Growth and characterization of L-Tartaric acid, an NLO material

S.A. Martin Britto Dhas\textsuperscript{a}, M. Suresha, G. Bhagavannarayana\textsuperscript{b}, S. Natarajan\textsuperscript{a,*}

\textsuperscript{a}Department of Physics, Madurai Kamaraj University, Madurai 625 021, India
\textsuperscript{b}Material Characterization Division, National Physical Laboratory, New Delhi 110012, India

Received 27 June 2007; received in revised form 7 August 2007; accepted 5 September 2007

Communicated by M. Schieber
Available online 14 September 2007

Abstract

Single crystals of L-Tartaric acid (C\textsubscript{4}H\textsubscript{6}O\textsubscript{6}), an organic nonlinear optical (NLO) material, have been grown by hanging seed solution and submerged seed solution techniques at room temperature. The crystal system has been confirmed from the single crystal X-ray diffraction analysis. The crystalline perfection was evaluated using high-resolution X-ray diffractometry (HRXRD). From this analysis, it was found that the quality of the crystal is quite good. The functional groups were identified using FTIR spectroscopy. UV–vis–NIR spectrum showed the absence of absorption in the wavelength region of 220–900 nm. The second harmonic generation efficiency is 89\% compared to that of standard potassium dihydrogen phosphate (KDP). The laser damage threshold value is much higher than that of KDP and closer to that of β-barium borate.

© 2007 Elsevier B.V. All rights reserved.

PACS: 61.10.Nz; 81.10.Dn; 81.10.—h

Keywords: A1. X-ray diffraction; A2. Growth from solution; B1. Organic compound; B2. Nonlinear optical materials

1. Introduction

Materials that possess optical nonlinearities have been studied extensively for their possible applications in various fields like telecommunication, optical computing, optical data storage and optical information processing. The generation of coherent blue light through second harmonic generation (SHG) from near infrared (NIR) laser sources is an important technological problem that has attracted much attention in the last few years. Potential applications lie in the fields of high-density optical data storage, high-resolution printing and spectroscopy [1,2]. Organic nonlinear materials are attracting a great deal of attention, as they have large optical susceptibilities, inherent ultra fast response times and high optical thresholds for laser power as compared with inorganic materials [3]. A number of such materials have been reported in literature for their potential applications [3–6]. In the present article, the bulk growth of the nonlinear optical (NLO) material, L-Tartaric acid and its crystalline perfection, spectroscopic and NLO properties are discussed. L-Alaninium maleate (LAM) [4] and L-Prolinium tartrate (LPT) [7] were the recently reported as NLO materials from our laboratory. Even though the SHG efficiency of L-Tartaric acid is slightly on the lower side than the above crystals, the laser damage threshold and thermal stability are of the same order. Also, L-Tartaric acid has higher solubility in water, could be crystallized into bigger sizes and costs much less in comparison with the amino acid-NLO materials. A number of tartaric acid complexes are known to possess NLO property [7–9]. However, to our knowledge, no systematic non-linear optical studies appear to have been carried out for the crystals of L-Tartaric acid (Fig. 1).

2. Experimental studies

2.1. Crystal growth

The selection of the solvent is an important step in the bulk growth of crystals from solution by slow evaporation
The size of the crystal depends on the amount of material available in the solution, which in turn is decided by the solubility of the material in that solvent. Hence, the solubility measurements of L-Tartaric acid were carried out in water and water + acetone (1:1) for various temperatures, viz., 27, 30, 35, 45, 55 and 60 °C. The temperature dependence of solubility is shown in Fig. 2. From the figure, it is seen that the solubility increases with the increase of temperature in both the cases but the solubility is much higher in water. Hence, water was selected as the solvent for the crystal growth experiments.

Commercially available L-Tartaric acid (S.D. Fine-chem, India) was used for the solubility measurements and growth. Initially, the material was purified by repeated recrystallization. Recrystallized L-Tartaric acid was dissolved in double-distilled water at 32 °C. After obtaining the saturation, the solution was filtered using micro filter paper and the solution was optimally closed using a perforated polythene sheet. Seed crystals were harvested within a week. A suitable seed crystal was selected from the harvested crystals. Two methods of crystallization were attempted to grow bulk crystals. In the first method, a saturated solution was prepared and the seed crystal was hung inside the solution that was optimally closed for controlled evaporation. A good quality transparent crystal of size of $31 \times 11 \times 6 \text{mm}^3$ was obtained in a period of 3 weeks. From Fig. 3, it is clear that the end portions of the crystal are of good quality than the middle portion which is not transparent and has lot of defects. It is due to the stress applied by the thread which was used to hang the seed crystal [10]. To avoid it, another technique, viz., submerged seed solution method, was used. In this method, the seed crystal was kept at the bottom of the vessel containing the saturated solution. A good-quality crystal of size $20 \times 15 \times 12 \text{mm}^3$ (Fig. 4) was obtained in the same period of about 3 weeks. Portions of this crystal sample were used for all the characterization studies described in the following paragraphs.

3. Crystal characterization

3.1. Single crystal X-ray diffraction

Nonius CAD-4/MACH 3 Diffractometer with Mo Kα (0.71073 Å) radiation was used to obtain the accurate cell parameters of the grown crystals at room temperature, by the least-squares refinement of the setting angles of 25 reflections. L-Tartaric acid was crystallized in the monoclinic system and the lattice parameters were found...
to be $a = 6.203(5)$ Å, $b = 6.018(3)$ Å, $c = 7.720(9)$ Å, $\beta = 100.10(2)^\circ$ and the space group is $P2_1$. These values agreed well with the reported values [11]. The density of the crystal was found to be 1.76 g/cm³ using floatation method and the melting point was found to be 170(2) °C using a melting point apparatus.

### 3.2. Multicrystal X-ray diffractometer

To reveal the crystalline perfection of the grown crystals, a multicrystal X-ray diffractometer (MCD) developed at National Physical Laboratory (NPL) [12] has been used to record the high-resolution diffraction curves (DCs). In this system, a fine focus (0.4 mm²; 2 kW Mo) X-ray source energized by a well-stabilized Philips X-ray generator (PW 1743) was employed. The well-collimated and monochromated Mo K$_{\alpha 1}$ beam obtained from the three monochromator Si crystals set in dispersive (+,−,−) configuration has been used as the exploring X-ray beam. This arrangement improves the spectral purity ($\Delta \lambda / \lambda \leq 10^{-5}$) of the Mo K$_{\alpha 1}$ beam. The divergence of the exploring beam in the horizontal plane (plane of diffraction) was estimated to be ≤3 arcsec. The specimen crystal is aligned in the (+,−,−,−) configuration. Due to dispersive configuration, though the lattice constant of the monochromator crystal(s) and the specimen are different, the unwanted dispersion broadening in the diffraction curve of the specimen crystal is insignificant. The specimen can be rotated about a vertical axis, which is perpendicular to the plane of diffraction, with minimum angular interval of 0.5 arcsec. The diffracted intensity is measured by using a scintillation counter, which is mounted with its axis along a radial arm of the turntable. The rocking or DCs were recorded by changing the glancing angle (angle between the incident X-ray beam and the surface of the specimen) around the Bragg diffraction peak position $\theta_B$ starting from a suitable arbitrary glancing angle (denoted as zero). The detector was kept at the same angular position $2\theta_B$ with wide opening for its slit, the so-called $\omega$ scan.

#### 3.2.1. High-resolution X-ray diffraction (HRXRD) analysis

Before recording the diffraction curve, to remove the non-crystallized solute atoms remaining on the surface of the crystal and also to ensure the surface planarity, the specimen was first lapped and chemically etched in a non-preferential etchant of water and acetone mixture in 1:2 volume ratio. Fig. 5 shows the high-resolution DC recorded for l-Tartaric acid specimen using (1 0 0) diffracting planes in symmetrical Bragg geometry by employing the multicrystal X-ray diffractometer described above, with Mo K$_{\alpha 1}$ radiation. As seen in Fig. 5, the DC is quite sharp without any satellite peaks which may otherwise be observed either due to internal structural grain boundaries [13] or due to epitaxial layer which may some times form, for example in case of complexing layers formed due to organic additives [14]. The full width at half maximum (FWHM) of the DCs is 14 arcsec, which is very close to that expected from the plane wave theory of dynamical X-ray diffraction [15]. The single sharp diffraction curve with very low FWHM indicates that the crystalline perfection is extremely good. The specimen is a nearly perfect single crystal without any internal structural grain boundaries and dislocations (or very low density of dislocations which could not be detected by high-resolution X-ray topography).

### 3.3. FTIR and UV–vis–NIR studies

The FTIR spectra of the crystal were recorded in the KBr phase in the frequency region of 400–4000 cm$^{-1}$ using a Jasco Spectrometer (FTIR, model 410) at a resolution of 4 cm$^{-1}$ and with a scanning speed of 2 mm/s. The recorded FTIR spectra (Fig. 6) were compared with the standard spectra of the functional groups [16]. The strong but broad peak at 3404 cm$^{-1}$ is due to the presence of O–H stretching in the carboxyl group. The very strong peak observed at 1737 cm$^{-1}$ indicates the presence of C=O. The peak at 1399 cm$^{-1}$ is assigned to C–H stretching. The weak peak at 1450 cm$^{-1}$ is due to the combination of C–O stretching and O–H deformation.

The UV–vis–NIR transmission spectrum of the crystal was recorded in the wavelength range of 190–900 nm and is shown in Fig. 7. It is seen that the UV transparency cutoff occurs around 220 nm and there is no remarkable absorption in the entire region of the spectra. It is an important requirement for NLO materials for possible applications [17].

### 3.4. Powder SHG and laser damage threshold measurements

The NLO conversion efficiency was tested using a modified setup of Kurtz and Perry [18]. A Q-switched Nd:YAG laser beam of wavelength 1064 nm was used with an input power of 2.0 mJ and pulse width of 10 ns, the repetition rate being 10 Hz. The crystals of l-Tartaric acid...
were ground to a uniform particle size of about 125–150 μm and then packed in a capillary of uniform bore and exposed to laser radiations. The output from the sample was monochromated to collect only the second harmonic (λ = 532 nm) and eliminate the fundamental, and the intensity was measured using a photomultiplier tube. A second harmonic signal of 40 mV was obtained, while the standard potassium dihydrogen phosphate (KDP) crystal gave an SHG signal of 45 mV/pulse for the same input energy. Higher efficiencies are expected to be achieved by optimizing the phase matching [19].

One of the decisive criteria for an NLO crystal to perform as a device is its resistance to laser damage, since high optical intensities are involved in nonlinear processes. Inorganic crystals are usually known to have high resistance to laser damage. The laser damage threshold studies on L-Tartaric acid have been carried out using a Q-switched Nd:YAG laser of 10 ns pulses at a wavelength of 1064 nm. The energy density was calculated using the formula

\[
\text{Energy density} = \frac{E}{A} \text{(GW/cm}^2\text{)},
\]

where \(E\) is the input energy measured in mJ and \(A\) is the area of the circular spot. The laser damage energy density was found to be 5.4 GW/cm². This value is in the higher range compared to the values reported for some known NLO materials (Table 1).

### Table 1

<table>
<thead>
<tr>
<th>Compound</th>
<th>SHG signal (mV)</th>
<th>Laser damage threshold (GW/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potassium dihydrogen phosphate (KDP)</td>
<td>45</td>
<td>0.2(^a)</td>
</tr>
<tr>
<td>Urea</td>
<td>270</td>
<td>1.5(^a)</td>
</tr>
<tr>
<td>Benzimidazole</td>
<td>202</td>
<td>2.9(^a)</td>
</tr>
<tr>
<td>β-Barium borate</td>
<td>180</td>
<td>5.0(^a)</td>
</tr>
<tr>
<td>L-Arginine phosphate</td>
<td>135</td>
<td>10.0(^a)</td>
</tr>
<tr>
<td>L-Prolinium tartrate</td>
<td>43</td>
<td>5.9(^b)</td>
</tr>
<tr>
<td>L-Alaninium maleate</td>
<td>55</td>
<td>4.9(^c)</td>
</tr>
<tr>
<td>L-Tartaric acid</td>
<td>40</td>
<td>5.4(^d)</td>
</tr>
</tbody>
</table>

\(^{a}\)Ref. [20].  
\(^{b}\)Ref. [7].  
\(^{c}\)Ref. [4].  
\(^{d}\)Present work.
4. Conclusions

Bulk NLO crystals of L-Tartaric acid were grown using hanging seed solution and submerged seed solution methods. The crystals were optically good and the crystalline perfection was tested by HRXRD. The optical studies showed the absence of absorption above the wavelength of 220 nm. The SHG efficiency is comparable to that of the standard KDP crystal but the laser damage threshold is much higher compared to that of KDP. The above experimental results, viz., bulk size, high melting point, extremely good crystalline perfection, optical transparency, SHG efficiency and high value of laser damage threshold show that L-Tartaric acid crystals may have possible NLO applications.

Acknowledgments

The authors thank the UGC-SAP and DST-FIST Programmes and S.A.M.B. thanks the Madurai Kamaraj University for the Research fellowship.

References