RESEARCH ARTICLE

Growth Aspect, Structural and Optical Properties of Unidirectional Growth of Potassium Hydrogen Maleate Single Crystal by Sankaranarayanan–Ramasamy (SR) Method

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Third order nonlinear optical semi-organic potassium hydrogen maleate single crystal was grown by Sangaranarayanan-Ramasamy (SR) method. The formation of the bonds in the crystal was confirmed by FTIR analysis. Thermal properties were analyzed, and found that the grown crystal is thermally stable up to 196°C. The transparency (74%) was assessed from the UV-Vis studies. The photo-luminescence spectral study revealed yellow emission in the wavelength region 500-650nm. The surface laser damage threshold value of the grown crystal was measured by using Nd:YAG laser. Z-scan technique was employed to observe the third-order nonlinear optical property of the grown crystal.

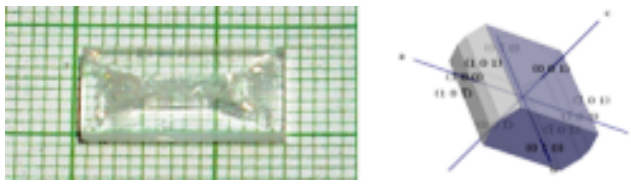
Introduction

Nonlinear optical materials are more important in the field of optical switching, optical storage data system, semi-conductors, piezoelectric applications, etc. The nonlinear is a phenomenon it leads to development of materials technology with various devices, the extensive amount of research developed on the optical crystals for second and third order nonlinear applications. The third order optical materials are used for all optical switching and sensor protection applications, concern nonlinear refraction and third order susceptibility [**1-2**]. In comparison with inorganic counterparts, organic crystals usually possess poor mechanical and thermal properties and are susceptible for damage during device processing. In order to overcome these difficulties the semi-organic materials which features the combined properties of both inorganic and organic crystals are considered suitable materials for device fabrication in semi-organic materials, polarizable organic molecules are bounded within inorganic host [**3**]. Sangaranarayanan and Ramasamy (SR) method is simplest and less sophisticated instruments. The advantages of this method are entire solution can be converted into crystal, selective orientation can be obtained and the growth rate of different planes can be measured [**4**]. In general, potassium hydroxide (KOH) is an inorganic compound that serves as a source of OH^- and highly nucleophilic anion which attacks the polar bonds in both inorganic and organic materials. At the room temperature, the OH groups are ordered and the environment about the K^+ centers is distorted with K^+ - OH^-.KOH forms a series of crystalline hydrates, namely the monohydrates $KOH.H_2O$, dihydrates $KOH.2H_2O$. Maleic acid or cis-butenedioic acid is a dicorboxylic acid with a large π-conjugation forming crystalline maleate with various organic and inorganic molecules.

Material synthesis and crystal growth

Growth of KHM crystal by conventional method

Equimolar ratio of Potassium hydroxide (5.6g, Merck 99%) and Maleic acid (11.6g, Merck 99%) were dissolved in de-ionized water and it was stirred continuously for 6 hr using a magnetic stirrer for homogeneity. The saturated solution was filtered and allowed for slow evaporation. The non-hygroscopic, free from inclusion, size up to 15 × 8 × 3 mm^3 single crystal was obtained in the period of 31 days. The photograph of as grown single crystal and morphology drawn using WinXMorph program are shown in **Fig. 1a** and **Fig. 1b**.



(a) (b)

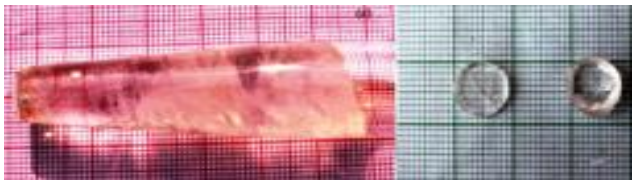
Fig. 1. Photograph of (a) as grown crystal and (b) Morphology of KHM crystal by conventional method.

Crystal growth by SR method

Experimental set up

The Sankaranaryanan and Ramasamy (SR) method consists of ring heater connected to the temperature controller for required solvent evaporation and it is positioned at the top of the growth ampoule which controls the spurious nucleations near the surface region of the solution during the entire growth period [**5**]. < 001 >

orientation of conventional grown single crystal was imposed into a glass ampoule as a seed. The saturated solution was filled into a seed loaded ampoule and temperature of top portion was maintained at 303K temperature. A good quality crystal of size 55 mm length and 0.4 mm diameter was harvested in the period of 74 days. The photograph of as grown KHM crystal, and the cut and polished crystals are shown in **Fig. 2a** and **Fig. 2b** respectively.



(a) (b)

Fig. 2. Photograph of (a) as grown crystal; (b) cut and polished KHM crystal by SR method.

Result and discussion

X-ray diffraction studies

The single crystal XRD analysis confirms that the grown crystal belongs to orthorhombic system with centrosymmetric nature having the space group Pbcm. The determined cell parameters are a = 4.6032 Å, b = 7.8518Å, c = 16.7404 Å, and α = β = γ = 90° with cell volume V = 573 Å^3. These observed crystal parameters are well matched with reported data [**6**].

FTIR analysis

FT-IR spectrum was recorded to identify the presence of functional groups in the KHM compound. The infrared spectrum (4000-400 cm^{-1}) was traced by using JASCO FTIR 410 spectrometer and the recorded spectrum is shown in **Fig. 3**. The sharp peak observed at 3419 cm^{-1} in the higher frequency range is associated with stretching of O-H group. The peak noted at 1579 cm^{-1} is due to asymmetric carboxylate ion. The presence of carboxylic groups confirmed through the stretching of C-C at 1471 cm^{-1} and C=O stretching found at 1370 cm^{-1} respectively. The intense peak observed at 1279 cm^{-1} is due to inplane bending of C-OH while C=O deformation observed at 701 cm^{-1}. The noted deformation peak for maleic acid observed at 551 cm^{-1}.

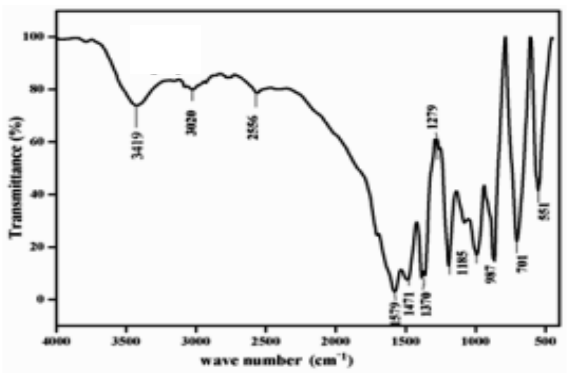


Fig. 3. FTIR spectrum of KHM crystal.

Thermal analysis

TGA and DSC studies of KHM material were carried out in the temperature range 20°C - 1000°C in nitrogen atmosphere using NETZSH STA 449F3 thermal analyzer. The thermograms traced simultaneously from TG-DSC measurements are shown in **Fig. 4**. It was observed that the compound is stable up to 196°C. The melting point was found to be 249°C with an endothermic peak. The weight loss of 28.17% is occurred in the temperature range 263°C - 310°C, due to the decomposition of carbon dioxide. The release of carbon monoxide and other volatile gases occurred in the temperature range 483°C - 515°C and the estimated weight loss is around 14.28%. The final stage of thermogram corresponds to the decomposition of residual species in the compound.

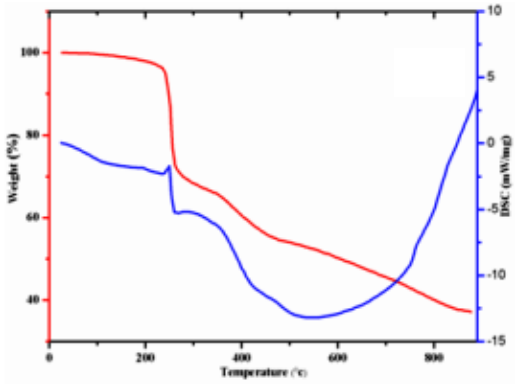


Fig. 4. TG/DSC thermogram of KHM crystal.

U V-Vis-NIR analysis

The grown KHM crystals with 1.5 mm thickness were used to record the spectra using T90+ UV/Vis spectrometer in the range 190-900 nm. The lower cut-off wave length of the grown crystal was observed at 304 nm and the transmittance value was found to be 74 %. Due to strong electronic bonding and anti-bonding transition there is no transmission of light in the UV region. The transparency of SR grown crystal showed higher value than the crystal grown by conventional method as shown in **Fig. 5**. The good optical transmittance of the crystals in the visible region suggests that the crystals can be used various optical and electronic applications.

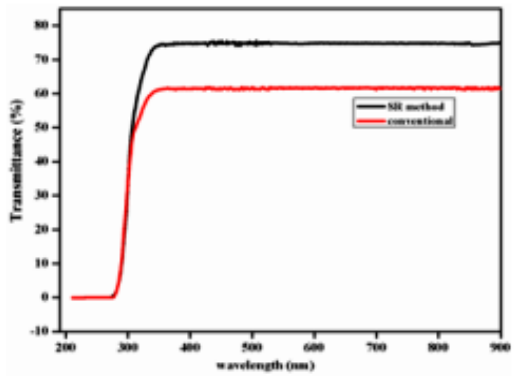


Fig. 5. UV-Vis transmittance spectra.

Photoluminescence studies

The KHM crystal was excited at 290 nm and the emission spectrum was recorded at room temperature in the range 500-650 nm and the sharp emission peak was observed at 585 nm as shown in **Fig. 6**. The crystal found to emit yellow light and hence it may be used as a light emitting material for LED application [**7**].

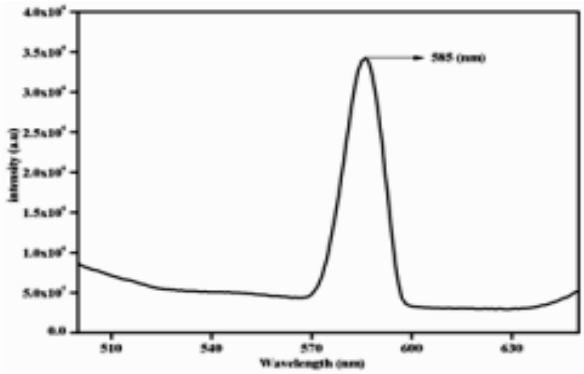


Fig. 6. Emission spectrum of KHM crystal.

Laser damage threshold measurement

Laser damage threshold of KHM crystal was measured by using Nd:YAG laser system, which delivered laser pulses at 1064 nm. The power density was calculated by using the relation [**8**],

$$P_{(d)} = E/\tau\pi r^2$$

where E is the input energy in mJ, τ is the pulse width and r is the radius of the beam. The multiple shot laser damage threshold energy density was estimated and found to be 2.73 GW/cm^2.

Z-scan studies

Third order nonlinear properties of the material can be ascertained by using Z-scan technique which provides magnitude and sign of the nonlinearity [**9**]. 1 mm thick grown crystal sample was fixed on a holder. In this measurement the crystal was moved far away from the focus (-Z) to the focus (Z = 0) and then moved to the same focus (+Z), the corresponding transmitted intensity of the sample was measured by photo-detector and digital photo meter. The crystal can be induced by the laser spectrum according to the materials nature; it shows either converging (self-focusing) or diverging (self-de-focusing) phenomena. From the closed aperture Z-scan mode the transmittance graph was appeared with a peak (p) followed by a valley (v) which implies the occurance of the self-de-focusing effect. The laser beam width was broad at the aperture, thus the transmittance was decreased. The change in transmittance between the peak and valley in Z-scan is $\Delta T_{p-v} = T_p - T_v$ where T_p and T_v are the normalized peak and valley transmittances as depicted in **Fig. 7**. From the open aperture Z-scan mode, the intensity of transmittance was found high at the focal point (Z=0) which is called saturable absorption as shown in **Fig. 8**. From the obtained Z-scan data, the difference between the peak and valley transmittances (ΔT_{p-v}) can be calculated. By employing closed aperture and open aperture Z scan data, nonlinear refractive index (n_2) and nonlinear absorption coefficient (β) can be estimated [**10-11**]. The effective third-order nonlinear refractive index (n_2) of grown crystal was found to be 8.18 × 10^{-8} cm^2/W and the nonlinear absorption coefficient (β) value was calculated as 0.37 × 10^{-4} cm/W. The nonlinear optical susceptibility (χ^3) was estimated to be 8.67 × 10^{-6} e.s.u.

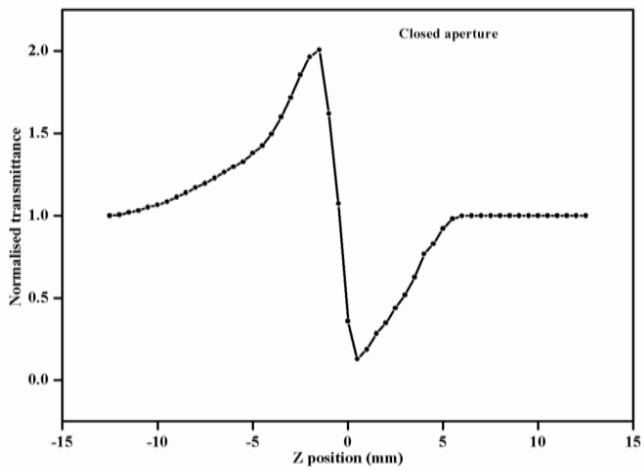


Fig. 7. Closed aperture mode Z-scan plot of KHM crystal.

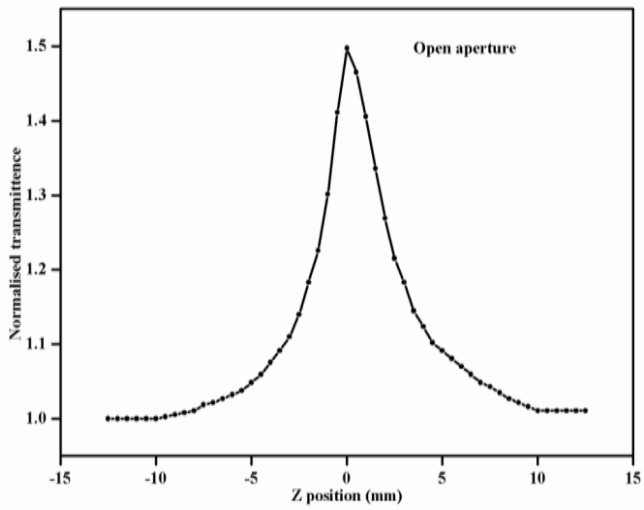


Fig. 8. Open aperture mode Z-scan plot of KHM crystal.

Conclusions

Unidirectional KHM crystal was grown by SR method with specific orientation <001>. The KHM crystal belongs to orthorhombic system with centrosymmetric space group Pbcm. The functional groups present in the crystal were identified from the FTIR analysis. The title compound is stable up to 196°C. The lower cutoff wave length (304 nm) showed a good transparency. Photoluminescence spectra reveal that the crystal shows the emission at 585 nm. The LDT value was found to be 2.73 GW/cm^2. Open aperture and closed aperture. Z-scan studies revealed the nonlinearity of the KHM crystal and open aperture analysis depicted the saturable absorption.

Keywords

Semi-organic compounds, crystal growth, SR method, TG-DSC, photoluminescence, Z-scan measurement.

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