

Investigations on Mechanical and Dielectric Properties of NLO material: 4-methoxybenzoin

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ABSTRACT

Organic nonlinear optical single crystals of 4-methoxy benzoin were grown by slow evaporation technique. The lattice parameters and crystal structure of the grown crystal were confirmed using single crystal X-ray diffraction analysis. Optical absorption range of the grown crystal was measured by UV-VIS-NIR spectrophotometer. Mechanical behavior was analyzed using Vicker's microhardness test. Microhardness studies revealed that the hardness of the grown crystal increases with an increase in load. Meyer's index number n was calculated and found that the material belongs to soft material category. The dielectric behavior of the crystal was carried out at different temperatures in the frequency range of 50 Hz to 5 MHz. The frequency dependence of dielectric constant and dielectric loss is found to be decreased with increase in frequency at different temperatures. Low dielectric loss shows that the grown crystal contains lesser defects manifesting the suitability of the crystal towards device applications.

Keywords: Solution growth, NLO, Single crystal XRD, UV-VIS-NIR Spectrophotometer, Microhardness, Meyer's index, Dielectric constant and Dielectric loss

1. INTRODUCTION

The Nonlinear optics (NLO) is now established as an alternative field to electronics for future photonic technologies. The fast growing development in the optical fiber communication systems have stimulated the search for new NLO materials that are capable of fast and efficient processing of optical signals and integrated optics [1]. Many optically active amino acids show high efficient optical second harmonic generation and are promising candidates for laser and optical communication technology [2]. The crystals capable of generating second harmonics must have a unit cell with no centre of inversion and this requirement is met by the crystals of pure amino acids since these molecules themselves are dissymmetric. The synthesis, structural, vibrational, optical and second harmonic generation (SHG) properties of single crystals of 4-methoxy benzoin have been reported earlier [3]. The present investigation, deals with the growth of 4-methoxy benzoin single crystals by slow evaporation technique. The grown single crystals were subjected to single crystal X-ray diffraction, optical absorption, microhardness and dielectric studies. The results of these investigations are discussed.

2. MATERIAL AND METHODS

Single crystals of 4-methoxy benzoin, an organic nonlinear optical material have been synthesized by a slow evaporation technique at room temperature yielded many small crystals. The defect-free, optically clear, and perfectly shaped tiny crystals were chosen as seeds for the growth experiment. From XRD studies, it is confirmed that 4-methoxy benzoin belongs to orthorhombic crystal structure with space group $Pca2_1$. The single crystalline nature is thus confirmed and the space group reveals that the material shows no inversion

symmetry (non-centrosymmetric). Optical absorption measurements were made using Perkin Elmer Lambda 35 UV-VIS-NIR spectrophotometer with a resolution of 2 nm in the region from 200 nm to 1000 nm to measure the absorption range of the crystal. The mechanical characterization of the 4-methoxy benzoin crystals have been examined using Vickers microhardness studies. The single crystals with flat and smooth faces were chosen for the static indentation tests and the same crystal was mounted on the base of the microscope. The indentations were made gently by varying the loads from 10 to 50 g for a dwell period of 10 s using both Vickers diamond pyramid indenter attached to an incident ray research microscope (Mitutoyo MH112, Japan). The intended impression of Vickers was approximately square in shape. The shape of the impression is dependent on the structure, face and materials used. After unloading, the length of the two diagonals was measured by a calibrated micrometer attached to the eyepiece of microscope. For each load, at least five well-defined indentations were considered and the average is taken as d . The dielectric measurements for 4-methoxy benzoin single crystals have been carried out using HIOKI 3532-50 LCR HITESTER. Carefully selected samples were cut using a diamond saw and polished using paraffin oil and fine grade alumina powder to obtain a good surface finish, and coated with conducting silver paste in order to increase the ohmic contact. The dielectric permittivity measurements were carried out with the sample placed inside a dielectric cell whose frequencies could be varied in a controlled manner for different temperatures 35 - 95°C, respectively.

3. RESULTS AND DISCUSSION

3.1 Single Crystal XRD

The study revealed that 4-methoxy benzoin single crystals belong to orthorhombic crystal system with a non-centrosymmetric space group $Pca2_1$. The lattice parameters were found to be $a=14.45 \text{ \AA}$, $b=14.08 \text{ \AA}$, $c=5.85 \text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$ with unit cell volume $V = 1192.62 \text{ \AA}^3$. These lattice parameters values are found to be in good agreement with the reported values [3].

3.2. Optical Studies

UV-VIS-NIR absorption spectrophotometer was used to record the absorption spectrum in the range between 200 nm and 1000 nm. From the observed spectrum (Fig.1), the lower cut-off wavelength is found to be 400 nm. The absence of absorption in the near infrared region provides the access to the laser wavelength of 1064 nm from Nd: YAG source for second harmonic generation. Hence, UV absorption studies reveal that the grown 4-methoxy benzoin crystal is one of the suitable materials for exhibiting second harmonic generation in the entire visible and near infrared region. The measured transmittance (T) was used to calculate the absorption coefficient (α) using the relation,

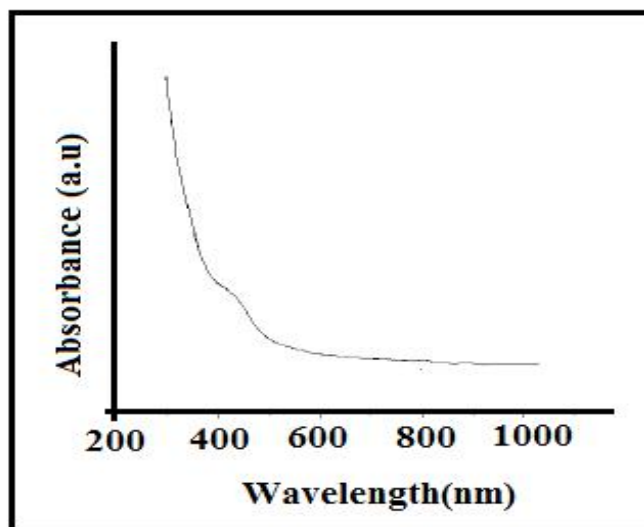
$$\alpha = \frac{2.3026 \log\left(\frac{1}{T}\right)}{t} \quad (1)$$

where T is the transmittance and t is the thickness of the crystal. As a direct bandgap of the crystal below study has an absorption coefficient (α) obeying the following relation,

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

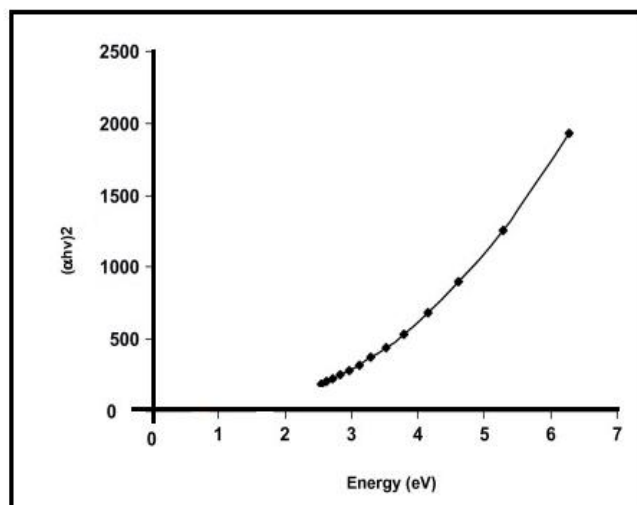
where E_g is the optical band gap of the crystal and A is a constant. The Tauc's plot of $(\alpha h\nu)^2$ against the photon energy ($h\nu$) at room temperature (Fig.2) shows a linear behaviour, (α -absorption coefficient and h -Planck's constant) which can be considered as an evidence of the indirect transition. Hence, assuming indirect transition between valence band and conduction band, the bandgap (E_g) is estimated by extrapolation of the linear portion of the

87 curve to the point $(\alpha h\nu)^2 = 0$ [4]. Using this method, the band gap of the 4-methoxy benzoin
88 crystal was found to be 3.50 eV. As a consequence of wide band gap, the grown crystal has
89 large transmittance in the visible region [5].
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Fig. 1. UV-VIS-NIR absorption spectrum of 4-methoxy benzoin crystal



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Fig.2. Band gap of 4-methoxy benzoin crystal

100 3.3 Microhardness study

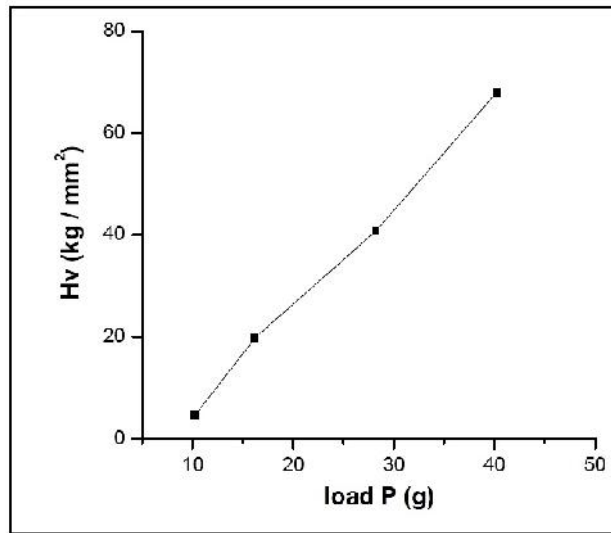
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The mechanical studies of crystals are evaluated by mechanical testing. The fastest and simplest type of mechanical testing is hardness measurement. Among the different testing methods, the Vickers hardness test is commonly used. Microhardness study was

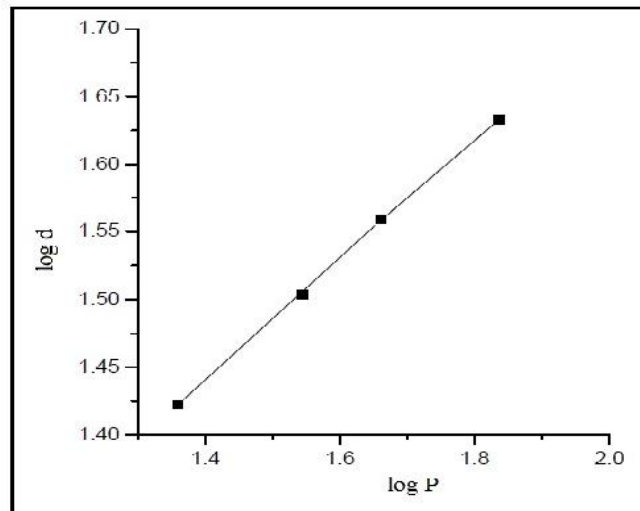
105 conducted using a Vickers microhardness tester fitted with a diamond pyramidal indenter.
 106 The applied load was varied from 10 to 50 g for a constant indentation period of 10 s. The
 107 Vicker's hardness number H_V is calculated using the relation
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$$109 \quad H_V = 1.8544 P / d^2 \text{ kg/mm}^2 \quad (3)$$

110 where P is the indenter load in kg and d is the diagonal length of the impression in mm . A
 111 graph was plotted for hardness versus load (Fig. 3) and $\log P$ versus $\log d$ (Fig.4). The plot
 112 of $\log P$ versus $\log d$ yields a straight line, and its slope gives the work hardening coefficient
 113 or the Meyers index number ' n '. The value of n is found to be 1.62 and since the value of n is
 114 less than 2, the hardness of the material is found to increase with the increase of load (Fig.4)
 115 which confirms the prediction of Onitsch [6] and also the reverse indentation size effect [7,8].
 116 From the Meyer's index number it is clear that the title material belongs to hard material
 117 category [9].



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 119 Fig. 3. Vickers hardness of 4MB as a function of applied load
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 122 Fig. 4. Plot of $\log d$ Vs $\log p$
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3.4 Dielectric Studies

The dielectric analysis is an important characteristic that can be used to bring knowledge based on the electrical properties of a material medium as a function of temperature and frequency. Based on this analysis, the capability of storing electric charges by the material and capability of transferring the electric charge can be measured. The dielectric properties are correlated with electro optic property of the single crystals, particularly when they are non-conducting materials [10]. Microelectronics industry needs low dielectric constant (ϵ_r) materials as an interlayer dielectric. The dielectric constant is calculated using the formula

$$\epsilon_r = \frac{Ct}{\epsilon_0 A} \quad (4)$$

where C is capacitance (F), t the thickness (m), A the area (m^2), and ϵ_0 the absolute permittivity in the free space having a value of $8.854 \times 10^{-12} \text{ Fm}^{-1}$. The frequency dependence of the dielectric constant at different temperatures is shown in Fig.5. It is found that the dielectric constant of 4-methoxy benzoin is high at low frequencies and it decreases with increasing frequency. This also indicates that the value of dielectric constant increases with increase in temperature. As the net polarization present in the material is due to ionic polarization, electronic polarization, dipolar polarization and space charge polarization. First two do not decrease very significantly with rise in temperature. Contribution of decrease in dielectric constant due to electronic polarization is very less. Dipolar polarization is also expected to decrease with temperature as it is inversely proportional to temperature. The contribution to polarizability to space charge depends on purity and perfection of crystals. At low temperature and high frequency we may take it as negligible. However it is significant in the low frequency region. As the temperature increases the contribution from space charge effect towards polarization may have tendency to increase. The high value of dielectric constant is attributed to high ionic conductivity. Most of the solid electrolytes have high dielectric constant [11]. The dielectric constant of a material is composed of four contributions such as electronic, ionic, orientational and space charge polarizations. All these may be active at low frequencies. In fact, the nature of the variation of dielectric constant with frequency indicates which type of contributions present in the sample. The decrease in dielectric constant with increase in frequency may be attributed to the dependence on the electronic, ionic, orientational and space charge polarizations. Fig. 6 shows the decrease of dielectric loss of 4-methoxy benzoin as a function of frequency. The dielectric loss decreases with increase in frequency at almost all temperatures but appears to achieve saturation in the higher frequency range of 1 MHz and above at all the temperatures. It is also observed that as the temperature increases, the value of dielectric constant also increases to a considerable value (Fig. 7). The same trend is observed in the case of dielectric loss versus temperature as well (Fig. 8). It is well observed that the dielectric loss decreases with increasing frequency. The low value of dielectric loss indicates that the grown crystals are good in quality [12]. The characteristic of low dielectric constant and dielectric loss with high frequency for a given sample suggests that the sample possesses enhanced optical quality with lesser defects and this parameter is of vital importance for various nonlinear optical materials and their applications [13].

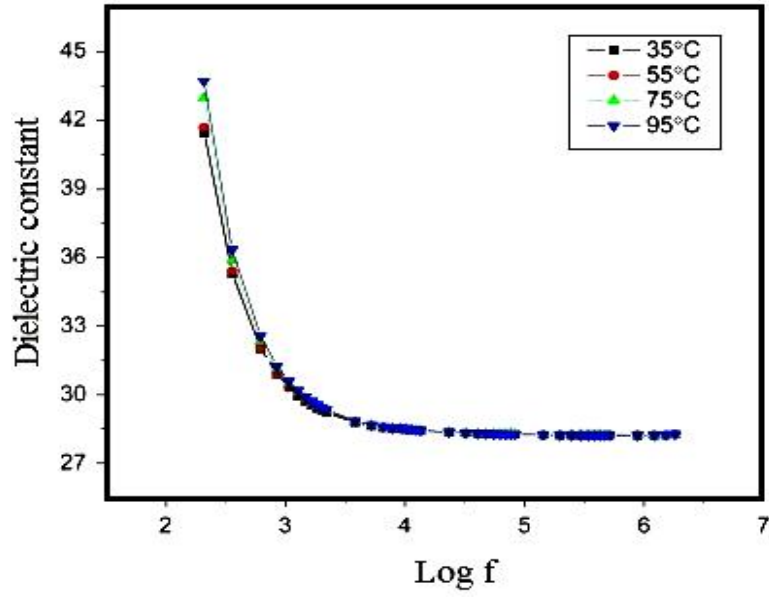


Fig. 5. Variation of dielectric constant with $\log f$

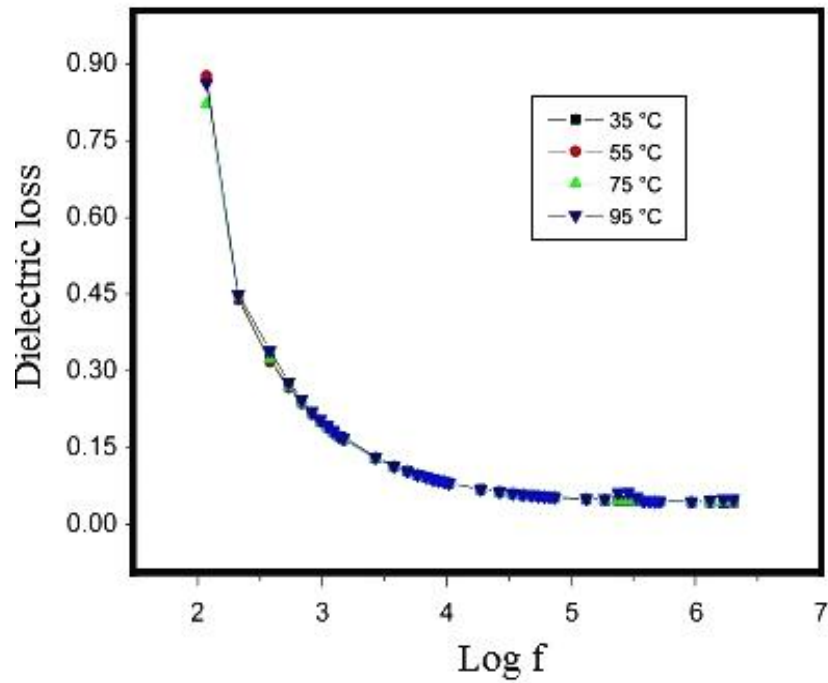


Fig.6. Variation of dielectric loss with $\log f$

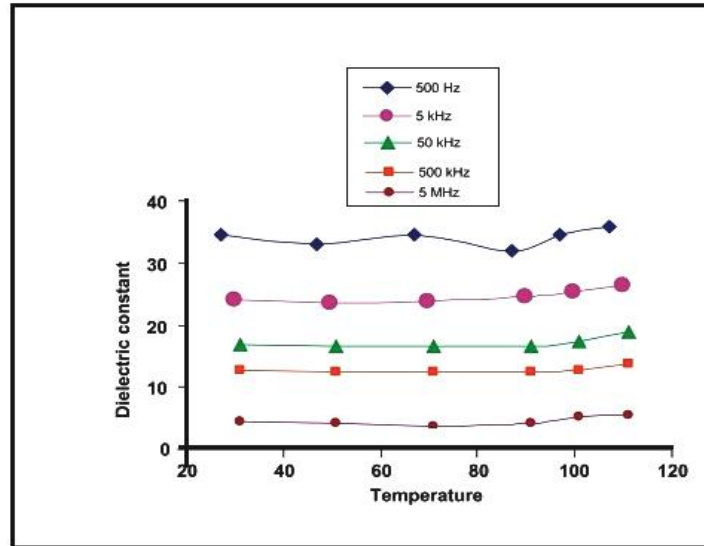


Fig.7. Temperature dependence of dielectric constant

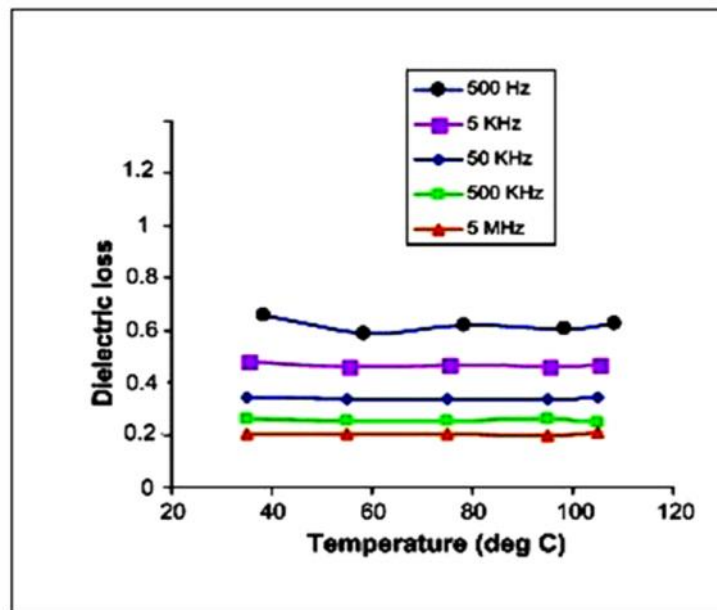


Fig.8. Temperature dependence of dielectric loss

4. CONCLUSION

The single crystals of 4-methoxy benzoin were grown by slow evaporation technique. The grown crystal is confirmed by X-ray diffraction analysis and it is found that the crystal belongs to the orthorhombic system with the space group $Pca2_1$. The optical absorption spectral analysis reveals that the crystal is transparent in the entire UV-VIS-NIR region with the lower cut-off wavelength as 400 nm. The optical bandgap for the grown crystal is found to be 3.50 eV. Mechanical hardness studies reveal that Vicker's hardness number increases as the load increases. The dielectric studies revealed that 4-methoxy benzoin has low dielectric loss with less power dissipation and hence this crystal can be used for optical applications. Dielectric studies reveal that both dielectric constant and dielectric loss decreases with increase in frequency. The dielectric characterization shows low value of dielectric constant at higher frequencies for these crystals.

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