Optical and electrical properties of a new organic NLO crystal: guanidinium L-monohydrogentartrate L-tartaric acid

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A new crystalline material guanidinium L-monohydrogentartrate L- tartaric acid (GuHTT) has been grown successfully. The optically nonlinear active single crystal is synthesized by slow evaporation technique. In this work, we discuss about the transmittance spectrum, optical band gap, optical constants, second harmonic generation efficiency, dielectric constant etc. in detail. The optical and electrical conductivity of the crystal have been calculated.

1. Introduction

Nonlinear optical materials have gained considerable attention due to their potential applications in high speed information processing, optical communications, optoelectronics and optical data storage [1,2] etc. Among them, organic materials are of more interest when compared to inorganic materials due to their high nonlinearities and rapid response in the electro optic effect. At present, many booming compounds are guanidinium cation based compounds. For instance, its derivatives and hydrogen bonded guanidinium complexes. The guanidinium ion is derived by protanation from the very strong base guanidine [3]. Successful examples of the recent research are compounds of guanidinum with orthoarsenic and phosphoric acids [4], guanidinium L-tartrate monohydrate [5] and zinc guanidinium sulfate [6]. Our attempts to discover a new NLO crystal with relatively large nonlinearity in our laboratory pave a way to synthesis guanidinium L-monohydrogentartrate L-tartaric acid.

2. Experimental

All materials are purchased with analytical grade and used without any pretreatments. Guanidinium carbonate and L-tartaric acid are dissolved in deionized water at a stoichiometric ratio 1:3. The prepared solution is stirred for 3 hours and allowed for slow evaporation at room temperature. Good optical quality guanidinium L-monohydrogentartrate L-tartaric acid (GuHTT) single crystal of dimension 39 x 9 x 5 mm^3 is harvested after a period of 25 days. Fig. 1(a) shows a photograph of grown single crystal. We polished the sample crystal with thickness of 2 mm to get the optical transmission spectrum and powdered the crystal to measure its second harmonic generation efficiency (SHG). The same thickness sample was used for the analysis of dielectric measurements for various frequencies and temperature using a HIOKI 3532-50 LCR HITESTER.

3. Result and discussion

The GuHTT crystal was subjected to single crystal X-ray diffraction studies using Enraf Nonius-CAD4 single crystal X-ray diffractometer with MoKα radiation (λ = 0.7107 Å) to estimate the lattice parameters values. The X-ray diffraction experiment shows that GuHTT crystal belongs to orthorhombic crystal system with non-centrosymmetric space group $P2_12_12_1$. The cell parameters of GuHTT crystal obtained are, a = 11.339 (3) Å, b = 11.146 (3) Å, c = 6.657 (3) Å and v = 841.3 Å^3. The obtained lattice parameter values are in good agreement with the reported literature values [7].

The optical transmission spectrum of the GuHTT single crystal from UV to NIR in the wavelength range from 200 to 2000 nm is recorded using Shimadzu UV-1061 UV-Vis-NIR spectrophotometer. The transmission spectrum of GuHTT crystal is shown in Fig. 1(b). Materials composed of L-tartaric acid often possess lower transparency cut off wavelength. Here, according to the experimental plot, GuHTT crystal has lower transparency cut off at 230 nm. It can be seen that the transmittance increases rapidly around 250 nm and leads to the efficient transmission (about 75 %) until 2000 nm. The dependence of optical absorption coefficient (α) on photon energy is analyzed in the high absorption region to obtain the energy gap as $(\alpha h\nu) = \beta (h\nu - E_g)^\gamma$ where β is a constant [8]. The γ is an index that characterized the type of optical transition and it is assumed to be ½ for allowed direct transition. From the functional dependence obtained for the absorption coefficient on photon energy, it may be seen

that the optical transition is a direct one. The graph between $(\alpha h\nu)^2$ and photon energy $(h\nu)$ has been plotted and shown in Fig. 2(a). The intercept obtained by the extrapolation of the linear portion of the plot gives the band gap energy of the GuHTT crystal and is estimated as 4.96 eV.
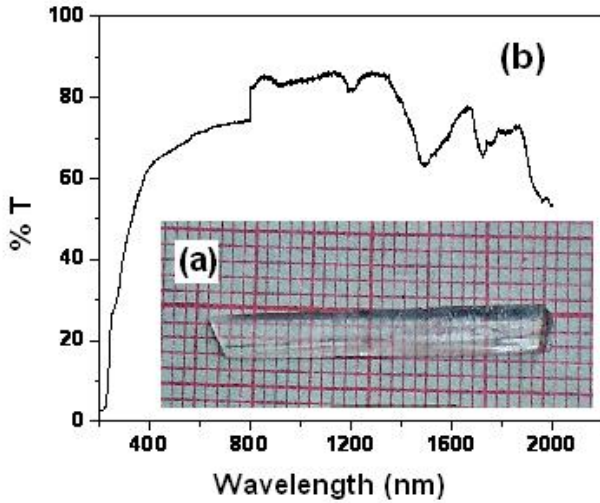

Fig. 1(a). As grown single crystal of GuHTT from aqueous solution. (b). UV-Vis-NIR transmittance spectra of GuHTT crystal.
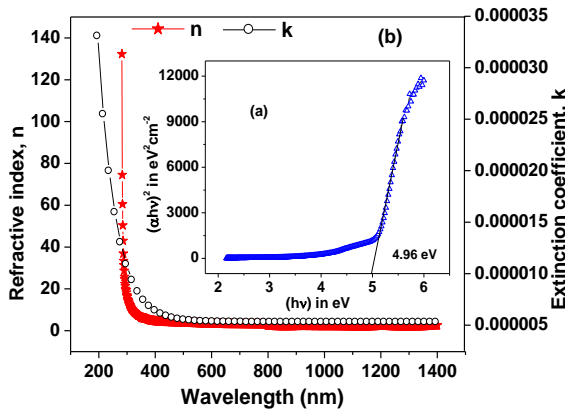

Fig. 2(a). Plot of $(\alpha h\nu)^2$ vs hv for GuHTT crystal. (b). Plot of Extinction coefficient and Refractive index vs wavelength for GuHTT crystal.

Kurtz and Perry technique [9] was used to investigate SHG of the grown crystal, which was considered as a valuable tool to evaluate homogeneity of the sample. A high intense beam of Nd: YAG laser (λ = 1064 nm) is directed in to the powder sample. The SHG efficiency is confirmed from the output of green light emission (λ = 532 nm). The SHG efficiency of GuHTT crystal is estimated as 21.7 mV for an input energy of 31 mJ/pulse, while the standard KDP crystal gives 14 mV for the same input energy. Thus, the SHG of GuHTT is 1.6 times that of standard KDP.

Optical constants, refractive index (n) and extinction coefficient (k) have also been estimated using the formula as reported earlier [10].

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2}$$

where k is related to the absorption coefficient by $k = \frac{\alpha\lambda}{4\pi}$.

The energy dependence of n and k for GuHTT crystal is shown in Fig. 2(b). The refractive indices and extinction coefficients are strongly dependent on the wavelength, especially in the UV region. The high refractive index at lower wavelength is due to the absorption of photon by the crystal. The value of refractive index and extinction coefficient remains stable above 300 nm as 2.1 and 5.26 x 10^{-6} at higher wavelength of 1200 nm.
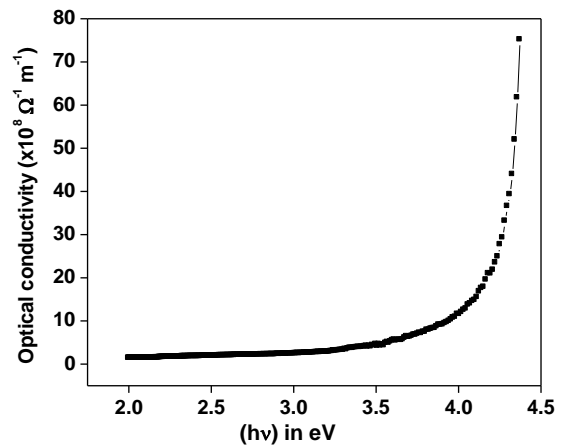

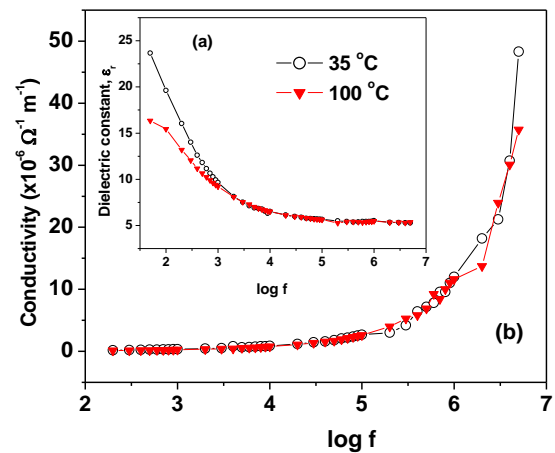Fig. 3. Plot of optical conductivity against photon energy.

Fig. 4(a). Variation of dielectric constant with frequency. (b) Plot of electrical conductivity versus frequency.

From the optical constants, the electric susceptibility (χ_e) is calculated as 0.351 at same wavelength of refractive index by using the relation [11] $\chi_e = (n^2-k^2-\varepsilon_0)/4\pi$, where ε_0 is the dielectric constant in free space. However the grown crystals associated with low dielectric loss inhibit the propagation of electromagnetic energy which aided conductivity. The optical conductivity (σ) of the crystal is calculated using the following relations [12,13], $\sigma = \alpha nc/4\pi$. The plot between the optical conductivity against photon energy is depicted in Fig. 3. The spectrum indicates that the optical conductance increases with increase of photon energy.

4. Dielectric studies

The dielectric properties of the optical materials are interconnected with electro-optic properties. The well cut and polished GuHTT crystal of dimension 9.9 x 9.4 mm^2 is used for dielectric measurements. The dielectric constant $\varepsilon_r = Ct/A\varepsilon_0$, where C is the capacitance, A is the area of cross section and t is the thickness of the crystal. The variations of dielectric constant (ε_r) as a function of frequency at different temperatures are shown in Fig. 4(a). The value of dielectric constant is high at lower frequencies and slightly decreases as frequency increases then remains very stable after 10 kHz. The value of ε_r at higher frequency is calculated as 5.4. The decrease in dielectric constant at higher frequencies is attributed to the absence of space charge polarization near the grain boundary interface [14, 15]. For a material to be a potential candidate for NLO applications, dielectric constant and dielectric loss (tan δ) must be kept as low as possible. The ac conductivity of the samples is calculated using the formula $\sigma_{ac} = \varepsilon_0\varepsilon_r\omega$ tan δ [16], where ω is the angular frequency ($\omega = 2\pi\nu$). Fig. 4(b) shows the variations of ac conductivity of GuHTT crystal with different temperatures for various frequencies. The low value of electrical conductivity is due to the decrease in mobility of the charge carriers due to ionic size, which leads to the change in electronic band structure. At higher frequency the ac conductivity increases sharply with increase of frequency (above 100 kHz). It reveals that the electrical conductivity is proportional to mobility and carrier concentrations. The conductivity and mobility of an electron can be related by $\sigma = n_d e\mu_e$, where μ_e is the mobility of electron and n_d is the number density of electron [17].

5. Conclusion

A new organic nonlinear optical single crystal of guanidinium L-monohydrogentartrate L-tartaric acid has been grown by slow evaporation technique. The grown crystals are subjected to optical and dielectric studies. The grown crystal has a wide transparency window from 230 to 2000 nm thus confirming the suitability of SHG. The optical band gap of GuHTT crystal is 4.96 eV. The powder SHG efficiency of GuHTT is about 1.6 times that of KDP.

The GuHTT crystal exhibits low dielectric constant and low dielectric loss which are most favorable properties for NLO applications. The optical and electrical conductivity of the grown crystal have been studied.

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