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Growth, Thermal, Dielectric, Linear and Nonlinear Optical Properties of L-Malic Acid Doped KDP Single Crystals

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ABSTRACT

Growth of bulk nonlinear optical (NLO) single crystals gained new significant with the advent of solid-state laser sources for opto-electronic applications. An optically transparent crystal of L-Malic acid doped KDP (LMKDP) potassium dihydrogen phosphate (KDP) has been grown from aqueous solution slow evaporation at room temperature. The crystallinity of the LMKDP crystals has been studied by powder XRD analysis. FTIR spectral analysis confirms the functional group in the synthesized compound. The second harmonic generation (SHG) efficiency was measured by using Kurtz powder technique. The dielectric behavior of grown crystals has been studied in the frequency range from 50 Hz to 50MHz. UV–visible absorption spectrum was recorded to study the optical transparency of grown crystal. Thermogravimetric analysis (TG) and differential thermal analysis (DTA) were used to study the thermal properties of the grown crystal.

Keywords: PXRD, FT-IR, FT-Raman, NLO studies, dielectric studies, UV-visible, TGA/DTA.

I. INTRODUCTION

In this modern era of information and technology with fast and high data storage capacity, data retrieving, processing and transmission demands the search of new NLO materials with unique physical properties. Hence, there is a great demand for synthesize the new NLO materials and grow their single crystals. KDP is among the most widely used NLO material. Potassium dihydrogen phosphate (KDP) crystals have created considerable interest because of its Piezo-electric, electrooptic, nonlinear optical properties and its extensive application in X-ray monochromators [1-3]. In addition to their large NLO response, the advantage of organic materials is that they offer high degree of synthetic flexibility to tailor their optical properties through the structural modification and they exhibit high laser damage threshold [4]. In single crystals form, the NLO materials display huge optical nonlinearity, which is of great interest for telecommunication, optical information processing and high optical data storage, etc., [5]. Many methods have been tried to improve the NLO properties of KDP crystal. With the aim of improving the second harmonic generation (SHG) efficiency of KDP, researchers have attempted to modify KDP crystals by doping different types of impurities. The present work, L-Malic acid of 0.2 molar percentages has been doped with KDP material. The grown L-Malic acid doped KDP (LMKDP) crystals were characterized by PXRD, FTIR, FT-RAMAN, NLO, Dielectric studies.

II. EXPERIMENTAL PROCEDURE

In the present work, L-Malic acid of 0.2 molar percentages has been doped with KDP material. The solution was thoroughly stirred for homogenization and then filtered into a borosil beaker using whatmann filter paper. It was porously sealed and placed in a dust free atmosphere for slow evaporation technique at room temperature. Single colorless and optically transparent crystals were harvested within 30 days.

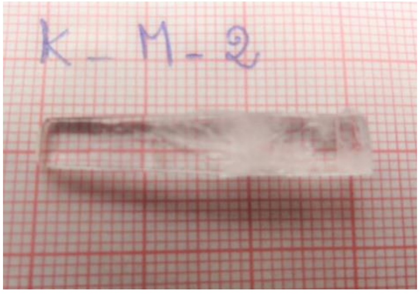

Figure 1. As grown single crystal of LMKDP

III. RESULTS AND DISSCUSION

3.1 Powder X-ray Diffraction Analysis.

Powder X-ray diffraction technique is a powerful tool to analyze the crystalline nature of materials. Powder X-ray diffraction analysis was carried out by using XPERTPRO X-Ray diffractometer with Cukα radiation (λ=1.5406 Å). The cell parameter values for LMKDP are a=b=0.634Å, c=0.524Å with the angles α=β=γ = 90° suggested that the LMKDP crystal crystallizes in tetragonal structure. The samples were scanned over the range 10 - 70°. The sharp and well-defined peaks at specific 2θ values indicate the high crystalline nature of the crystal. Powder XRD graph has been shown in the Figure 1.

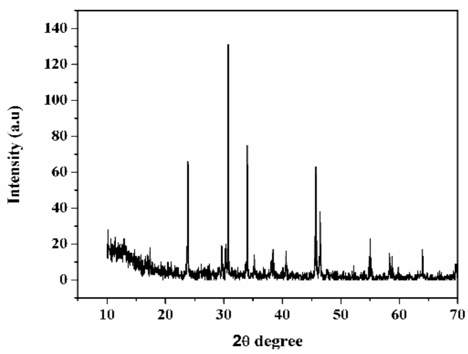

Figure 2. Powder XRD pattern of LMKDP crystals.

3.2 FT-IR Analysis.

FT-IR and FT-Raman spectra of LMKDP crystal were recorded and the spectrum of LMKDP crystals are shown in Fig.2. An intense band of strong absorption around 1217cm^{-1} and protonated by the carboxyl group (COOH) gives hydrogen bonding [6], which is attributed to O-H stretching vibration for the confirmative group of water on hydration. The functional groups of the LMKDP crystals have been identified by the spectrum. In the high frequency region of IR spectra, the sharp peaks observed at 618 cm^{-1} are described to PO_4 stretching vibration in the crystal. The O-H deformation and P=O stretching will be observed in the frequency of 1392 cm^{-1}. In FTIR the absorption band at 1392cm^{-1} is due to P-O-H bending vibration in the LMKDP.

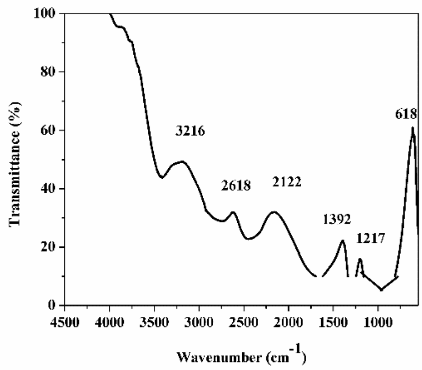

Figure 3. FT-IR spectral analysis of LMKDP Crystal.

3.3 SHG Analysis

Nonlinear optical measurements were carried out by using Kurtz powder technique. In order to confirmed the NLO property, the grown crystals were powdered and subjected to Kurtz and Perry powder technique, which is a powerful tool for initial screening of materials for SHG [7]. A Q-switched Nd: YAG laser beam of 1064 nm wavelength with 1.9 mJ/pulse input power, 8 ns pulse width and repetition rate 10Hz was used to estimate SHG efficiency of the grown LMKDP crystals. KDP crystalline powder was the reference material, the output of SHG range was compared and found that the SHG conversion efficiency of LMKDP is 1.4 times greater than that of reference KDP.

3.4 Dielectric Studies

Every material has a unique set of electrical characteristics that are dependent on its dielectric properties. The variation of dielectric constant and dielectric loss of the sample with frequency is studied at room temperature by H10K1 3532 LCR HITESTER in the frequency range 50 Hz to 50 MHz and is shown in Fig. 4 and Fig. 5. The high value of dielectric constant at high frequency may be due to the presence of all the four polarizations namely space charge, orientation, electronic and ionic. The dielectric characteristic of a crystal is determined by the dielectric constant and dielectric loss. The dielectric constant (ε ') and dielectric loss (ε '') of the sample were calculated using the following equation [8]:

$$\varepsilon' = c^*t/\varepsilon_o A \quad \text{-------------}1$$
$$\varepsilon'' = \varepsilon'/Q \quad \text{---------------}2$$

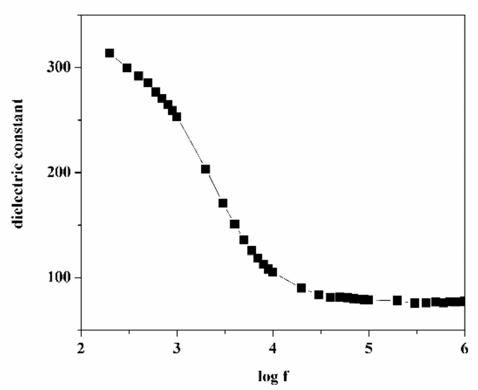

Figure 4. Dielectric constant Vs Log f of LMADP Crystal

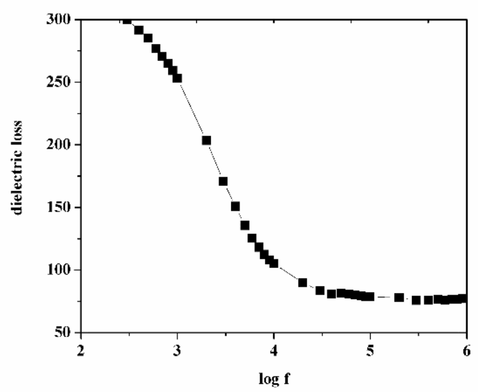

Figure 5. Dielectric loss Vs Log f of LMADP Crystal.

3.5 Optical Absorption Studies

The UV-Vis spectrum of LMKDP crystals were recorded by using Perkin Elmer UV-Vis spectrometer (Model: Lambda 35) in the wavelength range of 200-900 nm. Optical transparency range of single crystals plays a very important role in optical technology [9]. UV-Visible techniques are helpful in the investigation of NLO materials making it possible to check, both NLO responses and spectroscopic absorbance in the appropriate wavelength range [10]. The lower cutoff (286 nm) wavelengths are very important properties for the grown crystals [11]. This is one of the most desirable properties of the crystals for the device fabrication. The band gap of the crystal was evaluated by extrapolation of the linear part of the graph and found to be 4.98 eV

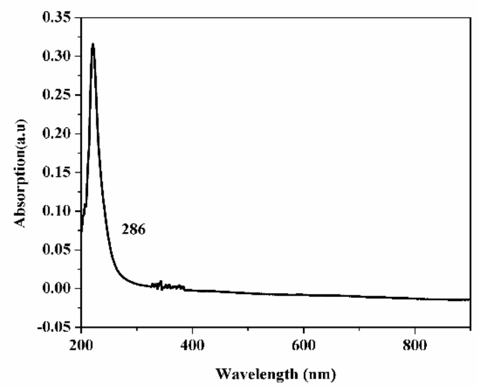

Figure 6. UV-vis absorption of LMADP Crystal.

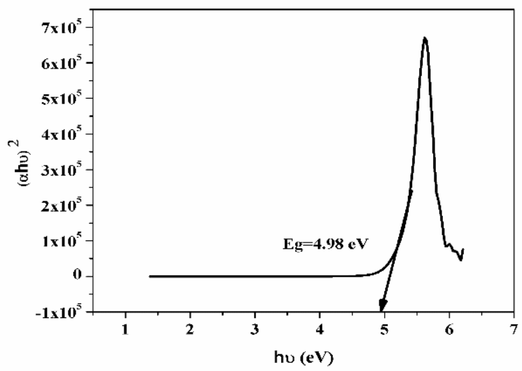

Figure 7. UV-vis band gap of LMADP Crystal.

3.6 Thermal Analysis

The thermal stability of the crystal is a very important factor for potential application. The thermal stability of the title compound was identified by thermogravimetric (TGA) and differential thermal analysis (DTA) studies simultaneously. Thermogravimetric analysis shows that LMKDP is very stable up to 199 °C and the weight loss starts at this temperature. It is observed from DTA thermogram that an endothermic event begins at 234°C and then sharp peak appears at 234°C and the second peak appears at 269°C. Good crystalline nature of the title compound is clearly noticeable from the sharpness of the endothermic peak. The sharp endothermic peak 234°C at is due to the decomposition of the sample desired by its DTA analysis and it coincides with the TG curve [12].

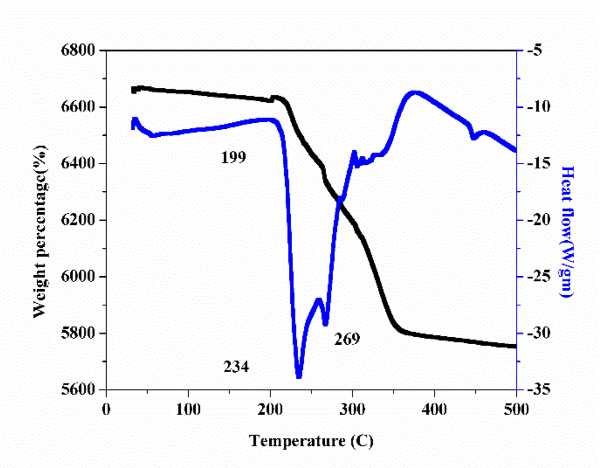

Figure 8. TG-DTA spectrum of LMADP Crystal.

3.7 Photoluminescence Studies

The photoluminescence (PL) intensity majorly depends on the excitation energy as well as on the intensity of the incident beam. In present analysis the LMKDP crystal has been photo-excited with an excitation wavelength of 361 nm and the EM spectrum was recorded with no delay in the range of 350 to 450 nm. Two emission peaks were observed in the spectrum at 361nm and 426 nm respectively. The results indicate that LMADP single crystal observed violet and blue fluorescence spectrum.

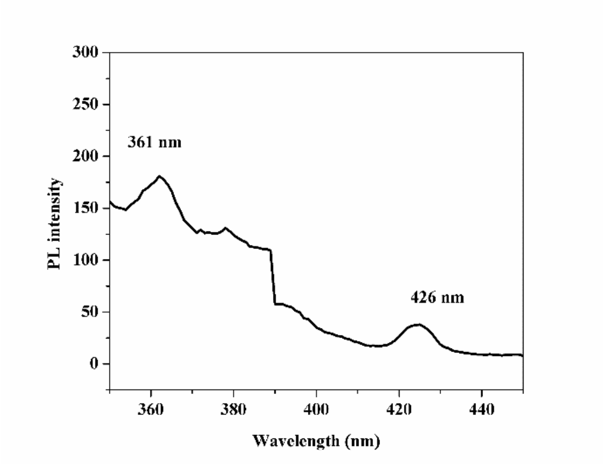

Figure 9. Photoluminescence Emission spectra of LMKDP crystal

IV. SUMMARY

The good-quality single crystals of LMKDP were successfully grown by slow evaporation method at room temperature. XRD studies reveal the tetragonal structure of the grown crystals. FT-IR spectrum confirm the presence of functional group in the grown crystal. The UV–Vis spectra showed that the crystals had a wide optical window, no absorbance and good optical transmittance in the entire visible region. The nonlinear optical studies confirm the SHG property of the grown crystal. The SHG efficiency of LMKDP is 1.4 times greater than that of reference KDP. The electrical property of the grown crystal was observed by the dielectric studies. TGA and DTA thermogram revealed the thermal stability of the materials. Photoluminescence studies show the excitation of LMKDP falls in violet and red fluorescence spectrum.

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