Growth, Optical, Mechanical and Dielectric Properties of Potassium Tetraborate Tetrahydrate Single Crystal

S. Sathiskumar¹, T. Balakrishnan², K. Ramamurthi³

¹,²,³ Crystal Growth Laboratory, PG & Research Department of Physics, Periyar EVR College (Autonomous), Tiruchirappalli – 620 023, Tamil Nadu, India

Abstract: Potassium tetraborate tetrahydrate (KTBTH) single crystals were grown by slow evaporation solution growth method at room temperature. The grown crystal was characterized by single crystal X-ray diffraction analysis. FT-IR and FT-Raman spectra were recorded to identify the functional groups. Optical transmission and absorption spectral studies were carried out to test the transmittance of the crystal in the UV – visible – NIR range. Optical parameters such as band gap energy and extinction coefficient of the grown crystal were calculated. Mechanical hardness of the grown crystal was estimated by Vickers microhardness test. Dielectric constant and dielectric loss of KTBTH crystal were calculated as a function of frequency at different temperatures. The a.c. resistivity and a.c. conductivity were obtained from the dielectric studies. Etching studies were carried out for different etching time. Kurtz powder second harmonic generation (SHG) test reveals that KTBTH possesses SHG efficiency of 0.4 times that of urea, thus shows it a potential candidate for optical second harmonic generation.

Keywords: Crystal growth, Optical properties, Mechanical properties, Dielectric constant

1. Introduction

Nonlinear optical (NLO) materials find applications in potential areas like optical modulation, optical switching, optical logic and optical memory, telecommunication, signal processing and optical internal connections [1]. In this regard inorganic borates have long been in the focus of researchers due to their interesting variety of structures, high laser damage threshold and high optical quality. The boron atom usually coordinates with either three / four oxygen (or) fluorine atoms to form [BO₃]³⁻ or [BO₄]⁵⁻ or [BF₄]⁻ groups [2]. Accordingly, the electronic orbitals of the boron atoms are hybridized to forming sp² structures with trigonal symmetry or sp³ structures exhibiting tetragonal symmetry. Moreover several of these two kinds of groups can be connected in different ways to form typical BₓOᵧ structures [3]. Thus the ability of boron atoms to form various structural possibilities makes the borates an attractive candidate in the field of nonlinear optics. Crystals containing the basic [BO₃]³⁻ and [BO₄]⁵⁻ groups are noncentrosymmetric [4]. Due to such special features of the borate groups, the search on the noncentrosymmetric crystal structures in borate family and the novel materials reported is about twice when compared to the families of other crystals [5]. In addition, borate crystals have the advantages of low absorption edge with high transmittance region and possessing high laser damage threshold and reasonable NLO coefficient. Extensive search has led to the discovery of many excellent materials such as β-BaB₂O₄ [6], LiB₃O₅ [7], ammonium pentaborate [8], potassium pentaborate [9], potassium boromalate [10], potassium boro succinate [11], rubidium bis – DL malatoborate [12] and strontium teribium triborate [13]. The single crystal structure of potassium tetraborate tetrahydrate (KTBTH) (K₂[B₄O₅(OH)₄]·2H₂O) was reported by Marezio et al. [14] and KTBTH belongs to orthorhombic crystal structure with the space group of P2₁2₁2₁, a noncentrosymmetric structure. Growth of KTBTH crystal and its thermal and linear optical properties of KTBTH were reported by Hellwig et al. [15] and Xingcheng Luo et al. [16]. In the present work studies on the growth, spectroscopic, linear and nonlinear optical, dielectric, etching and powder second harmonic generation efficiency of KTBTH crystal are carried out and presented.

2. Experimental

2.1. Crystal Growth

Potassium hydroxide (KOH) and boric acid (H₃BO₃) were dissolved in double distilled water at room temperature. Then the resultant solution was stirred well to obtain clear solution. The solution was filtered using Whatman filter paper and taken in a beaker. Beaker containing the solution was closed with polythene sheet containing small pinholes and it was kept in a dust free atmosphere. Solvent evaporation at room temperature yielded transparent single crystals of KTBTH of 5 mm × 4 mm × 3 mm size in a growth period of 10 days (Fig.1).

Figure 1: As grown KTBTH crystals
3. Characterization Studies

3.1 X-ray Diffraction Analysis

Single crystal X-ray diffraction intensity data were collected on a BRUKER NONIUS CAD4 single crystal X-ray diffractometer using monochromatized Cu Kα radiation (λ = 1.5408 Å) at 293K. The results show that the KTBTH belongs to orthorhombic system with unit cell parameters a = 6.855 (6.859) Å, b = 11.778 (11.774) Å, c = 12.894 (12.899) Å and they compare well with the corresponding reported values of Hellwig et al. [15] given in the parenthesis.

3.2 FT-IR and FT-Raman Spectral Analyses

Fourier transform infrared (FT-IR) spectral analysis of KTBTH single crystal was carried out between 4000 and 400 cm\(^{-1}\) using Perkin Elmer FT-IR spectrophotometer by KBr pellet technique at 300 K. FT-IR spectrum of KTBTH is shown in Fig. 2. The O–H asymmetric and symmetric stretching vibrational frequencies are observed at 3562 and 3378 cm\(^{-1}\) respectively. The peak at 1690 cm\(^{-1}\) is due to O–H bending vibration. The band observed at 1096 and 1000 cm\(^{-1}\) are due to B–O terminal asymmetric and terminal symmetric stretching vibrations respectively. The intense sharp peak observed at 1243 cm\(^{-1}\) is assigned to O–B-O terminal asymmetric stretching vibration. The O–B-O ring asymmetric bending vibration is observed at 712 cm\(^{-1}\). The peak observed at 449 cm\(^{-1}\) is attributed to B–O stretching vibration [17, 18].

3.3 UV–Vis–NIR Spectral Studies

UV–Vis - NIR optical transmission spectrum was recorded in the range of 190 – 1100 nm using THERMO SCIENTIFIC spectrophotometer. The transmittance and absorbance spectrum of KTBTH single crystal of thickness 3 mm is presented in Fig. 4. The crystal possesses high transmittance of 95 %, the essential properties of any crystal for NLO applications. The π–π* orbital transition occurs in the excitation of π electron requires smaller energy and hence, transition of this type occurs at longer wavelength. Lower cut off wavelength occurs at 200 nm and there is no absorption in the entire visible region. The optical absorption coefficient (α) is calculated using the relation [19],

\[
\alpha = \frac{1}{t} \log \left( \frac{1}{T} \right)
\]

(1)

<table>
<thead>
<tr>
<th>FT – IR</th>
<th>FT – Raman</th>
<th>Band assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>3562</td>
<td>-</td>
<td>O – H asymmetric stretching</td>
</tr>
<tr>
<td>3378</td>
<td>-</td>
<td>O – H symmetric stretching</td>
</tr>
<tr>
<td>1690</td>
<td>-</td>
<td>O – H bending</td>
</tr>
<tr>
<td>1475</td>
<td>1410</td>
<td>B – O terminal asymmetric stretching</td>
</tr>
<tr>
<td>1339</td>
<td>-</td>
<td>B – O asymmetric stretching</td>
</tr>
<tr>
<td>1243</td>
<td>-</td>
<td>O – B – O asymmetric stretching</td>
</tr>
<tr>
<td>1158</td>
<td>-</td>
<td>B – O terminal stretching</td>
</tr>
<tr>
<td>1096</td>
<td>1092</td>
<td>B – O terminal asymmetric stretching</td>
</tr>
<tr>
<td>1000</td>
<td>974</td>
<td>B – O terminal symmetric stretching</td>
</tr>
<tr>
<td>920</td>
<td>-</td>
<td>B – O ring stretching</td>
</tr>
<tr>
<td>831</td>
<td>-</td>
<td>B – O stretching</td>
</tr>
<tr>
<td>-</td>
<td>765</td>
<td>B – O ring stretching</td>
</tr>
<tr>
<td>712</td>
<td>695</td>
<td>O – B – O ring asymmetric bending</td>
</tr>
<tr>
<td>613</td>
<td>591</td>
<td>O – B – O terminal bending</td>
</tr>
<tr>
<td>564</td>
<td>568</td>
<td>O – B – O bending</td>
</tr>
<tr>
<td>496</td>
<td>-</td>
<td>O – B – O stretching</td>
</tr>
<tr>
<td>449</td>
<td>455</td>
<td>B – O stretching</td>
</tr>
</tbody>
</table>

Table 1: Comparison of FT – IR and FT – Raman spectral frequencies (cm\(^{-1}\)) of KTBTH crystal

Figure 2: FT – IR spectrum of KTBTH

Figure 3: FT – Raman spectrum of KTBTH
where $T$ is the transmittance and $t$ is the thickness of the crystal. The direct band gap of the crystal can be obtained from the absorption coefficient ($\alpha$) calculated using the relation [20],

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

where $E_g$ is the optical band gap energy of the crystal, $h$ is the Planck’s constant, $\nu$ is the frequency and $A$ is a constant. A plot of variation of $(\alpha h\nu)^2$ versus $h\nu$ shown in Fig. 5. $E_g$ is evaluated by extrapolating the linear portion of the graph. The direct energy gap is $\sim 6.3$ eV. The high value of band gap shows the crystal possesses dielectric behavior to induce polarization when powerful radiation is incident on the material. The absorption coefficient ($\alpha$) is related to the extinction coefficient $K$ by the relation [21]

$$K = \frac{\alpha \lambda}{4\pi}$$  \hspace{1cm} (3)

3.4 Microhardness Studies

The structure and molecular composition of crystals greatly influence their mechanical properties. Microhardness test is one of the simplest and best methods to understand the strength of the materials. Hardness of a material is a measure of resistance offered by the lattice for permanent deformation [22]. Shimadzu Vickers diamond pyramidal indenter was used for the microhardness studies. Microhardness measurements were made on the polished (100) plane of the KTBTH crystal. Load P was varied between 2 and 50g, and the time of indentation was kept constant (5s) for all trials. The diagonal lengths of indentation $d_1$ and $d_2$ were measured in $\mu$m for various applied load ($P$). The Vickers hardness number ($H_v$) was calculated using the relation [23]

$$H_v = \frac{1.8544P}{d^2} \text{kg/mm}^2$$  \hspace{1cm} (4)

Figure 4: UV – Vis – NIR transmittance and absorbance spectrum of KTBTH

Figure 5: Plot of $(\alpha h\nu)^2$ versus photon energy for KTBTH

Figure 6: Plot of extinction coefficient ($K$) vs. wavelength

Figure 7: Microhardness values versus load for KTBTH
where \( d \) is the average value of \( d_1 \) and \( d_2 \). The variation of Hv with the applied load \( P \) is shown in Fig. 7. It is observed that the microhardness value increases with the increase in the applied load. According to the normal indentation size effect (ISE), microhardness of crystals decreases with increasing load and for reverse indentation size effect (RISE) hardness increases with increasing load [24]. In the present work the plot obtained between log \( P \) and log \( d \) gives a straight line. The work hardening coefficient \( (n) \) was calculated from Fig.8 by the least square curve fitting method. The work hardening coefficient \( (n) \) calculated is 3.

Onitsch [25] concluded that if the value of \( n \) lies between 1 and 1.6 it refers to the hard materials and for soft materials it is above 1.6. Thus the KTBTH single crystal comes under the soft materials category. KTBTH exhibits the cracks for load \( (P) \) above 100g due to the release of internal stress generated locally by indentation. According to Meyer’s law,

\[
P = A d^n
\]

\( \text{(5)} \)

A plot of \((P/d)\) versus \(d\) gives a straight line Fig. 9, the slope of which gives the load independent microhardness. The slope \((P/d^2)\) multiplied by the Vickers conversion factor (1.8544) gives the value of load independent microhardness. In the present study the calculated load independent microhardness is 100 g / \( \text{mm}^2 \).

3.5 Dielectric Studies

The dielectric study was carried out using the instrument HIOKI 3532 – 50 LCR HITESTER in the frequency range from 50 Hz to 2MHz at different temperatures. KTBTH single crystal of dimension \( 0.5 \times 0.5 \times 0.2 \) (cm\(^3\)) was taken and its opposite faces of the crystal were coated with silver paste. Then the crystal was placed between the two copper electrodes to form the parallel plate capacitor. The dielectric constant \((\varepsilon)\) and dielectric loss \((\varepsilon'')\) were calculated using equations

\[
\varepsilon = \frac{Cd}{A\varepsilon_0}
\]

\( \text{(8)} \)

\[
\varepsilon'' = \varepsilon \tan \delta
\]

\( \text{(9)} \)

where \( C \) is the capacitance of the sample, \( d \) is the thickness of the crystal, \( \varepsilon_0 \) is the permittivity of free space (\( \varepsilon_0 \approx 8.854 \times 10^{-12} \) F / m) and \( A \) is the area of the sample. Experimental values of dielectric constant and dielectric loss of KTBTH crystal as a function of frequency is shown in Fig. 10 and Fig.11 respectively. From the figures it is observed that both the dielectric constant and dielectric loss decrease with increasing frequency. As the magnitude of dielectric constant depends on the degree of polarization of charge in the crystal and it arises from the contribution of different polarizations, namely electronic, ionic, orientation and space charge polarization [27, 28]. The large dielectric constant at low frequency is due to the presence of space charge polarization. Space charge polarization arises due to the mobile charge carriers impeded by interfaces. The space charge polarization depends on the bonding, structure, purity and perfection of the crystal [29]. The low value of dielectric constant at higher frequency is important for considering the materials for photonics, electro – optic and NLO applications. It is observed that the dielectric loss deceases with increasing frequency.
frequency. The a.c. resistivity and a.c. conductivity are calculated using the relations [30].

\[ \rho = \frac{A}{2\pi f C d} \] (10)

\[ \sigma = \frac{1}{\rho} \] (11)

The variation of a.c. resistivity and conductivity with the frequencies of applied field is shown in Fig.12 and Fig.13 respectively. As shown in Fig.12 the a.c. resistivity increases rapidly as frequency increases. Obviously the reverse trend is observed for a.c. conductivity (Fig. 13) of the grown crystal.

3.6 Chemical Etching Studies

The chemical etching studies were carried out on the grown single crystal using polarized optical microscope fitted with Motic camera. Etching is an important tool for the identification of the crystal defects, which is able to develop some of the features such as growth hillocks, etch pits and grain boundaries on the crystal surface and micro structural imperfections of the grown crystal. Quality crystals with minimum defects are essential fabrication of devices. Dislocations in crystal influence a number of physical properties like plasticity, mechanical strength, etc. [31]. Hence it is necessary to know the density and distribution of dislocations in the crystals. Chemical etching technique was employed for studying etch pit in the KTBTH crystal. Etching study was carried out on (110) plane of KTBTH crystal. KTBTH crystal was etched in diluted hydrochloric acid for duration of 5 and 10s. The etched samples were dried using tissue paper and etch pattern were observed. Fig. 14 shows the etch pattern on the (110) plane of grown KTBTH crystal for an etching time of 5s in diluted hydrochloric acid as etchant and it produces elongated rectangular hillock shaped well defined etch pits. Fig. 15 shows the etch pattern produced on the previously 5s etching.
face after an etching for additional 5 s. An increase of etch
time, does not make appreciable change in the morphology
of the etch pits.

Figure 14: Etching study on (110) plane of KTBTH crystal
(etch time of 5 s)

Figure 15: Etching study on (110) plane of KTBTH crystal
(etch time of 10 s)

3.7 Second Harmonic Generation

The second harmonic generation (SHG) efficiency test was
carried out by the powder technique proposed by Kurtz and
Perry [32]. A Q switched Nd:YAG laser beam of wavelength
1064 nm, with a beam energy of 0.680 J/pulse and a pulse
with of 8 ns with a repetition rate of 10 Hz was used. The
crystals are ground to powder and packed between two
transparent glass slides and exposed to laser radiation. The
second harmonic signal generated due to powdered crystal
was confirmed from the emission of green radiation (532
nm). The observed SHG efficiency of KTBTH is 0.4 times
that of urea crystal.

5. Acknowledgement

The authors T. B and S. S would like to acknowledge the
University Grant Commission (UGC), New Delhi, India for
providing financial support [project ref. No. 41 –
956/2012(SR)]. The scientific supports extended by
Sophisticated Analytical Instrument Facility (SAIF), Indian
Institute of Technology Madras, Chennai – 600 036, India,
and Department of Physics, B. S. Abdur Rehman University,
Vandalur, Chennai – 600 048, for providing facilities for
characterization.

References

267 – 271.
779 – 782.
[5] G. Heller, A survey of structural types of borates and
polyborates. Topics in Current Chemistry (Springer,
Berlin 1986)
[8] T. Balakrishnan, G. Bhagavannayakama, K. Ramamurthi,
S. Krishnan, Optics & Laser Techno. 43 (2011) 1229 -
1232.
Murugakoothan, P. Arulmozhichelvan, R. Jayavel,