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Growth and Characterization of Barium doped Potassium Hydrogen Phthalate Single Crystal

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ABSTRACT
The Non Linear Optical materials have acquired new significance with the advent of a large number of devices utilizing solid state Laser sources. Potassium Hydrogen Phthalate one of the Non Linear Optical material having superior non linear optical properties has been exploited for variety of application. In the present work, KHP single crystals were grown by slow evaporation technique with Barium metal ion as a dopant. The grown crystals were subjected to powder XRD analysis and the result shows that the Ba^{2+} ions does not alter the crystal structure, but it enter into the crystal lattice of pure KHP. The optical transparency of the grown crystal was studied by UV-Visible spectroscopy, the molecular structure was confirmed by FTIR analysis and its thermal stability by TG/DTA analysis. The improved SHG efficiency of barium doped Potassium Hydrogen Phthalate crystal could enhance the nonlinearity behaviour. In addition to this, the electrical parameter such as dielectric constant was studied in detail.

***Keywords* -** Crystal Growth, Dielectric constant, FTIR, KHP, SHG, Thermal studies, UV, XRD.

I. INTRODUCTION

The search for new conversion materials for various device applications has led to the discovery of many organic, inorganic and semi organic Non Linear Optical (NLO) materials. To improve the properties of the NLO materials, the semi-organic crystals have attracted considerable interest due to their electro-optic processes [1, 2]. Potassium Hydrogen Phthalate (KHP) with the chemical unit formulae $K(C_6H_4COOH\text{-}COO)$ is a semi-organic salt that belongs to the alkali acid phthalate series has an orthorhombic symmetry with the space group Pca21 and shows a perfect cleavage along (*010*) plane. KHP crystal plays an important role in the field of NLO and is used in quantitative X-ray Analysis [3-5]. Its higher chemical stability and economic viability with good kinetic growth properties have made to pay attention on it in past decades. The aim of the present work is to grow and to explain the effect of Ba^{2+} ion on thermal, optical and electrical properties of KHP.

II. EXPERIMENTAL

The barium doped KHP crystals were grown by the slow evaporation solution growth method. The KHP salt was dissolved in deionised water. The solution of KHP salt was prepared in a slightly under saturation condition at 30 ˚C. The solution was stirred well for three hours constantly using magnetic stirrer. With this solution, 1 mole percent of $BaCl_2$ was added as dopant, and then stirred well for another three hours. Then the solution was filtered using a filter paper. The solutions were kept undisturbed by covering with a thick sheet of paper for controlled slow evaporation.

Transparent, good quality barium doped single crystals of KHP were collected after 20-25 days. The photographs of grown crystals are shown in Fig. 1. The grown crystals were subjected to different characterization such as Powder XRD, UV-visible spectral studies, SHG efficiency and dielectric study.

Fig. 1. Photograph of 1 mole % $BaCl_2$ doped KHP.

III. RESULTS AND DISCUSSIONS

POWDER XRD ANALYSIS

The grown crystals were subjected to powder XRD analysis using *Philips X'pert Pro* with Cu Kα1 radiation (λ=1.54056 Å) for the phase analysis. The crystal belong to orthorhombic system and its cell parameters are a= 9.674 Å, b=13.291 Å, c=6.516 Å, V=837.8086 Å^3. The cell parameters were good agreement with the reported values from the database of International centre for Diffraction Data (ICDD) [6]. The powder XRD patterns for $BaCl_2$ doped KHP crystals is shown in Fig. 2 and it consist of peaks corresponds to KHP and no other peaks of other phase or element are detected for $BaCl_2$ doped KHP within the detection limit of the instrument. This is the evidence for the incorporation of Ba^{2+} ion into KHP and the doping does not changed the crystallinity of the material.

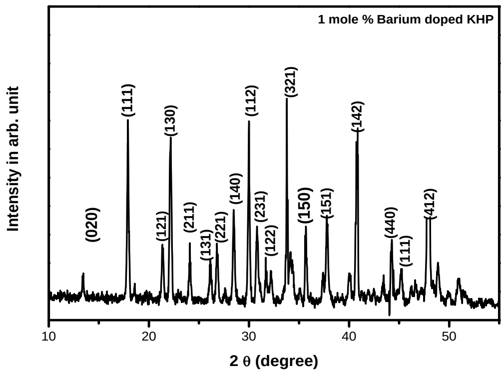

Fig. 2. Powder XRD pattern for $BaCl_2$ doped KHP.

UV –VIS SPECTRAL STUDIES

The UV –Vis spectral study is a special technique tool to determine the transparency, which is one of the requirements for the material to be optically active [7]. Optical transmission spectrum of BaCl2 doped KHP single crystals were recorded in the range 200-1600 nm using *Perkin Elmer mode Lambda-35* spectrophotometer. The recorded spectra are shown in Fig. 3. The crystal has sufficient transmission in the entire region which is an important requirement for a material to be optically active. The high transmission in the entire visible region and short UV cut off wavelength = 393 nm facilitates the grown crystal to be a potential nonlinear optical material for second harmonic generation of Nd:YAG laser [8] and the band gap energy of the sample was found to be 3.155 eV.

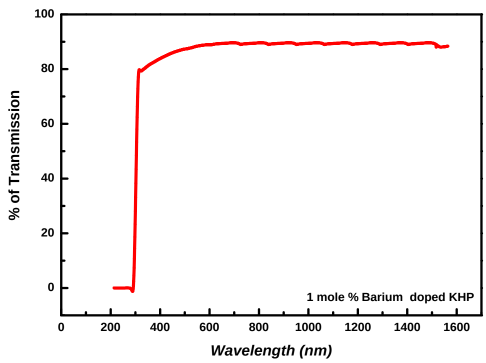

Fig. 3. The UV-Vis spectrum of $BaCl_2$ doped KHP.

FTIR SPECTRAL ANALYSIS

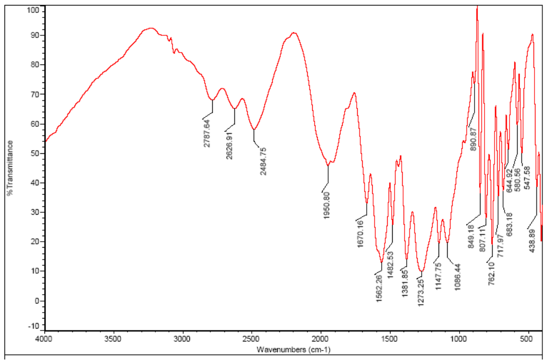

Fig. 4. The FTIR spectrum of $BaCl_2$ doped KHP.

Fig. 4 shows the FTIR spectra of $BaCl_2$ doped KHP single crystal in the range of 400-4000 cm^{-1}. A very slight shift in some of the characteristic vibrational frequencies is obtained and this is due to lattice strain produced as a result of doping. Also the presence of the functional groups in the compound has been confirmed by FTIR analysis.

TG/DT ANALYSIS

The TG/ DTA curves for $BaCl_2$ doped KHP crystal is shown in Fig. 5. It is noticed that there is a strong endothermic peak at 290.32 ˚C reveals the decomposition of doped KHP structure which is closer to the melting point of pure KHP (290.74˚C). It shows that the doping does not affect the thermal stability of the sample. There is an endothermic peak is observed at 505.01 ˚C, which shows the bulk decomposition of the compound at this temperature.

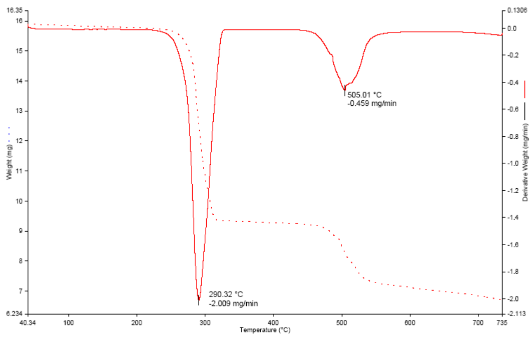

Fig. 5. The TG/DTA curve of $BaCl_2$ doped KHP.

SHG EFFICIENCY

The NLO property of the crystal was confirmed by the Kurtz and Perry powder technique. The transmitted fundamental wave was passed over a monochromator which separates 532 nm (second harmonic signal) from 1064 nm and absorbed by a $CuSO_4$ solution which removes the 1064 nm light. The green light was detected by a photomultiplier tube and displayed on a storage oscilloscope.

TABLE 1: SHG signals energy output.

Input P (J)	KDP ref (mJ)	KHP Pure (mJ)	doped KHP (mJ)
0.68	8.8	3.2	3.9

The powder SHG efficiency of $BaCl_2$ doped KHP crystal is compared with KDP and it was found that the SHG efficiency of $BaCl_2$ doped KHP was 0.44 times that of KDP and 1.22 times that of pure KHP (TABLE 1).

DIELECTRIC STUDY

Selected samples of $BaCl_2$ doped KHP crystal was polished in proper size and for good electrical contact opposite faces of the crystals were coated with good quality graphite. The samples were annealed in the holder assembly at 423 K before making observation. The Capacitance and dielectric loss were measured using Agilent 4284A Precision LCR meter in the range of 100 Hz to 1000 KHz from temperature 313 K to 423 K.

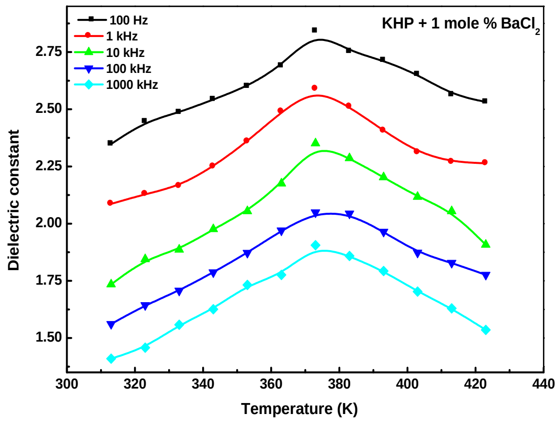

Fig. 6. Dielectric constant for $BaCl_2$ doped KHP.

The dielectric constant was calculated at different temperatures for different frequencies which are shown in Fig. 6. For $BaCl_2$ doped KHP crystals it can be noticed that the dielectric constant initially increases up to 373 K and then gradually decreases. This indicates that the crystal undergoes phase transition from paraelectric to ferroelectric at 373 K which is called Curie temperature of the doped crystal. The low value of the dielectric constant is essential parameter for the enhancement of NLO materials and hence these materials can be used as inter-metal dielectric material [9].

IV. CONCLUSION

The single crystals of pure and $BaCl_2$ doped KHP crystals were grown by low temperature solution growth method. The powder XRD confirms its structure and lattice parameters. The optical transparency of the grown crystal was studied by UV-Visible spectroscopy and the molecular structure was confirmed by FTIR spectral analysis. The TG/DTA analysis shows that the thermal stability was not affected by the dopant. The temperature dependent dielectric constant reveals the ferroelectric properties. The higher SHG efficiency and the low value of dielectric constant are the essential parameters for the enhancement of NLO properties.

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