP crystals.

Conclusion

For the first time, single crystal of CaBL was grown by solution growth- slow evaporation method. XRD data reveals that the CaBL crystal is orthorhombic with a P_{212121} space group. The lower cut off wavelength analyzed by UV-Vis spectrum was determined to be 230 nm. Optical constant studies and dielectric studies explain that this crystal suitable material to be used in opto-electronic and electro-optic devices. Fluorescence studies confirm that this crystal emits green light.

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