Structural, optical, mechanical and thermal properties of sodium borohydride doped potassium dichromate single crystal (SBHKDC)

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Abstract: Inorganic single crystal of SBHKDC was grown from well filtered aqueous solution by slow evaporation technique at room temperature. The transparent crystals were obtained over a period of 27 days. The grown crystals were characterized structurally, optically, thermally, mechanically and electrically. The lattice parameters, unit cell volume and crystalline were determined by single crystal and powder x-ray diffraction analysis. The functional groups present in the crystals were identified using Fourier Transform infrared spectral analysis. The Optical study was investigated by UV-Vis visible spectrum. The thermal stability of the compound was evaluated by Thermo gravimetric and differential thermal analysis. The dielectric constant and dielectric loss of the crystal were inspected in different temperatures. The mechanical property of the grown crystal is carried out using Vickers Hardness Indentation Test.

Keywords: Powder XRD, FTIR, UV, TGA/DTA, Dielectric loss and constant

1 Introduction

The fast development in the field of opto-electronics has stimulated the search for new nonlinear optical crystals for efficient signal processing. Frequency conversion materials can have a significant impact on laser technology, optical communication and data storage technology [8-10]. The new materials inspected for nonlinear optical applications had always been inorganic. Many inorganic crystals are well examined in terms of their physical properties. Since these materials are mostly ionic bonded and it is easier to synthesize. Inorganic materials often have high melting point and high degree of chemical inertness. High temperature oxide materials are well studied for diverse applications like piezo-electricity, pyro-electricity, Ferro-electricity and opto-electronics [11].

Most organic crystals have usually poor mechanical and thermal properties and are susceptible to damage during processing. Also it is difficult to grow bulk size optical quality crystals of these materials for device applications. But inorganic crystals have excellent mechanical and thermal properties [12]. Particularly inorganic borates exist in numerous structural types of some crystals such as KB₅. These borate crystals generally possess chemical stability, high damage threshold and high optical quality [13]. The borate compound materials are superior to other commonly used materials for UV applications [14]. In literature crystal structure and other characterization studies of sodium penta borate Na(H₅B₅O₁₀) were reported [11,15].

The crystal Potassium Dichromate (KDC) has desirable properties [16], the Pentavalent chromium metal ion is the high temperature resist [17], corrosive resistant materials [18], liquid crystal display [19,20], green pigment [21], catalyst material and so on [22,23]. With these potential sites it is desired to dope potassium Dichromate with sodium boro hydride in equal molar ratio.

2 Experimental

2.1 Material synthesis

The 99% purity of the Merc brand product of the major and mixed compound has taken in equal molar ratio as 1:1. First Potassium dichromate (KDC) was dissolved in Millipore water then the second compound sodium borohydride (SBH) was taken into pinch by pinch added in the KDC solution. The reducing agent of SBH reaction has
taken into clean atmosphere in room temperature and the reaction takes place beaker temperature is raised. When the reaction takes place the oxide removed. The non homogeneous solution is formed after deposition of some sediment; the chemical reaction takes place as follows,

$$2K_2Cr_2O_7 + 8NaBH_4 + D_2O \rightarrow 4Na_2CrO_4 + 4B_2O_3 + 4KOH$$

### 2.2 Growth of SBHKDC crystals

The saturated non-homogeneous solution was filtered ash less whatmann filter paper then the homogeneous solution is further double filtration process to avoid co-precipitation of multiple phases. The filtered clear yellowish solution was taken in a beaker and covered with good quality perforated polythene cover to restrict the fast evaporation it is kept at room temperature in a dust free compartment for slow evaporation.

After the period of 27 days, the colorful good quality yellowish crystal with dimension 14×7×4mm$^3$ was obtained, the harvested crystal shown in the figure 1. The grown SBHKDC crystal was crystal clear and the optimized crystal grown condition are presented in the Table 1.

#### Figure 1 As grown SBHKDC crystal.

#### Table 1. Optimized growth conditions of SBHKDC

<table>
<thead>
<tr>
<th>Major Compound</th>
<th>K$_2$Cr$_2$O$_7$ (KDC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dopant Compound</td>
<td>NaBH$_4$ (SBH)</td>
</tr>
<tr>
<td>Method of Growth</td>
<td>Slow Evaporation Technique</td>
</tr>
<tr>
<td>Solvent used</td>
<td>Millipore water of 18.2 MΩcm resistivity</td>
</tr>
<tr>
<td>Molar ratio</td>
<td>Equal (or) 1:1 of K$_2$Cr$_2$O$_7$ &amp; NaBH$_4$</td>
</tr>
</tbody>
</table>

| pH | 12 |
| Operate temperature | Room temperature |
| Period of growth | 27 Days |
| Dimension | 14×7×4 × mm$^3$ |
| Crystal color | Yellowish |

### 3 Results and Discussion

#### 3.1 single crystal X-ray diffraction analysis

As grown SBHKDC crystal was selected for single crystal XRD study. It was carried out using an Bruker X8 KAPPA APEX II single crystal X-ray diffractometer with Moku (λ=0.7107Å) radiation to identify lattice parameters. The intensity data were collected up and accurate unit cell parameters were obtained based on about 40 reflections selected for confirm the structure of the crystal system data gives on the Table 2. From the compared crystallographic data of KDC [16], it is found that SBHKDC crystal belongs to Cubic Structure.

#### Table 2 The single XRD unit cell parameters of the SBHKDC crystal

<table>
<thead>
<tr>
<th>Lattice parameters</th>
<th>Reported pure KDC Data [16]</th>
<th>Experimental data of SBHKDC Single crystal XRD</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (Å)</td>
<td>7.37</td>
<td>6.32</td>
</tr>
<tr>
<td>b (Å)</td>
<td>7.44</td>
<td>6.32</td>
</tr>
<tr>
<td>c (Å)</td>
<td>13.36</td>
<td>6.32</td>
</tr>
<tr>
<td>A</td>
<td>96.21</td>
<td>90º</td>
</tr>
<tr>
<td>B</td>
<td>97.96</td>
<td>90º</td>
</tr>
<tr>
<td>γ</td>
<td>90.75</td>
<td>90º</td>
</tr>
<tr>
<td>V (Å$^3$)</td>
<td>722.3</td>
<td>252</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Triclinic</td>
<td>Cubic</td>
</tr>
</tbody>
</table>

#### 3.2 Powder X-RAY diffraction analysis

The powder XRD study was carried out using a Rich-Seifert diffractometer with CuKα (λ=1.5406Å)
radiation. The indexed powder XRD pattern of the grown SBHKDC crystal is shown in Figure 2. The powdered SBHKDC sample was scanned over the range 10º to 90º at the rate of 1º per min. The grown SBHKDC crystal has taken powder X-ray diffraction pattern. All the observed and well defined Bragg’s sharp and strong peaks at specific 2θ angles show high crystalline of SBHKDC.

The FT-IR spectrum was recorded in the range 4000 - 400 cm⁻¹ by Potassium bromide (KBr) pellet technique. Some important FTIR sharp peaks shown as discus below, peak 541,624 cm⁻¹ is Cr – O Stretching [26], the major sharp peak is shown as(s) 873 cm⁻¹ is O-H Deformation. Vibrations at 940cm⁻¹, 1078 cm⁻¹ are the sharp peaks denotes the B-O terminal symmetric and asymmetric stretching [24], 2205 – 2351 cm⁻¹ B-H Stretching, 2033cm⁻¹ Several (w) overtone bends, 1605cm⁻¹ H-O-H Bending, 1462cm⁻¹ In-plane O-H bending, 1201cm⁻¹ D-O-D Bend [25]. [s-Strong, w- Weak]

### Table 3. Band assignments of SBHKDC crystal FT-IR spectra

<table>
<thead>
<tr>
<th>Wave number (cm⁻¹)</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>3366</td>
<td>Strong O – H stretch</td>
</tr>
<tr>
<td>3261</td>
<td>O – H Symmetric stretching</td>
</tr>
<tr>
<td>3155</td>
<td>H bonded O – H stretch</td>
</tr>
<tr>
<td>2678</td>
<td>O – D Stretching</td>
</tr>
<tr>
<td>2351</td>
<td>B – H Stretching</td>
</tr>
<tr>
<td>2205</td>
<td>B – H Stretching</td>
</tr>
<tr>
<td>2033</td>
<td>Several weak overtone bends</td>
</tr>
<tr>
<td>1605</td>
<td>H – O – H Bending</td>
</tr>
<tr>
<td>1462</td>
<td>In-plane O – H bending</td>
</tr>
<tr>
<td>1402</td>
<td>H – O – D Bend</td>
</tr>
<tr>
<td>1201</td>
<td>D – O – D Bend</td>
</tr>
<tr>
<td>1078</td>
<td>B – O terminal asymmetric</td>
</tr>
<tr>
<td>940</td>
<td>B – O terminal symmetric</td>
</tr>
<tr>
<td>873</td>
<td>O – H deformation</td>
</tr>
<tr>
<td>726</td>
<td>O – H out-of-plane deformation</td>
</tr>
<tr>
<td>624</td>
<td>Cr – O Stretching</td>
</tr>
<tr>
<td>541</td>
<td>Cr – O Stretching</td>
</tr>
</tbody>
</table>

3.3 Fourier Transformation Infrared Spectroscopy (FTIR)

The IR spectrum is providing a fingerprint for identification of a substance Infra-red spectroscopy is effectively used to identify the functional groups and determine the molecular structure of the synthesized compounds. The SBHKDC crystal’s FT-IR spectrum is shown in Figure 3.

3.4 Linear Optical Property Studies (UV-Vis)

The UV-Vis spectra potential of SBHKDC inorganic compound single crystals are mainly used for optical applications. The optical transmittance spectrum of the crystal has been recorded in the region 200-1100 nm and shown in Figure 4. The crystal has been found to be clear, in the UV region and has the lower cutoff wavelength at
268 nm, while the material can be used as sensor property in the region 268 to 1000 nm. In this significant transparency in the visible region indicates the strong fitness of the material for the frequency conversion application. The optical transmission spectral studies confirmed that the crystal has high transmission about 94%. The Figure 4 shows the grown SBHKDC crystal is generally better optical switching property which is an essential consideration for the NLO crystals.

![Figure 4](image)

**Figure 4** Optical transmission spectrum of SBHKDC inorganic crystal.

### 3.5 Thermal Analysis (TGA/DTA)

The Differential thermal analysis (TGA/DTA) of SBHKDC crystal were carried out with the help of TG/DTA 6200 SII EXSTAR 6000 (Figure 5) using a ceramic alumina (Al2O3) crucible as reference. A sample of weight 9.84 mg was taken in a crucible.

![Figure 5](image)

**Figure 5.** TGA/DTA Curves of SBHKDC crystal.

The temperature range of 100 to 800°C recorded at a rate of 20 °C/min in the thermal properties of SBHKDC inorganic crystal in nitrogen (N2) atmosphere. The DTA curves show that the melting point of SBHKDC crystal is 361.5 °C. Corresponding TGA curve of the given data is shown straight line indicates the maximum weight loss is 0.3% up to 800°C. The reason is Transition metal of Chromium (Cr) is highly thermal stability around 1000 °C [26]. So, it is most useful to high temperature industrial applications. The DTA curve shows that the material has high thermal stability. The DTA line shows two exothermic peaks are shown in figure 5. The exothermic peaks observed at 361.5°C and 571°C. The endothermic peak at 555.5°C is shown in figure 5.

### 3.6 Dielectric Studies

The dielectric properties are correlated with the electro-optic property of the crystals the capacitance and dielectric loss were measured using the conventional parallel plate capacitor method with the frequency range 50 Hz to 1 MHz using the Agilent 4284A LCR meter at various temperatures ranging 40°C to 358 °C. A good quality as grown crystal of 4 mm thickness was electrode on either side with graphite coating to make it behave like a parallel plate capacitor. The dielectric constant is one of the basic electrical properties of solids. The variations of the dielectric constant and dielectric loss with log of frequency at different temperatures are shown in figures 6(a) and (b) respectively.

#### 3.6.1 Dielectric Constant

The grown SBHKDC crystal dielectric constant measured in four different temperatures from 40 - 85°C, from the figure 6 (a) shown below. The dielectric constant decreases with increasing frequency and becomes almost saturated beyond 3.5 KHz for all temperatures. The decrease in dielectric constant of SBHKDC crystal at low frequencies may be attributed to the dependence of electronic, ionic, orientation and space charge polarizations [27-29]. The space charge contribution will depend on the low frequency region. Hence the larger values of dielectric constant exhibited by sample at low frequencies may be attributed to space charge polarization arising due to the crystal defects at grain boundary interfaces. At low frequencies, the charge on the defects...
can be rapidly redistributed so those defects closer to the positive side of the applied field become positively charged. This leads to a screening of the field and an overall reducing in the electric field [30]. As capacitance is inversely proportional to the field, this reduction in the field for a given voltage results in the increased value of capacitance when the frequency is lowered. However, at high frequency, the defects no longer have enough time to rearrange in response to the applied voltage, and so the capacitance decreases.

**3.6.2 Dielectric Loss**

The variations of dielectric loss (\(\tan \delta\)) with frequency are shown in Figure 6 (b). It is observed that the dielectric loss decreases with increasing frequency. Similar trend was observed for all the recorded temperatures.

**Figure 6 (a)** Dielectric constant (\(\epsilon\)) of SBHKDC in organic crystals

**Figure 6 (b)** Dielectric losses (\(\tan \delta\)) of SBHKDC inorganic crystals

**3.7 Microhardness Studies**

Vickers micro hardness studies carried REICHERT POLYVAR 2 hardness attachment – Micro – Duromat 4000E. The hardness of the material depends of different parameters such as lattice entry, Debye temperature heat of formations and inter-atomic distance [31-33], during the static indentation were made at room temperature with a constant indentation time of 10s for all indentations. An indentation process, the external work applied by the indenter is converted to a strain energy component to the volume of the resultant impression and the surface energy component proportional to the area of the resultant impression.

\[
H_v = 1.8544 \left(\frac{p}{d^2}\right) \text{kg/mm}^2
\]

Where, \(H_v\) is the Vicker’s hardness number kg/mm², ‘\(p\)’ is the applied load and ‘\(d\)’is the average diagonal length of the indentation impression in millimeter and 1.8544 is a constant of a geometrical factor for the diamond pyramid.
Figure 7(b) Variation of log P against log d for SBHKDC crystal.

The SBHKDC in organic crystal hardness test were observed in three different loads applied from 25 to 100 g on the hardness and were calculated using the relation. At lower loads there is an increase in the hardness number. Initially the hardness number is increase then decrease with increase of load.

The relation between load (P) and diagonal length of indentation (d) is given by Mayer’s law which is given below

\[ P = a d^n \]

Where ‘a’ and ‘n’ are constant for a particular material Figure 4.7(b) shows the variation of log p with log d. Slope of the line can be obtained and it is known as Mayer’s index number (or) work hardening coefficient (n). Further the material which is confirm, if n > 1.6 is the soft material and if n < 1.6 is the hard material [34]. The grown SBHKDC crystal hardness coefficient is calculated by the slope of ‘log p’ and ‘log d’ using Mayer’s formula, work hardness coefficient

\[ n = \frac{dy}{dx} \]

The value of hardness coefficient is n= 0.04 for SBHKDC crystal it is less than 1.6 therefore the SBHKDC crystal has hard nature.

4. Conclusions

The Single crystal of SBHKDC, an inorganic crystal has been successfully grown from an aqueous solution using slow evaporation technique at room temperature. The harvested grown yellowish crystal dimension is 14×7×4 mm³. The single crystal X-ray diffraction study is confirms the structure of the crystal is perfect cubic and the unit cell parameters of the given SBHKDC crystals is α=β=γ= 90° and a=b=c= 6.32. The Powder X-ray diffraction pattern shows the good crystalline nature of the grown crystal. The functional groups of the grown SBHKDC crystal has confirm the Chromium, boron and hydrogen assignments. The UV-Vis cut off wavelength is found to be at 268 nm, and 94% of transmittance shown well optical property. TG/DTA studies revealed that the crystal is thermally stable up to 361.5 °C. The weight loss of the material is 0.3% of the up to 800 °Cshows the high thermal stability of grown crystal. The grown crystal's dielectric properties have been studied. The mechanical properties of the grown crystal have been studied.
References


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**Competing Interests:**

The authors declare that they have no competing interests.

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