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### Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy



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## Growth, crystalline perfection and characterization of benzophenone oxime crystal

dielectric studies and microhardness analysis.

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ABSTRACT

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#### ARTICLE INFO

Article history: Received 1 December 2011 Received in revised form 10 February 2012 Accepted 17 February 2012

Keywords: Organic compound High resolution X-ray diffraction Single crystal growth FT-IR Dielectric properties

#### 1. Introduction

Oximes of carbonyl compounds are important because of their use in the purification and characterization of carbonyl compounds and also their use in organic synthesis as intermediates and medicinal chemistry [1–4]. Different oximes and their metal complexes have shown versatile bioactivity as chelating therapy agents, as drugs and as inhibitors of enzymes [5]. The bulk growth and properties of benzophenone, substituted benzophenone and its derivatives [6–16] have been extensively studied. The second harmonic generation efficiencies of some benzophenone derivatives properties of benzophenone oxime have not been reported so far to the best of our knowledge. In the present study, BPO was purified and grown as a single crystal using solution growth technique and the grown crystals were characterized by various techniques.

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#### 2. Experimental

#### 2.1. Synthesis and crystal growth

Single crystals of benzophenone oxime (BPO) have been grown by slow evaporation solution growth

technique from ethanol at room temperature. The single crystal X-ray diffraction study reveals that the

crystal belongs to monoclinic system and cell parameters are, a = 9.459 Å, b = 8.383 Å, c = 26.690 Å, v = 2115

Å<sup>3</sup> and  $\beta$  = 92.807°. The structure and the crystallinity of the materials were further confirmed by powder X-ray diffraction analysis. The various functional groups present in the molecule are confirmed by FT-IR

analysis. The TG/DSC studies reveal the purity of the material and the crystals are transparent in the entire

visible region having a lower optical cut-off at ~300 nm. The crystalline perfection was evaluated by high-

resolution X-ray diffraction (HRXRD). The crystal is further characterized by Kurtz powder technique,

The BPO was synthesized according to the reported method [19] with an yield of  $\sim$ 90%. The product was purified by repeated recrystallization from hot rectified spirit (m.p.  $\sim$  146° C).



are reported by Frazier et al. [17] and Cockerham et al. [18]. The growth, crystalline perfection, thermal, mechanical and dielectric

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BPO single crystals were grown using slow evaporation solution growth technique at room temperature. A saturated solution of BPO in ethanol was prepared and the solution stirred for 2–3 h at room temperature to obtain a homogeneous solution. A beaker containing BPO solution was tightly covered with a thin polythene sheet to control the evaporation rate of the solvent and kept

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Fig. 1. Photographs of as-grown BPO crystals.

undisturbed in a dust free environment. Numerous tiny crystals were formed at the bottom of the container due to spontaneous nucleation. Macroscopic defect-free crystals of BPO were harvested after 4 days after attaining a suitable size and shape. The photographs of the as-grown BPO crystals are shown in Fig. 1.

#### 3. Results and discussion

#### 3.1. Single crystal X-ray diffraction

The as-grown benzophenone oxime crystals were subjected to single crystal X-ray diffraction analysis using Bruker AXS (Kappa Apex II) X-ray diffractometer with MoK<sub> $\alpha$ </sub> radiation ( $\lambda$  = 0.71073 Å) to determine unit cell dimensions. The grown crystal is found to crystallize in the monoclinic system with space group  $P_{2_1}/n$ . The obtained unit cell parameters are listed in Table 1 and the unit cell parameters are in good agreement with the reported values [20].

#### 3.2. Powder X-ray diffraction analysis

As-grown BPO crystal was finely powdered and subjected to powder XRD analysis using a Philips Xpert Pro Triple-axis X-ray diffractometer at room temperature using a wavelength of 1.540 Å and a step size of 0.008°. The samples were examined with CuK<sub> $\alpha$ </sub> radiation in a 2 $\theta$  range of 10°–70°. At room temperature all the observed reflections were indexed. The indexed powder XRD pattern of the as-grown BPO crystal is shown Fig. 2. The well defined Bragg's peaks at specific 2 $\theta$  angles show good crystallinity of the materials.

#### 3.3. High-resolution X-ray diffraction analysis

To evaluate the crystalline perfection of the specimen crystals, high-resolution X-ray diffraction (HRXRD) analysis was carried

Table 1	
Single crystal XRD data for as-grown BPO crystal.	

Parameters	Reported value <sup>a</sup>	Present study
a (Å)	9.466	9.459
b (Å)	8.369	8.383
<i>c</i> (Å)	26.71	26.690
α(°)	90	90
β(°)	92.89	92.807
γ (°)	90	90
Volume (Å <sup>3</sup> )	2113	2115
System	Monoclinic	Monoclinic



Fig. 2. Powder XRD patterns of BPO crystal.

out. A multicrystal X-ray diffractometer developed at National Physical Laboratory (NPL), New Delhi [21] was used to record highresolution rocking or diffraction curves (DCs). In this system, a fine focus (0.4 mm × 8 mm; 2 kW Mo) X-ray source energized by a wellstabilized Philips X-ray generator (PW 1743) was employed. The well-collimated and monochromated  $MoK_{\alpha 1}$  beam obtained from the three monochromator Si crystals set in dispersive (+, -, -) configuration has been used as the exploring X-ray beam. The diffracted intensity is measured by using a scintillation counter. The DCs were recorded by changing the glancing angle (angle between the incident X-ray beam and the surface of the specimen) around the Bragg diffraction peak position  $\theta_{\rm B}$  (taken zero as reference point) starting from a suitable arbitrary glancing angle ( $\theta$ ). The detector was kept at the same angular position  $2\theta_{\rm B}$  with wide opening for its slit, the socalled  $\omega$  scan [22]. Before recording the diffraction curve, to remove the non-crystallized solute atoms remained on the surface of the crystal and also to ensure the surface planarity, the specimens were first lapped and chemically etched in a non-preferential etchant of water and acetone mixture in 1:2 volume ratio.

Fig. 3 shows the high resolution X-ray diffraction curve recorded for (0 2 0) diffracting planes using  $MoK_{\alpha 1}$  radiation for a typical BPO single crystal specimen in symmetrical Bragg geometry. On careful observation, the curve does not seem to be a single peak. The solid line (convoluted curve) is well fitted with the experimental points represented by the filled circles. On deconvolution of the diffraction curve, it is clear that the curve contains an additional peak which is 320" away from the higher intensity peak. The additional



Fig. 3. HRXRD curves recorded for BPO crystal.



Fig. 4. FT-IR spectrum of BPO crystal.

peak corresponds to an internal structural low angle boundary. For a better understanding, the schematic of a structural grain boundary is given as the inset of Fig. 3. As seen in the inset two regions of the crystal are misoriented by a finite angle say  $\alpha$ , known as tilt angle. Tilt angle may be defined as the misorientation angle between the two crystalline regions on both sides of the structural grain boundary. The two regions may be perfect. If the value of  $\alpha$ is  $\leq 1'$ , we may call it as very low angle boundary. If  $\alpha > 1'$  but less than a deg, we call it as low angle boundary. For more details of such structural grain boundaries including their effect on physical properties, reference is made available elsewhere [22,23]. The angular separation between the two peaks gives the tilt angle  $\alpha$  which is 320" for the specimen crystal as seen in the figure. The FWHM (full width at half maximum) of the main peak and the low angle boundary are respectively 430 and 760". These relatively higher values reveal the fact that both the regions of the crystal are not that perfect. These types of structural defects are probably generated in the crystals due to mechanical/thermal fluctuations occurred during the growth process and/or also due to fast growth [24]. It may be mentioned here that such minute defects could be detected with well resolved peaks in the diffraction curve only because of the high-resolution of the diffractometer, characterized by very low values of wavelength spread i.e.  $\Delta\lambda/\lambda$  and horizontal divergence for the exploring or incident beam, which are respectively around 10<sup>-5</sup> and much less than 3" of the multicrystal X-ray diffractometer used in the present studies.

#### 3.4. FT-IR analysis

The FT-IR spectrum was recorded for BPO crystal using an AVATAR 330 FTIR by KBr pellet technique in the range of 400–4000 cm<sup>-1</sup> (Fig. 4). An absorption band in the region 3000-3100 cm<sup>-1</sup> is due to C–H stretching frequency of aromatic ring. The band at 1490 cm<sup>-1</sup> is due to C=C stretching frequency of aromatic ring. The broad band appeared at 3250 cm<sup>-1</sup> is due to –OH stretching frequency of benzophenone oxime.

#### 3.5. Optical studies

Optical absorption spectrum of the grown benzophenone oxime single crystal was recorded in the wavelength region from 100 to 1200 nm using Perkin-Elmer Lambda 35 UV-vis spectrophotometer. The as-grown benzophenone oxime single crystal was polished and the good transparent single crystal with 2 mm thickness was used for the optical studies. The spectrum (Fig. 5) shows that the absorption is minimum in the entire visible region and cut-off wavelength is around ~300 nm. The UV cut-off wavelengths of the



Fig. 5. UV-vis spectrum of BPO crystal.

#### Table 2

UV cut-off  $(\lambda_{max})$  benzophenone and its derivatives.

System	UV cut-off (nm)	Reference
Benzophenone	~391	[6]
Benzophenone hydrazone	~340	[10]
Benzophenone semicarbazone	~280	[11]
Benzophenone oxime	~300	Present study

BPO crystal and some other benzophenone derivatives are given in Table 2.

#### 3.6. Mechanical studies

The crystal with 2 mm thickness was used for microhardness measurements using Reichert 4000E Ultramicrohardness tester. Vickers microhardness number  $H_v$  was calculated using the relation,  $H_v = 1.8544(P/d^2)$  kg/mm, where P is the applied load, d is the diagonal length of the indentation impression and 1.8544 is a constant factor for the diamond pyramid. The hardness number increases with increase of load (Fig. 6). The relation between load P and indentation length d is represented by Meyer's law  $P=Ad^n$ , where n is the Meyer index of work hardening exponent and A is constant for a given material. Since the value of n is greater than 2, the hardness of the material is found to increase with the increase of load confirming the prediction of Onitsch [25]. The n value of



Fig. 6. The plot of Vickers hardness number (kg/mm<sup>2</sup>) vs load (g) for BPO crystal.



Fig. 7. TG/DSC curve of BPO crystal.

as-grown BPO crystal is 5.74 and the crystal belongs to the soft material category.

#### 3.7. Thermal studies

The TG/DSC analysis of BPO crystal was carried out between 20 and 800 °C in the nitrogen atmosphere (Fig. 7). It shows that there is no physically adsorbed water in the molecular structure of the crystal. TG curve illustrates a single stage weight loss ~200 to 300 °C due to decomposition of BPO into fragments and their subsequent volatilization. In DSC, a sharp endothermic peak at ~149 °C is due to the melting point of the material and it was confirmed by using Sigma instrument melting point apparatus (146 °C). A high intense exothermic peak appearing close to ~200 °C is matching with the major weight loss in TG curve. The sharpness of the endothermic peak shows good degree of crystallinity and purity of the as-grown crystal.

#### 3.8. Dielectric properties

Dielectric measurements were carried out by the parallel plate capacitor method as a function of temperature for various frequencies using a Precision LCR meter (AGILENT 4284 A model). Fig. 8(a)–(c) is the plots of dielectric constant ( $\varepsilon_r$ ), dielectric loss  $(\tan \delta)$  and AC conductivity  $(\sigma_{ac})$  versus temperature at different frequencies. It can be seen that dielectric parameters, viz. dielectric constant, dielectric loss and AC conductivity increase with the increase in temperature. The  $\varepsilon_r$  and tan  $\delta$  values decrease with increase in frequency while  $\sigma_{ac}$  increases with increase in frequency. The dielectric constant of material is generally composed of four different types of contributions like ionic, electronic, orientational and space charge polarizations. The large value of dielectric constant at low frequencies may be due to contribution of all these polarizations. The decreased dielectric constant at higher frequencies could be due to the reduction in the space charge polarization. Space charge polarization is generally active at lower frequencies and high temperatures indicating the purity and perfection of the grown crystal [26]. The increase in conductivity could be attributed to reduction in the space charge polarization at higher frequencies [27]. In the present study, dielectric constant varying proportionally with temperature is essentially due to the temperature variation of the polarizability [28]. The low  $\varepsilon_r$  value dielectric materials have potential applications in microelectronic industries.

#### 3.9. Second harmonic generation (SHG) efficiency

The SHG test on the crystal as performed by Kurtz powder SHG method [29]. An Nd:YAG laser with a modulated radiation of 1064 nm was used as the optical source and directed on the powdered sample through a filter. The grown crystals were ground to



**Fig. 8.** (a) Plot of dielectric constant vs temperature (K) for BPO crystal. (b) Plot of dielectric loss vs temperature (K) for BPO crystal. (c) Plot of AC electrical conductivity vs temperature (K) for BPO crystal.

a uniform particle size of  $125-150 \mu$ m and then packed in a micro capillary of uniform bore and exposed to laser radiation. Contrary to earlier reports [18] no green light emission is observed. This is in tune with the single crystal XRD observations of this specimen crystallizing in a centrosymmetric space group [20]. It has been established that benzophenone oxime is a dimer and the centrosymmetry could be due to this structural arrangement. A pseudo symmetrical dimer, held together in the crystal by van der Waals interactions, is formed by means of O-H…N hydrogen bonds. Contrary to the belief that the hydrogen bonding generally leading to noncentrosymmetric structures, the NLO inactivity of benzophenone oxime has been experimentally observed. It has been reported that benzophenone [7], benzophenone hydrazone [10],

#### Table 3

SHG output of benzophenone and its derivatives.

System	SHG efficiency	Reference
Benzophenone Benzophenone hydrazone Benzophenone semicarbazone	3 times higher than KDP 10 times higher than KDP (Green light emission)	[7] [10] [11]
Benzophenone thiosemicarbazone	0.52 times that of Urea	[13]
Benzophenone oxime	(No green light emission)	Present study

benzophenone semicarbazone [11] and benzophenone thiosemicarbazone [13] exhibit SHG emitting a green light on exposure to 1064 nm Nd:YAG laser (Table 3). In these crystals there is a favorable molecular arrangement facilitating nonlinearity.

#### 4. Conclusions

Single crystals of benzophenone oxime (BPO) were grown from their ethanol solution using slow evaporation solution growth technique for the first time. The product formation was qualitatively confirmed by FT-IR. The powder X-ray diffraction and HRXRD studies reveal the structure and crystalline perfection of the grown crystal. The additional peaks in HRXRD indicate the formation of low angle structural grain boundaries. Thermal analysis confirms no decomposition of the crystal up to the melting point. The optical absorption shows excellent transmission in the entire visible region. The dielectric constant, dielectric loss and AC conductivity establish a normal behavior. Mechanical study on the crystals confirms the hardness behavior of the material. Studies reveal that this crystal is a promising material for the device fabrications in microelectronic industries.

#### Acknowledgement

One of the authors, K. Muthu is thankful to CSIR, New Delhi, for the award of a Senior Research Fellowship.

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