

Optical Studies on L-Tartaric acid and L-Prolinium Tartrate

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Abstract

Bulk-size single crystals of the nonlinear optical (NLO) materials: L-tartaric acid (LTA) and L-prolinium tartrate (LPT) were grown from aqueous solution using a home made crystal growth setup. Characterization of the crystals was investigated using single crystal X-ray diffraction. UV-vis-NIR spectra showed that the crystals have excellent transparency in the visible and infrared regions. Tentative assignments were made for the IR absorption peaks. The birefringence of the crystals was measured in the visible region and it was found to be varying with wavelength. Photoluminescence excitation studies showed that the emission occurred at 397 and 375 nm respectively, for LTA and LPT. The second harmonic generation (SHG) conversion efficiency of the powder samples of the crystals were measured as about 40% and 95% respectively, compared to that of the standard KDP crystals.

Keywords

L-Tartaric Acid; L-Prolinium Tartrate; MKN Setup; UV-vis-NIR; IR Spectra; Birefringence; SHG

Introduction

In recent years, several studies dealing with organic, inorganic and semiorganic materials for nonlinear optics (NLO) have been reported, due to the increasing need for cheap and easily processable materials for applications in photonics. Among these, organic nonlinear materials will be the key elements for future photonic technologies. A number of such materials have been reported in literature for their applications as NLO materials [Pal, Kar, Bocelli and Rigi, 2003, Natarajan, Martin Britto Dhas and Ramachandran, 2006]. L-Tartaric acid (LTA) and L-Prolinium tartrate (LPT) are good organic nonlinear optical materials. Reports are already available on the growth of the single crystals of LTA using slow evaporation, hanging seed, submerged

seed solution techniques and Sankaranarayanan-Ramasamy method [Suresh and Arivuoli, 2011, Martin Britto Dhas, Suresh, Bhagavannarayana and Natarajan, 2007, Ramesh Kumar, Gunaseelan, Kumararaman, Bhagavannarayana and Sagayaraj, 2011]. Recently, the unidirectional growth of LTA using a home made crystal growth setup (MKN setup) and its characterization were reported from our laboratory [Moovendaran and Natarajan, 2013]. Crystals of LPT were grown using submerged seed solution method by Martin Britto Dhas and Natarajan (2007), from our laboratory. The present communication deals with the following: (i) the growth of bulk-size single crystals of LTA and LPT using the MKN setup, (ii) their characterization using single crystal X-ray diffraction, UV-vis-NIR and infrared (IR) spectroscopic methods, (iii) measurements of birefringence and second harmonic generation (SHG) efficiencies and (iv) photoluminescence (PL) studies.

Crystal Growth Experiments

A new setup was designed in our laboratory to conduct several crystal growth experiments simultaneously [Moovendaran, Kalyana Sundar and Natarajan, 2011]. The home made setup (named as MKN setup) is made up of two large tanks and consists of several ampoules, dimmerstat, temperature controller, heating coil and thermometer. Constant temperature and uniform temperature gradient were maintained to increase the growth rate and quality of the crystal grown. The details of this setup and the growth of LTA single crystal have been reported elsewhere [Moovendaran and Natarajan, 2013]. LPT was synthesized using L-proline and L-tartaric acid taken in the equimolar ratio. The reactants were thoroughly dissolved in distilled water using a

magnetic stirrer to yield a homogenous solution. Good quality transparent single crystals grown by slow evaporation solution technique (SEST) were harvested from this solution after a period of about 14 days. A transparent good quality crystal (from the crystals obtained using the SEST) of size about 5 x 3 x 2 mm was selected as the seed crystal for single crystal growth along the [020] direction and fixed at the bottom of the ampoule. An aqueous saturated solution of LPT was prepared and transferred into the growth ampoule. A transparent crystal of LPT having a length of 35 mm and diameter of 15 mm was grown in a period of about 22 days. The average growth rate was found to be about 1.5 mm per day. The photograph of the cut and polished plates of the single crystals are shown in Fig. 1.

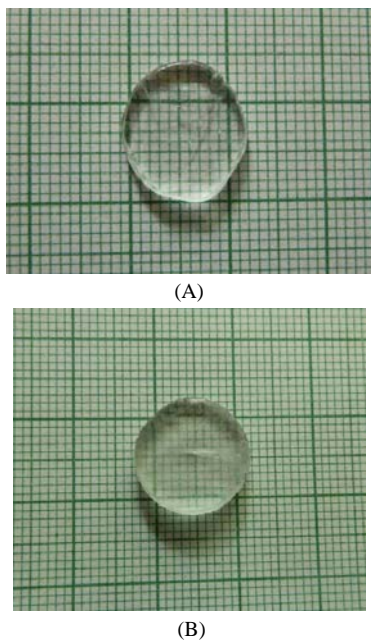


FIG. 1 PHOTOGRAPH OF THE CUT AND POLISHED PLATE OF (A) LTA (B) LPT

Results and Discussion

Single Crystal X-ray Diffraction

The crystals were subjected to single crystal X-ray diffraction studies using an Enraf Nonius CAD-4/MACH 3 diffractometer, with MoK α radiation (0.71073 Å). The accurate cell parameters at room temperature (25°C) were obtained from the least-squares refinement of the setting angles of 25 reflections. These values [Table 1] are in good agreement with those previously reported [Subha Nandhini, Krishna Kumar and Natarajan, 2001, Okaya, Stemple and Kay, 1966], confirming the identity of the crystals. It has been already known that both these

crystals crystallize in the monoclinic system with the space group P2₁. The densities of the crystals were determined by using the floatation method [Table 1].

TABLE 1 LATTICE PARAMETERS AND DENSITY OF LTA AND LPT

Crystal	a (Å)	b (Å)	c (Å)	β (°)	Density (gm/cm ³)
LTA	6.204 (3)	6.017 (3)	7.720 (8)	100.13 (2)	1.77 (2)
LPT	5.009 (2)	17.684 (9)	6.523 (3)	100.36 (3)	1.55 (1)

UV-vis-NIR Transmission Spectrum

The transmittance of the grown crystals (2 mm thickness) was measured using a Perkin-Elmer Lambda-35 spectrophotometer in the wavelength range of 200–1100 nm with a slit of width 2 nm and scan speed of 240 nm/min. The optical transmittance (Fig. 2) of LTA and LPT single crystals are 49% and 40% respectively. In both the cases, there is a strong absorption around 230 nm. The useful transmission extends from 230 to 1100 nm, which is essential for applications requiring blue/green light. It is an important requirement for NLO materials for possible applications. The optical absorption coefficient (α) was calculated from the transmittance using the following relation:

$$\alpha = \frac{2.303 \log (1/T)}{t}$$

where T is the transmittance and t, the thickness of the crystal. Owing to the optical energy gap, the crystal has an absorption coefficient obeying the following relation for high photon energies (h ν):

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

where A is a constant, E_g, optical band gap of the crystal, α , the optical absorption coefficient and h ν , the energy of the incident photon. The band gap of the crystals was calculated by plotting ($\alpha h\nu$)² against h ν (Fig. 3) and extrapolating the linear portion near the onset of absorption edge to the energy axis [Tauc, 1974]. The band gap energy of LTA and LPT were found to have the values of 5.0 and 4.5 eV, respectively.

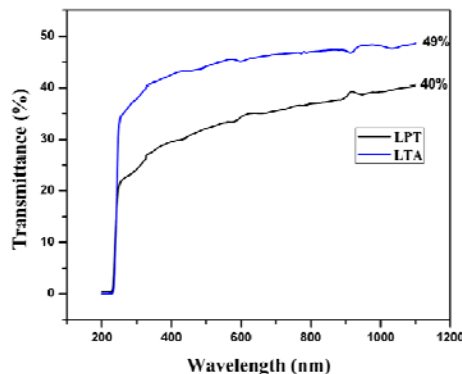


FIG. 2 TRANSMISSION SPECTRUM OF LTA AND LPT

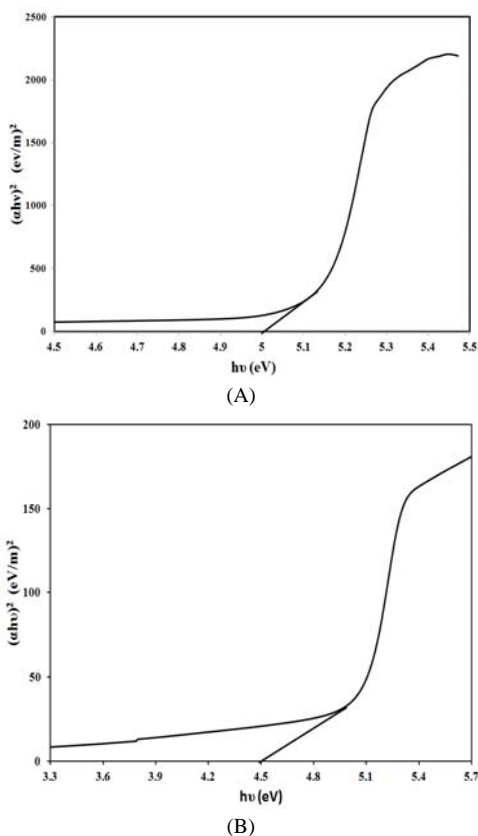


FIG. 3 TAUC'S PLOT FOR (A) LTA (B) LPT

IR Spectroscopic Studies

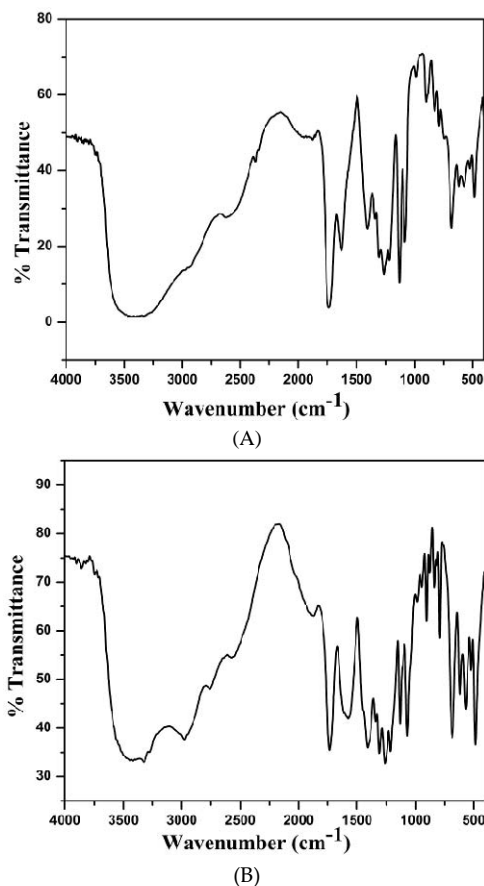


FIG. 4 IR SPECTRA OF (A) LTA (B) LPT

The IR spectra (Fig.4) of the samples were recorded in KBr phase in the frequency region of 400 to 4000 cm^{-1} , using a Jasco spectrometer (FTIR, model 410) under a resolution of 4 cm^{-1} . The recorded IR spectra were compared with the standard spectra of the functional groups [Socrates, 1980]. In the case of LTA, the strong and 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 1736 cm^{-1} indicates the presence of C=O. The weak peak at 1406 cm^{-1} is due to the combination of C-O stretching and O-H deformation. In the case of LPT, the peaks at 3323 and 2976 cm^{-1} are due to the N-H and CH_2 symmetric stretching. The presence of C=O is evident from the strong and sharp peak at 1732 cm^{-1} . The peaks at 1262 and 1214 cm^{-1} are due to the presence of carboxylic group in the tartrate anion.

Birefringence Studies

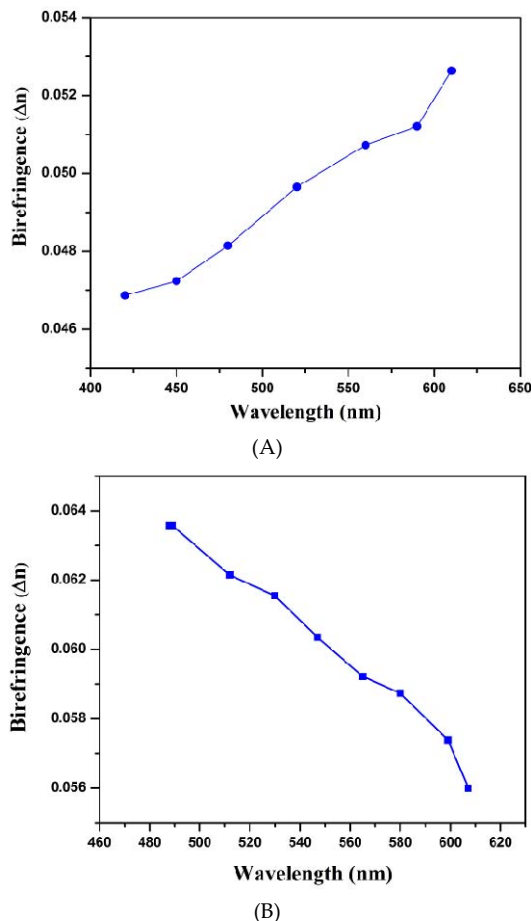


FIG. 5 GRAPH SHOWING THE VARIATION OF BIREFRINGENCE AGAINST WAVELENGTH FOR (A) LTA (B) LPT

Birefringence measurement is a precise technique to investigate the optical homogeneity in NLO crystals [Kar, Verma and Bartwal, 2009] and the value of birefringence is an important parameter to calculate phase matching angles [Fischer, Ohmer, Schunemann and Pollak, 1995].

In the present work, the modified channel spectrum (CS) method has been employed for quantitative assessment of the optical quality of the crystals of LTA and LPT grown in the MKN setup. The crystals were carefully cut and polished to get thin plates with thickness less than 1 mm. The details of the experimental setup are available elsewhere [Vijayan, Nagarajan, Slawin, Sashidharan Nair and Bhagavannarayana, 2007]. The values of the birefringence have been calculated by finding the absolute fringe order for particular wavelength and computed using the relation: $\Delta n = k\lambda/t$, where λ is the wavelength in nm, t , the thickness of the crystal in mm and k , the fringe order [Bhoopathi, Jayaramakrishnan, Ravikumar, Prasanyaa and Karthikeyan, 2012]. The graph showing the variation of birefringence (Δn) against wavelength (λ) is presented in Fig.5. It is seen that the value of birefringence of LTA crystal (0.398 mm thickness) lies between 0.0469 and 0.0526 in the wavelength range of 420-610 nm; the corresponding values for LPT being 0.0636 and 0.0560 (for a crystal of thickness 0.586 mm). Such a nominal variation of birefringence over a wide range of wavelength shows that these crystals may be useful in second harmonic generation (SHG) and polarization devices.

Photoluminescence Studies

Photoluminescence (PL) is the phenomenon in which electronic states of solids are excited by light of particular energy and the excitation energy is released as light. The photon energies reflect the variety of energy states that are present in these materials. The PL spectra were recorded using a Fluoromax-4 spectrofluorometer (HORIBA JOBIN YVON) having a 450W high pressure Xenon lamp as the excitation source. Fig. 6 shows PL emission spectrum recorded in the range of 300-450 nm with an excitation wavelength of 230 nm. It is seen that the crystals have a blue-violet fluorescence and the emission occurs at 397 and 375 nm, respectively.

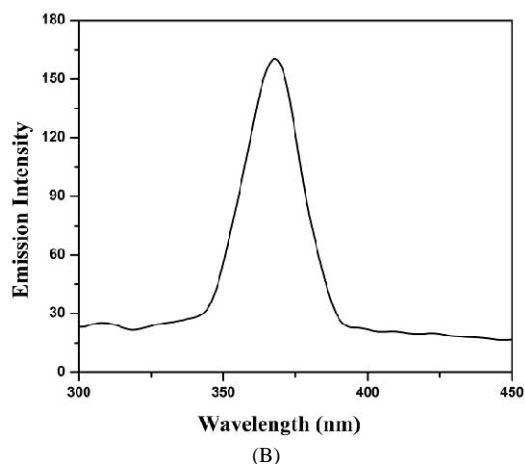
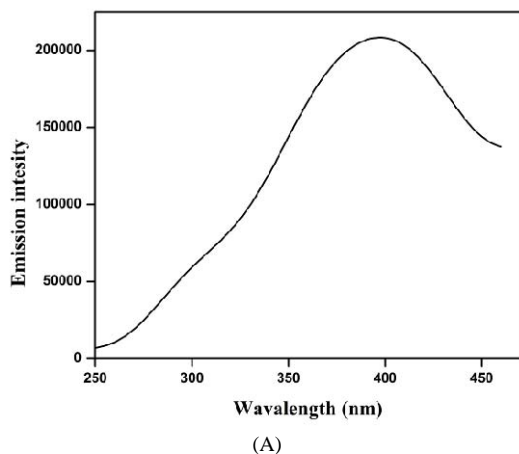


FIG. 6 EMISSION SPECTRUM OF (A) LTA (B) LPT

Second Harmonic Generation (SHG) Conversion Efficiency

The second harmonic generation (SHG) conversion efficiency was tested using a modified setup of Kurtz and Perry [Kurtz and Perry, 1968]. The fundamental beam of wavelength 1064 nm from a Q switched Nd:YAG laser was used with an input power 2.3 mJ and pulse width 10 ns, the repetition rate being 10 Hz. The output from the sample was monochromated to collect only the second harmonic ($\lambda=532$ nm), eliminating the fundamental and the intensity was measured using a photomultiplier tube. Second harmonic signals of 4.0 and 9.5 mV for LTA and LPT respectively, were obtained for an input pulse of energy 2.3 mJ. But the standard KDP crystals gave a SHG signal of 10 mV/pulse for the same input energy. Hence, it is seen that the SHG efficiency of LTA and LPT crystals are about 40% and 95% respectively, compared to that of the standard KDP crystals. The efficiency of frequency conversion will vary with the particle size and the orientation of the crystallites in the capillary tube [Porter, Ok, Bhuvanesh and Shiv Halasyamani, 2001].

Conclusions

Single crystals of L-tartaric acid and L-prolinium tartrate were grown using a home made crystal growth setup (MKN setup) and characterized by single crystal X-ray diffraction. The UV-vis-NIR spectra revealed that the crystals possess good optical transmittance in the entire visible region. Tentative assignments were made for the IR absorption peaks. The crystals showed very low variation in the value of birefringence over a wide wavelength range. PL studies showed that both the crystals had a blue-violet fluorescence. The SHG efficiency of LTA and LPT crystals were found to be about 40% and 95%

respectively, compared to that of the standard KDP crystals. The above results show that these materials may have some applications as NLO materials.

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Dr. S. Natarajan was born at Muthupettai (Tamilnadu State), India in 1949. He obtained the B.Sc. and M.Sc. degrees from the University of Madras and the Ph.D (1979) (all in Physics) from the Madurai Kamaraj University, India

Joining as a Lecturer in 1976, he was

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