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Enhancement of Mechanical, Electrical, Optical and Structural properties based on Potassium Hexacyano Ferrate single crystals

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ABSTRACT: Single crystal of potassium hexacyano ferrate (PHF) have been successfully grown by the slow evaporation technique at room temperature which has dimensions 13 ×10 ×3 mm3. The grown crystal was characterized structurally, optically, thermally, mechanically and electrically. Lattice parameters of the grown crystal were determined by X-ray diffraction analysis. The functional groups present in the crystal were identified using Fourier Transform Infrared spectral analysis. UV-Vis-NIR spectrum was recorded to estimate the UV cut-off wavelength and transparency. Second harmonic generation study confirms the NLO property. Thermal stability and decomposition of the crystal has been studied by TG/DTA analysis. Microhardness measurement indicates that the grown crystal exhibits normal indentation size effect. The frequency and temperature dependence of dielectric constant and dielectric loss were also studied.

Keywords: Single crystal XRD, powder XRD analysis, FT-IR, UV-Vis-NIR spectrum, thermal analysis, microhardness and dielectric properties.

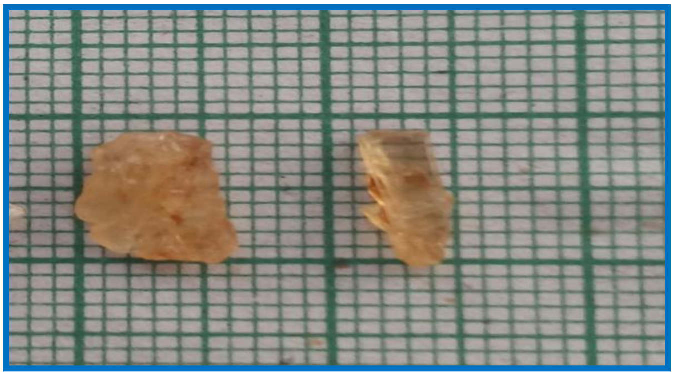
1 Introduction

In last few decades, the researchers are interested in non- linear optical material, due to their application in the field as optical communication, signal processing instrumentation [1]. The organic NLO material plays an important role in second harmonic generation, electro optic modulation [2, 3]. Extremely large number of organic compounds with non localized - electron system large dipole moment has been synthesized to realize the nonlinear susceptibilities [4, 5]. Many investigations are being carried out to synthesize new material. With large second order optical nonlinearities in order to satisfy, day to day technological demands [6-9]. In search of new frequency conversion materials, recent interest focused on inorganic materials due to their NLO properties [10-12]. From the literature survey investigation are focused on potassium hexacyano ferrate material due to its various desired applications.

2. Experimental Procedure

2.1. Synthesis of PHF single crystal

Saturated solution of on potassium hexacyano ferrate $K_4Fe(CN)_6{\cdot}3H_2O$ (PHF) was prepared at room temperature. The solution was continuously stirring for 4 hours at 35°C then the solution was filtered using Whatman filter paper and transferred into a petri dish. They are allowed to evaporate slowly in room temperature. The PHF single crystals of average size 13×10×3 mm3 were harvested after the 18 days as



shown in figure 1.

Figure 1 synthesis of PHF single crystal

2.2 Characterization

Characterization of potassium hexacyano ferrate single crystal such as structural, mechanical, optical, thermal has been carried out in this present investigation. The cell parameters were measured by single crystal XRD studies. Mechanical behavior was analyzed using Vickers micro hardness test. The NLO property of the grown crystal was confirmed by Kurtz and ferry powder SHG method [13]. Dielectric constant and dielectric loss measurements were carried out at different temperatures and frequencies.

3. Results and Discussion

3.1. Single Crystal X-Ray Diffraction Studies

A fine quality PHF crystal was kept on a Xcalibur Eos diffractometer at 293(2) K. Single crystal X-ray diffraction analysis of these single crystal have been carried out and the unit cell parameters are given in Table 1.

Table 1. The lattice parameter of grown PHF Crystal

Lattice parameter	Obtained values
Crystal system	Triclinic
Space group	P
a (Å)	7.401
b (Å)	7.487
c (Å)	13.436
α	96.25°
Β	98°
ɤ	90.85°
V(Å3)	733

3.2. FT-IR Studies

The FT-IR spectral study is used to identify the different functional groups present in the compound of the grown crystal. The FT-IR spectrum of PHF crystal was recorded in the IR region 400–4000 cm-1 from KBr pellets on a Perkin Elmer FT-IR spectrometer as shown in Fig.2.

The band 3439cm-1 has been assigned to the NH– symmetric and asymmetric stretch. The 2506, 2292 cm-1 is characteristic of OH stretch. The other peak at 2118 cm-1 is assigned to C=C stretch. The peak at 1822 cm-1 represents the C=O symmetric & asymmetric stretch, and the peak at1631 cm-1 represents C=O stretching. The peak at 1390 cm-1 is assigned to CH3 C-H bending. The peak at 1103 cm-1 is assigned to C-O stretching. The very strong peak observed at 791 cm-1 is attributed vibration of the C-H bend. The peak at 593 cm-1 is assigned to C-Br stretching. The predominant peaks appeared may be due to the vibrations involved in metal atoms in the crystal [14].

3.3. Linear Optical Studies

The linear optical studies of potassium hexacyano ferrate (PHF) were carried out using UV-VIS NIR spectrum

From the UV-Vis spectral study, a transmission coefficient is determined. The optical transmission spectrum of PHF crystal was recorded in the range 200-1000 nm. The recorded spectrum is shown in fig.2. From the optical spectra the UV cut off wavelength is 306 nm and the transmittance percentage is 97 %.

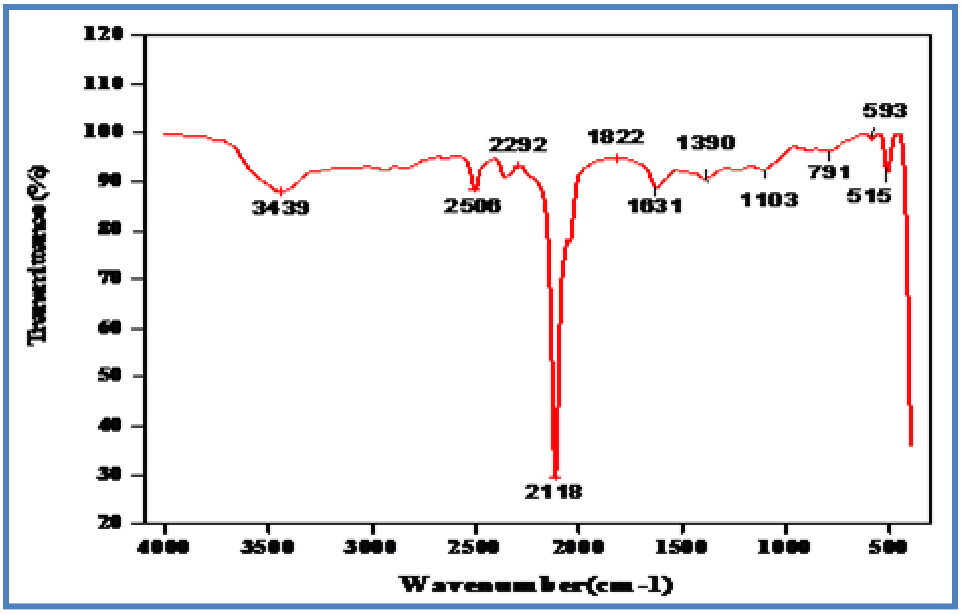


Fig.2. FT-IR Spectrum of pure PHF crystal

The high transmission in the entire visible region and short UV-cutoff wavelength evident that the grown crystal PHF to be a potential candidate for non- linear optical applications.

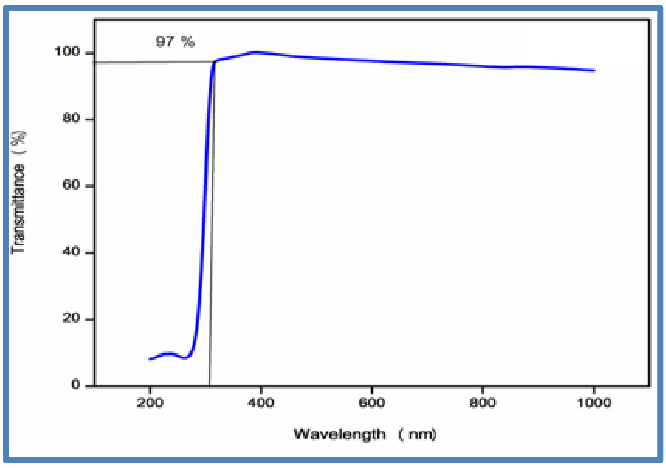


Fig.2. UV-Vis transmittance spectrum of PHF crystal

3.4 Thermal Analysis

In order to study the thermal stability of the grown crystal, thermogravimetric (TG) and differential thermal analysis (DTA) has been carried out using a Seiko TG-DTA 6200 model thermal analyzer in an inert nitrogen atmosphere. A powdered sample of about 15 mg was used for the analysis in the temperature range of 30–800°C with a heating rate of 20°C/minute. The TG-DTA pattern recorded for the PHF crystal is as shown in Fig.3.

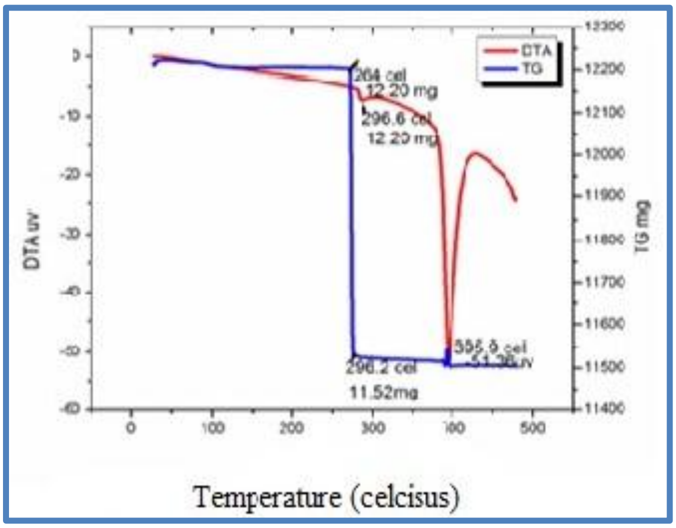


Fig. 3 Thermal Analysis (TG-DTA) PHF Crystal

From the TG curve, there is a weight loss at 296.2°C. The sharp endothermic peak around 395.9°C is assigned to the melting point of the PHF. The exothermic peaks are good agreement with TG trace.

3.5 Non-Linear Optical Property Studies

The powdered sample prepared from the grown crystal was subjected to the SHG test by Kurtz and Perry powder technique and the efficiency of the energy (frequency) conversion is confirmed by the emission of green light. The KDP sample was used as the reference material. The SHG efficiency estimated for both the crystals are given in the Table. 3

Table 3 SHG Efficiency of PHF Crystal

Sample	Output	SHG efficiency
KDP	8.8	0.14
PHF crystal	1.2	

It is observed from Table 3 the SHG efficiency of a mixed crystal, when compared with KDP it is low SHG efficiency. NLO efficiency of PHF crystal has found to be 14% when compared to standard KDP. SHG efficiency has to be increased for enhancing the NLO property for future work.

3.6 Dielectric Studies

Dielectric is an important property, which its ability to support an electrostatic field while dissipating minimal energy in the form of heat. The variation of dielectric constant and dielectric loss with a log of frequency for the crystal PHF different temperatures have been recorded as shown in Fig.4a & 4b. Figures show that the dielectric constant and the dielectric loss are both inversely proportional to the applied frequency at low-frequency range.

At 85°C, the dielectric constant of PHF has high value in the low-frequency range. The variation in the dielectric loss with a frequency within the temperature range 40°C to 85°C is shown in Fig.4a. At low temperature (40°C) the dielectric loss has a high value; at high temperature (85°C) the dielectric loss has a low value. At 55°C, the dielectric loss of PHF has high value in the low-frequency range (ie.50 Hz). The low value of dielectric loss at high frequency for PHF crystal suggests that the sample possess enhanced optical quality with fewer defects and this parameter is of vital importance for NLO materials in their application [15]

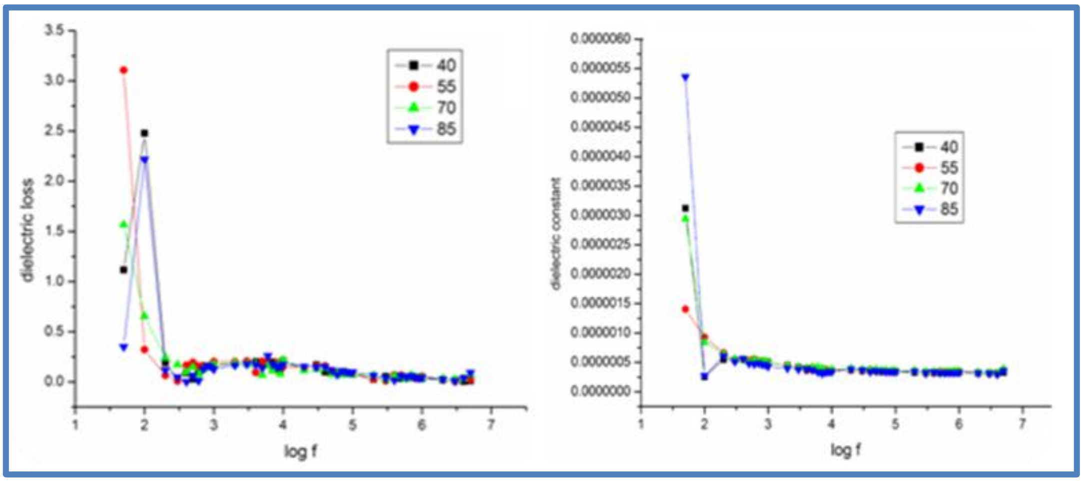


Fig.4a. Log f vs. dielectric loss of PHF **Fig.4b.** Log f vs. dielectric constant of PHF

3.7 Microhardness Studies

Micro hardness testing is one of the best methods for an understanding the mechanical properties of materials, the transparent polished crystal free from cracks was selected for hardness measurement .the indentation, where made soon the felt surface with the load ranging from 25gm to 100gm using Shimadzu make-model-HMV_2 filed with Vickers pyramidal indenter and attached to an incident light microscope. The indentation time was kept as 5s for all the loads. The Vickers hardness (Hv) was calculated from the relation.

Hv = 1.8544p/ d2 kg/mm2

Where p is the applied load in kg and d is the average length in mm and Hv is in kg/mm2 the variation of Vickers and MOHS hardness value with increasing load decreasing as shown in Fig.5a.It is observed from the graph, that the hardness value increases with increase in the applied load. Above 50gm, the hardness suddenly decreases, as cracks developed in the material. This may due to the relax of internal stresses generated locally by indentation [16].

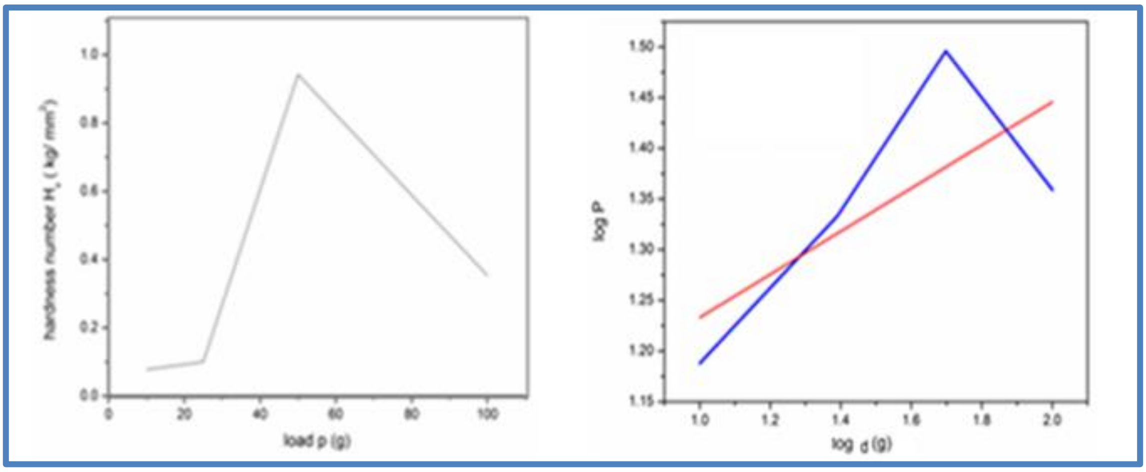


Fig.5a. Variation of HV vs. Load of PHF **crystal** **Fig.5b.**The plot of log p vs.log d of PHF crystal

Meyer's index number was calculated from Meyer's law, which relates the load and indentation diagonal length as the p = K x d n, where k is the material constant and n is Meyer's index. In order to find the value of 'n,' a graph of load p against load d is platted as shown in Fig.5b. From the slope of Meyer's index numbers 'n' was calculator too be 0.212. According to on its criteria the value of 'n' lies between 1 and 1.6 of hard material and is greater than 1.6 for hard material [17]. The 'n' values calculated in the percent study is <1.6 suggesting that the potassium hexacyano ferrate III crystal belongs category of hard material.

4. Conclusion

Synthesis, growth and characteristics of PHF crystal were studied. The PHF crystal was grown from aqueous solution by a low evaporation method. From the single crystal, XRD reveals PHF crystal belongs to Triclinic and possesses P space group. The functional groups are confirmed by FTIR analysis. The optical transmission spectrum has been recorded in the wavelength region between 200 nm and 1000 nm. From the NLO study was carried out and it reveals the PHF crystal has 0.14 times NLO efficiency than that of KDP. The grown crystal was thermally stable up to 296° C. The grown crystal shows excellent electrical, dielectric constant and mechanical properties.

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Competing Interests:

The authors declare that they have no competing interests.

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