An investigation on optical, mechanical and thermal properties of nickel sulphate hexahydrate single crystal – a UV band pass filter

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An investigation on optical, mechanical and thermal properties of nickel sulphate hexahydrate single crystal – a UV band pass filter

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Abstract

Nickel sulphate hexahydrate (NSH) crystal is known to be an excellent material for UV light band-pass filter applications. In this research work, good quality and enhanced size of NSH single crystal has been effectively grown by implementing Sankaranarayanan – Ramasamy (SR) method. After a prolonged period of 185 days, a fine quality of transparent as well as improved size single crystal of NSH with dimension 220 mm in length and 12 mm in diameter has been successfully harvested. The grown crystal has been subjected to various characterizations as that of single crystal X-ray analysis to confirm the crystal system with unit cell parameters, UV-Vis analysis to know the transmission spectrum, FTIR spectral analysis to find out the functional groups and photoluminescence study to affirm the green emission of the crystal. NSH crystal falls into the category of soft material as identified by microhardness study and etching study confirms that it has good quality as the surfaces are almost free of defects. Photoacoustic spectroscopy has been utilized to find the thermophysical parameters. The resultant value of thermal diffusivity is compared with few other familiar nonlinear optical materials such that it is asserted by the observed superior value of NSH single crystal that it is an added advantage for band-pass filter and harmonic generation applications.
Keywords: NSH crystal, optical, mechanical properties, etching, photoacoustic spectroscopy

1. Introduction

There has been considerable interest noticed over the years in the field of filter construction which propelled many of the researchers to plunge into the task of identifying material of required characteristic nature so that these could be very well be established for the possible applications. Nickel sulphate hexahydrate (NSH) is a crystal identified with the required characteristics so that it was especially developed for filter construction by Mcbride et al. [1], optical rotation by Stadnicka et al. [2] and a circular dichroic by Grinter et al. [3] in the visible region. Owing to possession of the much needed spectroscopic properties, the crystal could be utilized for transmission-band filters as it exhibits large transmission band in middle ultraviolet region. The crystal shows discontinues spectrum between the ultra violet to near infrared wavelength region so that it can be utilized for optical filters which has been elucidated by Hemmati et al. [4] and it is commercially available in the market as the crystals are extensively utilized in sensors which have the added advantage to approximate accurate range of missiles. There are different types of devices that make use of ultraviolet (UV) filters which select the specific range of wavelength of light to pass through. Such types of UV light filters are mainly applied for the warning systems to indicate the approach of missiles as investigated by He and Chen et al. [5]. Nickel sulfate hexahydrate crystal is one of the best examples for possessing high transmission efficiency (>80%) which is over the range between 250 nm and 340 nm, modest transmission for 450 nm < 600 nm, and strong absorption for all other region of higher wavelengths so that it is contemplated as an UV light filter which has been already reported by Singh and Youping et al. [6, 7]. In modern days, the knowledge of enlargement and classification of Tutton salts has been drawing significant reflections owing to their applications in the field of

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energy storage applications, ultra violet light filters, solar collectors, and also in missile approach caution systems [8]. There are many single crystals which exhibit band-pass filter properties and optical properties with high thermal stability such as ammonium cobalt nickel sulphate hexahydrate [9], cesium nickel sulphate hexahydrate [10], rubidium nickel sulphate hexahydrate [11], iron nickel sulphate twelve hydrate [12], potassium cobalt nickel sulphate hexahydrate [13], ammonium iron sulfate hexahydrate [14], potassium and ammonium zinc sulfate hydrate [15] and zinc magnesium ammonium sulfate hexahydrate [16]. NSH crystal finds its way as a transmission band-pass filter and also as it is an adaptable compound; it is widely used in several fields as that of petroleum, machinery, chemical, industrial and electronics sectors [17, 18].

In recent years, photoacoustic technique has found itself in a prominent position emerging as a powerful mechanism by which accurate estimation of thermal, optical and electronic properties are possible for a vast range of solid materials and also in particular for semiconductors [19-21]. Photoacoustic method is one of the non-contact and nondestructive techniques and it requires no precise sample treatment. Thermal properties of materials are very much essential to be understood for enormous amount of applications such as laser, optical technology and optical communications. In the present study, a crystal clear greenish bulk size NSH single crystal has been successfully accomplished by implementing Sankaranarayanan - Ramasamy (SR) method with the size of 12 mm diameter and 220 mm length that could be achieved for a growth period of 185 days. In slow evaporation solution growth technique, the shape of the crystal cannot be controlled, while in SR method a crystal can be grown in a particular shape as well as plane such that NSH single crystal has been grown along the plane (001). Also in SR technique, considerably large amount of water is used for the heat reservoir so that the temperature fluctuation of the environment doesn’t affect the growth of the crystal.
Hence, we chose this method to grow the title crystal. As of now, with the known literature, the grown crystal is found to be the largest in size among the reported NSH single crystals grown by SR method and in addition, to the best of our knowledge, no one has so far reported photoacoustic spectroscopic studies of NSH single crystal that is very much required for band pass filter and harmonic generation applications. Furthermore, optical, mechanical and etching studies have been performed for the grown NSH single crystal.

2. Experimental Section

2.1 Preparation of NSH seed crystal

Nickel sulfate hexahydrate (NSH) of high quality and purity obtained commercially was the starting material as solute and saturated solution was prepared using double distilled water as the solvent. In order to get a homogeneous solution, magnetic stirring was performed continuously for 2 hours in such a way that the obtained saturated solution was filtered into a beaker with the help of filter paper. Thereafter, the beaker was covered by a ‘polyethylene’ sheet with punched holes on it so as to enable controlled evaporation. Then, the beaker was kept at a place which was free from dirt and external disturbance. After a period of 2 days, crystals started growing and the crystals were monitored daily and after a week the grown crystals were recrystallized and the process was repeated few more times so that the solution was purified and thereafter it was allowed for crystallization. These crystals were grinded and used for the preparation of saturated solution and allowed for slow evaporation. After 30 days, a greenish good quality transparent seed crystal was selected and used for bulk unidirectional growth employing SR method.

2.2 NSH crystal growth by SR method
NSH crystal was grown by SR method. Briefly, a borosilicate glass container was used for SR setup and distilled water was filled in the glass container so as to be used as the reservoir of heat. A ring shaped heater possessing nichrome coil was attached at the top most portion of the container and it was connected with proportional integral derivative (PID) temperature controller (±1 °C) so that the heat reservoir could be maintained with a temperature gradient. For this experiment, a good quality transparent seed crystal of NSH was selected and mounted at the base of the ampoule. The prepared saturated solution at ambient temperature was poured steadily into the seed mounted ampoule and thereafter a perforated aluminium foil was used to cover the mouth of the ampoule so as to enable controlled evaporation. The temperature of the top portion of the borosilicate container was set at 40 °C with an accuracy of ±1 °C and the bottom portion was maintained at ambient temperature. As the ampoule was highly transparent the growing crystal could be very clearly seen which enabled every stage of growth to be monitored all through the growth period. After 3 days, it was observed that NSH crystal started growing so that appropriate monitoring and care was periodically given for avoiding power fluctuation during the entire period of crystal growth. The whole experimental setup was placed at an area which was vibration free and without any external disturbances. After a period of 185 days, a good quality, transparent and enhanced size single crystal of NSH (001) plane [4] with the dimensions of 220 mm in length and 12 mm in diameter was harvested and its photograph is shown in Fig. 1(a). The cut and polished NSH crystal of 1 mm thickness is shown in Fig. 1(b) and the remaining part of the grown crystal was used for further characterizations.
3. Results and Discussion

3.1 Single crystal X – ray Analysis

Single crystal XRD study was enabled for the grown NSH crystal by subjecting it to Enraf Nonius CAD4 – F single crystal X – ray diffractometer equipped with graphite monochromated Mo Kα (λ= 0.71073 Å) radiation performed at ambient temperature. Single crystal XRD analysis reveals that the crystal falls into the category of tetragonal crystal system possessing the unit cell parameters of \( a = 6.7837 (8) \text{ Å}, b = 6.7837 (11) \text{ Å}, c = 18.2774 (5) \text{ Å} \). \( \alpha, \beta \) and \( \gamma = 90^\circ \), which is in good accord with the reported data \[22\].
3.2 UV – Vis – NIR Spectrum

Varian Cary 5E UV – Vis – NIR spectrophotometer was utilized for recording UV – Vis – NIR transmittance spectrum of the crystal performed for the wavelength region 200 – 1100 nm. NSH has four transmission peaks owing to n-π* electronic transition positioned at 457 nm, 482 nm, 525 nm and 852 nm as shown in Fig. 2 and remaining wavelengths experience strong absorption such discontinuous spectral trait mostly happening due to absorption of hydrated transition metal ions. The crystal illustrates accurate transmission spectrum of a material performing as band pass filter between 360 nm to 400 nm and 606 nm to 744 nm. For the grown crystal, the transmission is close to 100 % at 250 nm and about 81% at 482 nm which are much higher than already reported values (73 % at 250 nm and 52% at 482 nm) [4].

![Fig. 2 UV – Vis –NIR transmittance spectrum of NSH crystal](image_url)
3.3 FTIR spectral analysis

FTIR analysis was performed so as to categorize the functional groups available for the grown NSH crystal which was executed using Cary 630 (ATR) FTIR spectrometer technique. To realize the probable functional groups, recording of FTIR spectrum for the crystal was carried out between the range 400 and 4000 cm\(^{-1}\). FTIR spectrum as obtained for NSH crystal is portrayed in Fig. 3 and the functional group data are listed in Table 1.

![FTIR spectrum of NSH crystal](image)

**Fig. 3** FTIR spectrum of NSH crystal
Table 1. Functional group data for NSH grown crystal

<table>
<thead>
<tr>
<th>Wavenumber cm(^{-1})</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>3340</td>
<td>OH asymmetric stretching</td>
</tr>
<tr>
<td>2244</td>
<td>Intermolecular hydrogen bonding between the water molecules</td>
</tr>
<tr>
<td>2073</td>
<td>Intermolecular hydrogen bonding between the water molecules</td>
</tr>
<tr>
<td>1631</td>
<td>H(_2)O deformation</td>
</tr>
<tr>
<td>1141</td>
<td>SO(_4) triply degenerate mode</td>
</tr>
<tr>
<td>1103</td>
<td>SO(_4) triply degenerate mode</td>
</tr>
<tr>
<td>981</td>
<td>SO(_4) degenerate mode</td>
</tr>
<tr>
<td>765</td>
<td>H(_2)O bending</td>
</tr>
<tr>
<td>628</td>
<td>SO(_4) degenerate mode</td>
</tr>
<tr>
<td>560</td>
<td>SO(_4) triply degenerate mode</td>
</tr>
<tr>
<td>444</td>
<td>SO(_4) triply degenerate mode</td>
</tr>
</tbody>
</table>

3.4 Photoluminescence (PL) study

PL spectrum of NSH was recorded with the help of Cary eclipse photospectrometer and the intensity of the observed spectrum is very much reliant on the crystalline and structural quality of the crystal. In general, PL materials are matter which modifies incident energy into electromagnetic radiation for the range of visible or IR regions. Materials of this region are predominantly utilized in the field of lighting technologies and medical diagnostics [23, 24]. The emission wavelength with broad luminescence is experienced at 486 nm, 495 nm, 505 nm and 521 nm for the excitation wavelength 360 nm as exhibited in Fig. 4. To calculate the band gap energy, the formula \( E_g = \frac{hc}{\lambda} \) is used. Here h is the Planck’s constant, \( \lambda \) is the wavelength and c
is the velocity of light of luminescence. The computed band gap energy values are 2.55 eV, 2.5 eV, 2.45 eV and 2.38 eV for the respective PL emission wavelengths. The empirical wavelengths of 486 nm, 495 nm, 505 nm and 521 nm denote that the crystal has green emission.

![Fig: 4 PL spectrum for emission of NSH crystal](image)

3.5 Microhardness Studies

Fine polished NSH single crystal was put under investigation for Microhardness measurement at ambient temperature accomplished by Shimadzu HMV – 2000 hardness tester which is generally attached to an indenter of diamond pyramid capable of making indentation on loading. Varying loads of P ranging between 10 and 100 g in steps of 10 g was applied fixing the time of indentation as 10 s for all observations. With the help of a microscope, the diagonal lengths of the respective indentations were recorded. Using the formula $H_v = 1.8544 \left( \frac{P}{d^2} \right)$
kg/mm², the Vickers microhardness (Hᵥ) number was computed, where P represents the applied mass in kg and d is the average length of indentation impression measured along the diagonal in mm. Fig. 5 illustrates the plot drawn between load P and Hᵥ (Vickers microhardness number) of NSH crystal. Observing the plot, it is obvious that the material’s hardness increases on increasing the applied load which confirms the phenomenon of reverse indentation size effect (RISE) exhibited by the crystal [25, 26]. The applied load and the resulting diagonal length obtained from the indentation are related by Meyer’s law which is \( P = Ad^n \), where \( n \) refers to the Meyer’s index and A denotes the constant of given material. The Meyer’s index which is also known as the work hardening coefficient (n) was obtained from the graph plotted between log P and log d as portrayed in Fig. 6. The datum of n was calculated from the slope out of the straight line obtained and it is identified as 2.02 which is much lesser than the reported value (4.80) [27]. The less value of the hardness may be due to the better crystalline quality of the present crystal [28] also the hardness value depends on the plane for non-centrosymmetric crystals. As per Onitsch [29], the value of n has to be lying between 1 and 1.6 so as to be in the category of hard materials and n has to be higher than 1.6 for the category of soft materials. Thus the datum of n acquired makes it to be known that NSH crystal falls into the type of soft material.
Fig. 5 Microhardness behavior of NSH crystal

Fig. 6 Meyer’s plot for NSH crystal
3.6 Chemical Etching Studies

Chemical etching, known to be a powerful tool, is widely used to examine the growth defects such as etch spirals, hillocks, rectangular etch pits etc., created on the crystal surface [30]. Fine polished NSH single crystal was put under etching process utilizing double distilled water as the etchant performed at ambient temperature. Gentle soaking of the crystal surface was enabled in the etchant for the time period of 20 s and immediately dried utilizing a high quality tissue paper. At once, the sample was put under a polarized optical microscope possessing a high resolution Motic camera so as to analyze the microstructure. Linear and lengthened lines of etch pits were noticed to have started on the surface of the crystal of NSH as shown in Fig. 7a. As the etching time was raised to 40 seconds it was recorded that uniform line-shaped etch pits were developed (Fig. 7b). This study corroborates that, on etching, the crystal obtains elongated straight line structure. Etching images confirm that NSH crystal has good quality as evidenced by the surfaces and it is also seen that the plane is without any notable defects.

![Etch Patterns of NSH crystal with water as etchant (20 seconds)](image)
3.7 Photoacoustic spectroscopic studies

The occurrence of sound as and when a solid sample is irradiated with non static (pulsed or modulated) light is known as photoacoustic (PA) effect. For the present investigation, finely polished nickel sulphate hexahydrate (NSH) single crystal of 1 mm thickness was selected to be mounted on the cell which is acoustic free. NSH crystal is illuminated by the modulated light radiation emanated from a 250 W halogen lamp and the modulated light enforces temperature fluctuations in the medium. As the temperature fluctuation rapidly increases it results into periodic difference of temperature creating pressure waves which can be detected by using a sensitive microphone. PA signal amplitude versus square root of chopping frequency is plotted as shown in Fig. 8. The plot implies that when the chopping frequency is on the rise the amplitude slowly decreases and also it is very significantly evident that the PA signal is dependent on $\omega^{-1}$. Thermal diffusivity of the crystal has been computed as $0.8398 \times 10^{-6}$ (m$^2$/s) at ambient temperature by curve fitting method which is depicted in Fig. 8 [31]. The thermal
diffusivity of the grown NSH crystal, along with the comparison of few prominent NLO crystals, is given in Table 3.

![Graph showing variation of PA signal amplitude for dissimilar square root of chopping frequency for NSH crystal](image)

**Fig. 8** Variation of PA signal amplitude for dissimilar square root of chopping frequency for NSH crystal
Table 3 Thermal diffusivity of NSH single crystal

<table>
<thead>
<tr>
<th>Materials</th>
<th>Thermal diffusivity $\times 10^{-6}$ (m²/s)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiTaO₃</td>
<td>1.3000</td>
<td>[32]</td>
</tr>
<tr>
<td>BBO</td>
<td>0.4241</td>
<td>[33]</td>
</tr>
<tr>
<td>TGS</td>
<td>0.2400</td>
<td>[34]</td>
</tr>
<tr>
<td>LAP</td>
<td>0.4436</td>
<td>[35]</td>
</tr>
<tr>
<td>NSH</td>
<td>0.8398</td>
<td>[ Present work]</td>
</tr>
</tbody>
</table>

From the observed data, we assert that the thermal diffusivity of NSH is greater than that of few reported values such as Barium Borate (BBO), Tri Glycine Sulphate (TGS) and L-Arginine Phosphate (LAP). However, the thermal diffusivity of NSH crystal is less than Lithium Titanium Oxide (LiTaO₃) crystal. Hence, the identified high value of thermal diffusivity for NSH crystal is an added advantage so that it can be used in high power radiation exposure environments [36].

4. Conclusion

NSH single crystal was grown successfully with enhanced size by employing Sankaranarayanan – Ramasamy (SR) method. X-ray analysis for NSH single crystal was experimented so as to confirm that the crystal system is tetragonal and UV-Vis- NIR Spectrum analysis shows that the maximum transmission of the crystal is around 80% at visible region and almost zero transmittance between the regions of 360 nm to 400 nm and 606 nm to 744 nm. FTIR spectral analysis corroborates occurrence of functional groups. NSH single crystal exhibits
green light emission which is observed from the photoluminescence spectral analysis. The microhardness value rises with rise in load and the Meyer’s index number determined for the crystal asserts that the crystal belongs to the category of soft material. The crystal exhibits uniform straight line structure as obtained from etching analysis which also proves that NSH crystal has fewer defects on surface. Using photoacoustic spectroscopy analysis, the thermal diffusivity of NSH single crystal was found out and compared with few other well-known prominent crystals and the value is higher than that of few familiar crystals. Consequently, the high value of thermal diffusivity for NSH crystal makes it suitable for UV band pass filter and harmonic generation applications.

References


