CHAPTER 5

GROWTH OF POTASSIUM TETRA BORATE (K$_2$B$_4$O$_{11}$H$_8$) SINGLE CRYSTALS BY LOW TEMPERATURE SOLUTION GROWTH METHOD AND ITS CHARACTERISATION

5.1 INTRODUCTION

The choice of selecting a particular crystal growth technique depends on the physical and chemical properties of the material to be crystallized and the suitability of the technique to grow the desired crystal. The parameters such as the growth kinetics, size, shape, purity, quality and the cost involved in producing the crystals also play a vital role (Pamplin 1979). Solution is a homogeneous mixer of a solute and a solvent. Solute is the component present in a smaller quantity. For a given solute, there may be different solvents. Apart from high purity starting materials, solution growth requires a good solvent. The solvent must be chosen taking into account the factors such as, moderate solubility for the given solute, must not react with the solute, good solubility gradient, low viscosity, low volatility and low corrosion.

Growth of crystal from solution is mainly a diffusion-controlled process; the medium must be less viscous to enable faster transport of the growth units from the bulk solution by diffusion. Hence, a solvent with less viscosity is preferable (Ohara 1973). Solution is a homogeneous mixer of a solute in a solvent. Solute is the component present in a smaller quantity. For a given solute, there may be different solvents. Apart from high purity starting materials, solution growth requires a good solvent.
The solvent must be chosen taking into account of the following factors:

(i) moderate solubility for the given solute
(ii) must not react with the solute
(iii) good solubility gradient
(iv) low viscosity
(v) low volatility and
(vi) low corrosion

If the solubility is too high, it is difficult to grow bulk single crystals and if it is too small then the solubility restricts the size and growth rate of the crystals. The solubility data at various temperatures are essential to determine the level of supersaturation. Hence, the solubility of the solute in the chosen solvent must be determined before starting the growth process. If the solubility gradient is very small, slow evaporation of the solvent is the other option for crystal growth to maintain the supersaturation in the solution.

5.2 LOW TEMPERATURE GROWTH METHODS

Low temperature solution growth can be subdivided into the following categories as in Figure 5.1.

![Figure 5.1 Classification of low temperature solution growth methods](image)

5.2.1 Slow Cooling Method

Slow cooling is the best method to grow good quality crystals by aqueous solution technique. However, the limitation of slow cooling method
is the need to use a range of temperature. The possible range of temperature is usually narrow and hence much of the solute remains in the solution at the end of the growth run. To compensate this effect, large volume of solution is required. Wide range of temperature may not be desirable because the properties of the grown crystal may vary with temperature. Even though this method requires a precise temperature control system, it is widely used with great success.

5.2.2 Solvent Evaporation Method

Generally the solvent evaporation solution growth technique has been widely used to grow several types of crystals at ambient temperature using water as solvent. In solvent evaporation method, the temperature is fixed and provision is made for evaporation. The evaporation technique has an advantage that the crystals grow at a fixed temperature. But inadequacies of the temperature control system still have a major effect on the growth rate. This method can effectively be used for materials having very low temperature coefficient of solubility.

5.2.3 Temperature Gradient Method

Temperature gradient method involves the transport of materials from a hot region containing the solute material to be grown to a cooler region, where the solution is supersaturated and the crystal grows. Some of the main advantages of this method are as follows,

(i) crystal grows at a fixed temperature

(ii) insensitive to changes in temperature provides both the source and growing crystal undergo the same change and

(iii) economy of solvent and solute
On the other hand, a small temperature difference between the source and the crystal zones has a large effect on the growth rate.

5.3 GROWTH OF K$_2$B$_4$O$_{11}$H$_8$ SINGLE CRYSTALS

In the present study potassium tetraborate tetrahydrate - K$_2$B$_4$O$_{11}$H$_8$ [K$_2$[B$_4$O$_5$OH]$_4$].2H$_2$O] single crystals (Marezio et al 1963, Hellwig et al 2000) are grown by low temperature solution growth, using solvent evaporation method at room temperature. For the growth of K$_2$B$_4$O$_{11}$H$_8$, potassium hydroxide (KOH) and boric acid (H$_3$BO$_3$) were used as the starting materials. Saturated solution was prepared at room temperature using potassium hydroxide and boric acid with a molar ratio of 7:10 and dissolved in double distilled water. The prepared solution was filtered using a micro-filter. The filtered solution was taken in the vessels and dried in dust-free atmosphere with perforated covering. Potassium tetraborate tetrahydrate crystals were grown during the process of solvent evaporation from a Petri dish. The crystals are harvested with good dimensions after a few weeks as shown in Figure 5.2.

Figure 5.2 As grown crystals of K$_2$B$_4$O$_{11}$H$_8$
5.4 CHARACTERIZATION OF K$_2$B$_4$O$_{11}$H$_8$ CRYSTALS

5.4.1 X-ray Diffraction Analysis

X-ray powder diffraction pattern of the K$_2$B$_4$O$_{11}$H$_8$ crystal was recorded by SIEFERT X-ray diffractometer using CuK$_α$ ($\lambda = 1.540$ Å) radiation in the angular range of $2θ = 10$ to 80°. The X-ray studies were carried out at room temperature. The sample was scanned for a $2θ$ range 10-80 degree at a scan rate of 1 degree /min. The formation of K$_2$B$_4$O$_{11}$H$_8$ compound is confirmed through the powder XRD pattern which is in agreement with the reports in the literature (Marezio et al 1963). The indexed X-ray diffraction pattern of the material is shown in Figure 5.3.

![Figure 5.3 Powder X-ray diffraction pattern of K$_2$B$_4$O$_{11}$H$_8$](image)

5.4.2 Single Crystal X-ray Diffraction Analysis

The single crystal X-ray diffraction data of the K$_2$B$_4$O$_{11}$H$_8$ single crystal was collected using an Enraf-Nonius CAD – 4 diffractometer, with graphite monochromated CuK$_α$ radiation source. From single crystal X-ray
diffraction analysis and is determined that the material crystallizes in orthorhombic space group P2\(_1\)2\(_1\)2\(_1\) and the unit cell dimensions are a = 6.852 Å, b = 11.774 Å, c = 12.897Å. The crystallographic parameters are given in the Table 5.1.

**Table 5.1 Crystal data of potassium tetraborate tetrahydrate**

<table>
<thead>
<tr>
<th>S. No</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Chemical formula K(_2)[B(_4)O(_5)(OH)(_4)](\cdot)2H(_2)O</td>
</tr>
<tr>
<td>2</td>
<td>Cell parameters a = 6.852Å, b = 11.774 Å, c = 12.891Å</td>
</tr>
<tr>
<td>3</td>
<td>Crystal system Ortherhombic</td>
</tr>
<tr>
<td>4</td>
<td>Space group P2(_1)2(_1)2(_1)</td>
</tr>
<tr>
<td>5</td>
<td>Molecular weight 305.50</td>
</tr>
<tr>
<td>6</td>
<td>Z 4</td>
</tr>
<tr>
<td>7</td>
<td>Density 1.946 g/cm(^3)</td>
</tr>
</tbody>
</table>

**5.4.3 FTIR Spectral Analysis**

The presence of the functional groups was qualitatively analyzed by the Infrared spectrum. The powdered crystal of K\(_2\)B\(_4\)O\(_11\)H\(_8\) was subjected to FTIR studies to confirm the presence of functional groups and coordination of ligands. The spectrum was recorded in the range 400 - 4000 cm\(^{-1}\) as shown in the Figure 5.4. From FTIR spectrum both the absorption bands of BO\(_3\) group and the absorption bands of BO\(_4\) group are observed. The stretching and bending modes of O-H are observed from the bands at 3370 and 1622 cm\(^{-1}\). The wave numbers of fundamental vibrations of the BO\(_3\) group are grouped into four separate regions and is observed from the bands 915 – 982, 1298-1312, 687 – 710, 660 cm\(^{-1}\) are assigned to the symmetric and asymmetric stretching, and symmetric and asymmetric bending modes respectively. The characteristics peak of BO\(_4\) is observed from the bands at 797 to 810, 1045 – 1125, 563 – 578 cm\(^{-1}\). The results obtained from the FTIR spectrum are in comparable that of the previous reports (Xingcheng Luo et al 2009). Thus the
FTIR spectrum shows all the fundamental vibrations of $\text{K}_2\text{B}_4\text{O}_{11}\text{H}_8$ and confirms the formation of the compound.

![FTIR spectrum of $\text{K}_2\text{B}_4\text{O}_{11}\text{H}_8$](image)

**Figure 5.4 FTIR spectrum of $\text{K}_2\text{B}_4\text{O}_{11}\text{H}_8$**

### 5.4.4 Thermal Analysis

Thermal stability of $\text{K}_2\text{B}_4\text{O}_{11}\text{H}_8$ is studied by DTA analysis using PerkinElmer thermal analyser (Model STA 6000). The $\text{K}_2\text{B}_4\text{O}_{11}\text{H}_8$ sample was subjected to the analysis from room temperature to 900 °C in nitrogen atmosphere at a heating rate of 10 °C/min. From the DTA graph it is observed that the endothermic peak at 790 °C corresponds to the melting of the solid phase as in the Figure 5.5.
Figure 5.5 DTA pattern of potassium tetraborate tetrahydrate

5.4.5 UV-VIS-NIR Analysis

Nonlinear optical effects can be used for the generation of new optical frequencies, which are not available with existing lasers, in particular compact blue coherent light sources (Bosshard et al 1995). Transmission spectra are of much importance for NLO materials, since an NLO material can be used in optical devices only if it has a wide transparency range. The UV-VIS-NIR spectral transmittance was recorded with an as-grown single crystal of K$_2$B$_4$O$_{11}$H$_8$ with 5 mm thickness in the wavelength range of 200-2500nm. Shimadzu UV–Vis–NIR spectrophotometer (Model 3600) was employed to record the spectrum. The recorded transmission spectrum is shown in Figure 5.6. The lower cutoff wavelength for the K$_2$B$_4$O$_{11}$H$_8$ crystal was observed to be less than 200 nm. The as-grown crystal is more than 60% transparent in the UV and visible regions. The presence of a wide transmission in the UV and visible regions enables sufficient transmission of the higher order harmonics of Nd: YAG lasers.
5.4.6 Etching Analysis

Etching analysis is widely used to study the growth pattern of the single crystals. Etching of surfaces using desirable solvent gives more information about the surface features. Patterns observed on surfaces like spirals, hillocks, and slip pattern, etc., yield considerable information on the growth process and growth mechanism of the crystal. For this study, Leica Q Win optical microscope was employed to study the surface features of the as-grown crystal.

From the analysis one can able to find the formation of the etch pits and its growth characteristics. The as grown K$_2$B$_4$O$_{11}$H$_8$ crystals etched for 5 using water as the etchant. Figures 5.7 (a) and (b) show the surface micrographs of the K$_2$B$_4$O$_{11}$H$_8$ crystal with 80x and 100x magnification. From the etch patterns, growth hillocks were observed from the surface micrograph of the as grown crystals and were found to be rectangular in shape with step
growth pattern. The formations of rectangular etch patterns indicate the two-dimensional nucleation mechanism (Sangwal 1987).

![Etch patterns of K$_2$B$_4$O$_{11}$H$_8$ Crystal](image)

**Figure 5.7** (a) and (b) Etch patterns of K$_2$B$_4$O$_{11}$H$_8$ Crystal

### 5.4.7 Powder SHG Test

The effective second order susceptibility at 1064 nm fundamental wavelength was evaluated using Kurtz-Perry powder technique (Kurtz et al 1968), which is considered to be a valuable technique for initial screening of materials for second harmonic generation. The crystal was illuminated using the instrument Scan jet laser source of Nd: YAG laser using the first harmonics output of 1064 nm with the pulse width of 8 ns. The second harmonic signal generated with the crystal was confirmed from the emission of intense green radiation by the crystal. From this SHG test, it is observed that the crystal efficiently converts the IR pump wavelength to visible region and hence this crystal can be useful in the frequency doubling applications and for other non-linear optical devices.
5.5 CONCLUSION

The growth of potassium tetra borate single crystals by low temperature solution growth method was carried out using solvent evaporation technique at room temperature. Potassium hydroxide (KOH) and boric acid (H$_3$BO$_3$) was used for the crystal growth using double distilled water as the solvent. The powder XRD pattern and FTIR spectrum confirms the formation of potassium tetra borate compound. The crystal is subjected to single crystal XRD and is found that it crystallizes in orthorhombic crystal system with P2$_1$2$_1$2$_1$ space group with lattice parameter values $a = 6.852$ Å, $b = 11.774$ Å and $c = 12.897$ Å. From the DTA measurements, the melting of the compound is observed at 790 ºC. UV-VIS-NIR study was carried out and is observed that the crystal possess the UV-cut off less than 200 nm and the transparency of the crystal is more than 60% in the UV and visible region. From the etching analysis, it is observed that the crystal possess step growth pattern. Kurtz powder technique is used to find the SHG property of the material and the material is said to be NLO active.