Thermophysical and Optical Properties of L-Tartaric Acid Crystal

Thirupathy Jayapalan, Sahaya Jude Dhas Sathiyadhas, Jose Michael, Balachandar Settu, and Martin Britto Dhas Sathiyadhas Amalapushpam*

Thermal properties play a vital role particularly for the materials which are used in high power laser irradiation. Photoacoustic technique is very much feasible to find out the thermal transport properties of solid materials. In the present work, nonlinear optical (NLO) single crystal of L-tartaric acid (LTA) was grown by Sankaranarayanan-Ramasamy (SR) method for dimensions of 140 mm in length and 11.5 mm in diameter. The grown LTA crystal has been subjected to UV-Vis-NIR spectral study to analyze the optical transmittance and absorbance characteristics. The thermal characterization studies were performed using photoacoustic spectrometer (PAS). Thermal characterization involves measurement of thermal parameters such as thermal diffusivity, thermal effusivity, thermal conductivity and specific heat capacity. The experimental results of photoacoustic spectrometer show that the thermal diffusivity of LTA is higher than the reported values of a few other well known NLO materials.

1. Introduction

Over the last few years, photoacoustic method has been considered as an important tool for faultless analysis of the thermal transport properties of solid materials, mainly semiconductors.[11–13] Photoacoustic spectrometer (PAS) is one of the nondestructive photothermal methods that make use of the identification of pressure fluctuation produced due to periodical thermal waves in the sample caused by the chopped or modulated light. Photoacoustic (PA) techniques are valuable since the signal generated depends on the quantity of heat produced in the sample and how fast the heat spreads. PA tool is also used to analyze parameters such as crystallinity degree, defects, microstructure effects and impurities.[14–18] The knowledge of thermal properties is essential for crystals which are exposed to high power laser irradiation and particularly for nonlinear optical (NLO) crystals. NLO is a proactive area which has been already acquainted with the frontline research so that it could emerge as the field of centre stage owing to its current developments in photonics, optical computing and optical communication. Furthermore, it could also supplement in providing the key functions of frequency shifting, optical modulation, optical switching, optical logic and optical memory for the emerging technologies in the areas such as telecommunications, signal processing and optical interconnections.[19] Organic non-linear materials are always in demand and continue to generate a great deal of interest as they have large optical susceptibilities, inherent ultra fast response times and high optical thresholds for laser power in comparison with their counterparts of inorganic materials. L-Tartaric acid (LTA) crystal is one among the potential NLO materials which has a good second harmonic efficiency that makes it to be compared with the standard materials of L-arginine,[10] L-histidine[11] and glycine.[12] In addition to that, it has large threshold damage energy of 5.4 GW cm$^{-2}$ which is quite higher than already reported values of a few well known NLO materials.[13–17] The major shortcoming of crystalline organic NLO materials is the difficulty in growing bulk size single crystals of high optical quality and also the fragile nature of these crystals causing them tough to be processed.[18] Though the growth and characterization of LTA crystals were already reported by few researchers,[13,19–21] its thermal properties are not found in the literature. As these properties play a vital role for the quality and stability of the output of NLO crystals, the acquired knowledge would add value for the device fabrication. Even though these properties can be determined by other methods such as laser flash method, we prefer photoacoustic spectrometer as it is a non-destructive testing and surface analytical tool. Furthermore, it is an effective technique to measure the absorption coefficient and thermal properties of weak absorption or opaque and diffuse materials in which conventional photoelectric measurement is not feasible.[22–25] In the present investigation, L-tartaric acid bulk single crystal has been grown by Sankaranarayanan-Ramasamy (SR) method with the dimensions of 140 mm length and 11.5 mm diameter which is larger in size compared to...
previous literature results.\cite{19,26} In addition to that, the thermal characterization of the sample has also been investigated and reported for the first time and the results are discussed in detail.

2. Experimental Section

2.1. Preparation of Seed Crystal

The most basic requirement of high quality crystal growth is the purification of the raw material. Recrystallization process is one of the best methods to improve the quality and purity of the material. The saturated solution of ‘AR’ grade L-tartaric acid was prepared and then allowed for slow evaporation. After a few days, many small sized crystals were harvested and these crystals were powdered and re-crystallized. The re-crystallization process was continued for a few more times and thereafter an optically transparent, well defined and good quality single crystal was chosen and used as seed for the unidirectional crystal growth purpose.

2.2. Crystal Growth by SR Method

For the growth of LTA single crystal, Sankaranarayanan-Ramasamy (SR) method\cite{27} was employed and the experimental setup consists of a borosilicate glass container which was filled with distilled water serving as heat reservoir. A ring heater made of nichrome along with a proportional integral derivative (PID) temperature controller (±1 °C) was fixed at the top portion of heat reservoir to establish the desired temperature gradient. The temperature was maintained at 40 °C at the top of the heat reservoir and the bottom portion was kept at room temperature. A glass ampoule with a V-shaped tapered bottom was designed and fabricated at author’s laboratory and the seed crystal of (110) plane\cite{19} was placed at the bottom of the ampoule and exposed to the solution of LTA so as to initiate further growth. The saturated solution of LTA was slowly poured into the ampoule without disturbing the seed crystal’s position. The top portion of the ampoule was closed with the help of a ‘polyethylene’ sheet consisting of pin holes for controlled evaporation. The whole setup was placed in a vibration free environment and the growth was monitored on daily basis. The seed crystal started growing after 3 days and the growth rate of the crystal was measured as 1.60 mm per day. The LTA crystal was optically transparent during the entire period of crystal growth and proper care was taken to avoid power failure by supplementing the experimental set up with power back up. After a period of 85 days, a transparent and good quality single crystal of LTA with dimensions of 140 mm in length and 11.5 mm in diameter was harvested as shown in Figure 1. The cut and polished section with 1 mm thickness of LTA crystal are shown in Figure 2.

3. Results and Discussion

3.1. Optical Transmission Spectral Analysis

The optical absorption spectrum of LTA crystal was recorded in the range 200–1200 nm using Varian Cary 5E UV-Vis-NIR spectrophotometer. Figure 3 shows the UV-Vis-NIR spectrum recorded with transparent single crystal of LTA of thickness 3 mm. It is observed that the lower cut-off of LTA crystal is at 236 nm and the crystal is found to be transparent in the region of 250–1200 nm. The optical absorption coefficient (α) was calculated using the following relation,

\[
\alpha = \frac{1}{t} \log \left( \frac{1}{T} \right)
\]
where, $T$ is the transmittance and $t$ is the thickness of the crystal. The crystal has absorption co-efficient ($\alpha$) obeying the following relation for high photon energies ($h\nu$):

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

Figure 3. UV-Vis-NIR absorbance and transmission spectrum of LTA.

Figure 4. Plot of ($\alpha h\nu$)$^2$ vs. photon energy of LTA.

where, $E_g$ is band gap and $A$ is constant. The graph between ($\alpha h\nu$)$^2$ and $h\nu$ is shown in Figure 4 and it gives the band gap of the crystal as 5.45 eV. As a consequence of wide band gap, the grown crystal has large transmission in the entire visible region.[28]

3.2. Photoacoustic Spectrometer (PAS)

The thermal properties of LTA crystal were determined by a photoacoustic spectrometer which was indigenously designed and constructed in our laboratory. The block diagram of the photoacoustic spectrometer is shown in Figure 5. The sample in an acoustic free cell is irradiated by the collimated and modulated light from a 250 W halogen lamp and thereby obtained modulated light generates temperature difference followed by pressure fluctuations in the medium. A microphone, which is controlled by sound recording software, is placed very close to the sample.

Figure 5. Block diagram of experimental setup of photoacoustic spectrometer.
Figure 7. Variation of PA signal amplitude for different square root of chopping frequencies.

Figure 8. Specific heat capacity plot for LTA crystal.

to pick up these fluctuations and an associated amplifying system produces an electrical signal whose amplitude is monitored over a range of modulation frequencies. This spectrometer was calibrated using standard samples such as quartz, BK7 and KDP crystals of dimension 10 × 10 × 1 mm³.

The PA signals for different chopping frequencies were obtained as shown in Figure 6 and the variation of PA signal amplitude for the square root of chopping frequency is depicted in Figure 7. The plots show that as the chopping frequency is increased the amplitude gradually decreases and also the $\omega^{-1}$ dependence of the PA signal is very much evident.

From Figure 7, thermal diffusivity of the crystal has been calculated by using the curve fitting method,[29] then thermal conductivity and thermal effusivity have been derived from the following equations.[30,31]

\[
k = \alpha \rho c_p \tag{3}
\]

\[
e = \rho c_p \sqrt{\alpha} \tag{4}
\]

where, $k$, $\alpha$, $\rho$, $c_p$ and $e$ are thermal conductivity, thermal diffusivity, density, specific heat capacity and thermal effusivity of the crystal, respectively. Since specific heat capacity is needed for thermal conductivity and thermal effusivity calculations, specific heat experiment was performed for the sample and the plot is shown in Figure 8. The specific heat capacity is found to be varied from 0.9 to 1.3 J g⁻¹ °C⁻¹ when the temperature is varied from 0 °C to 120 °C. Though the difference is small, the variation is linear. Since the specific heat is linear, the thermal properties such as thermal diffusivity, thermal conductivity and thermal effusivity will also be linear. It is favorable character for device fabrication since the properties are predictable.

Thermal diffusivity of LTA is calculated as 0.6384 $\times$ 10⁻⁶ m² s⁻¹ at the room temperature and other thermal parameters of LTA are also derived and listed in Table 1 which is provided with the values of popular NLO materials for comparisons. It is quite clear that the thermal diffusivity of LTA is higher than the reported values of few other well-known NLO materials such as Barium Borate (BBO), L· Arginine Phosphate (LAP) and Tri Glycine Sulphate (TGS). The high value of thermal transport properties of a material maximizes the formation of conductive networks and in turn it minimizes the thermal barrier resistance along the heat flow path so that the material could be saved from thermal shock generated by pulsed laser irradiation.[36] Hence, the high value of thermal transport properties of LTA crystal makes it suitable for many applications such as photonic, optical computing, optical communication etc.

4. Conclusion

Optically transparent single crystal of L-tartaric acid of length 140 mm and 11.5 mm diameter was grown successfully by SR method with a growth rate of 1.64 mm per day. The optical and

<table>
<thead>
<tr>
<th>Materials</th>
<th>Thermal Diffusivity x 10⁻⁶ (m² s⁻¹)</th>
<th>Thermal Effusivity x 10³ (J m⁻² K⁻¹ S⁻¹/²)</th>
<th>Thermal Conductivity (W m⁻¹ K⁻¹)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>BBO</td>
<td>0.4241</td>
<td>1.2285</td>
<td>0.8000</td>
<td>[32]</td>
</tr>
<tr>
<td>LAP</td>
<td>0.4436</td>
<td>0.8858</td>
<td>0.5900</td>
<td>[33]</td>
</tr>
<tr>
<td>TGS</td>
<td>0.2400</td>
<td>1.0574</td>
<td>0.5180</td>
<td>[34]</td>
</tr>
<tr>
<td>LiTaO₃</td>
<td>1.3000</td>
<td>3.4205</td>
<td>3.8000</td>
<td>[35]</td>
</tr>
<tr>
<td>LTA</td>
<td>0.6384</td>
<td>1.4052</td>
<td>1.1229</td>
<td>[Present study]</td>
</tr>
</tbody>
</table>

Table 1. Thermal parameters of L-Tartaric acid crystal.
thermophysical properties of the grown crystal were analyzed by UV-Vis spectrometer and photoacoustic spectrometer, respectively. The results show that the grown crystal is optically good quality single crystal with the transmission of nearly 65% in the entire visible region. The photoacoustic studies show that the thermal diffusivity of LTA crystal is $0.6384 \times 10^{-6} \text{ m}^2 \text{s}^{-1}$ which is higher than that of well known NLO materials such as barium borate (BBO), L-arginine phosphate (LAP) and tri-glycinesulphate (TGS). The higher value of thermal diffusivity is a favorable property for optical switching, optical modulation and laser applications. The above results show that LTA crystal can be utilized for optical devices and laser applications.

**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**

L-tartaric acid, photoacoustic spectroscopy, specific heat capacity, thermal conductivity, thermal diffusivity, thermal effusivity

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