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Effects of cadmium metal ion doping on the thermal, optical and electrical properties of potassium hydrogen phthalate single crystals.

A. C. Sajikumar[1*] and V.T.Jisha[2]

[1]Department of Physics, Malankara Catholic College, Mariagiri, Tamil Nadu, India.
[2]Physics Research Centre, S.T. Hindu College, Nagercoil, Tamil Nadu, India.
**Corresponding author*

Abstract

Cd doped Potassium Hydrogen Phthalate (KHP) single crystals were grown by slow evaporation method under room temperature. The grown crystals were subjected to powder XRD analysis and confirm its structure and lattice parameters. The optical transparency of grown crystal was studied by UV-Visible spectroscopy and the molecular structure was confirmed by FTIR analysis. TG-DTA studies reveals thermal decomposition and weight loss. The SHG efficiency of Cd doped KHP crustal could enhance nonlinearity behaviour. In addition the electrical parameters such as dielectric constant, dielectric loss and activation energy confirm the NLO property.

Keywords: KHP, Crystal growth, Thermal study, SHG, NLO, Dielectric constant

1. INTRODUCTION

Non Linear Optical (NLO) materials find a variety of applications such as frequency conversion, light modulation, optical switching, optical memory devices and optical second harmonic Generation (SHG) [1-5]. The non linear optical crystal of Potassium Hydrogen Phthalate (KHP) with the chemical formulae $K(C_6H_4COOH\text{-}COO)$ is the simplest occurring semi-organic salt that belongs to the alkali acid phthalate series has an orthorhombic symmetry with the space group Pca21 [6] and shows a perfect cleavage along (*010*) plane. Its higher chemical stability and economic viability with good kinetic growth properties have made to pay attention on them in past decades. As a result, very good semi organic NLO material like KHP have been developed and are found to be suitable for a number of applications [7]. Many authors have used some techniques for a variety of materials characterisations .As for the metallic part focus is on the group II B metals (Zn, Cd, Hg) usually have high transparency in uv region because of their closed d^{10} shell. Potential NLO materials like bis thiourea cadmium chloride (BTCC), Trially thiourea Cadmium chloride (TATCC) [8] are examples of this approach. The addition of some metal ions is expected to influence the growth kinetics, habit modification and the large size single crystal. The presence of small amount of impurities such as Ni^{2+}, Mg^{2+}, Co^{2+} and Li^{2+} plays an important role in the growth rate, habit modification of the crystal and its chemical properties [9].

The aim of the present work is to grow optically transparent, good quality KHP crystal by doping divalent metal Cd^{2+} ion and to describe the result of growth, uv visible, NIR transmittance, optical, NLO and dielectric studies. The addition of Cd^{2+} ion is expected to influence the growth, kinetics, habit modification and its properties.

2. CRYSTAL GROWTH

Commercially available KHP salt (AR grade) was dissolved gradually in deionised water until a saturated solution was obtained. The calculate amount of 1 mol % $CdCl_2$ was added to the solution and stirred for 5 hours. The solution was filtered and crystallization was allowed to take place by slow evaporation under room temperature. Colorless and transparent crystal of size was harvested after a period of about 30 days. The grown crystals were shown in fig.1.

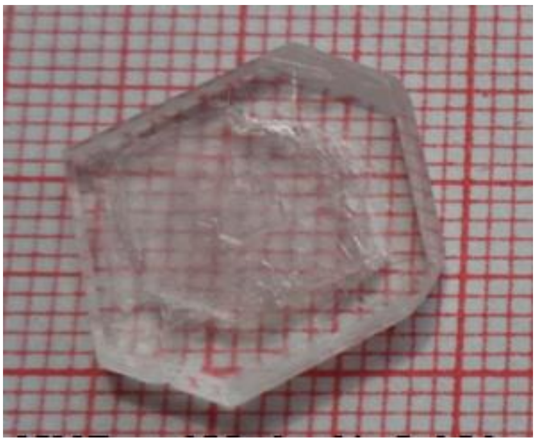

Fig. 1 Photograph of CdCl2 doped KHP crystals.

3. CHARACTERIZATION

The grown Cd doped KHP crystals was subjected to various characterization viz, powder x ray diffraction, UV spectral study, FTIR analysis study, NLO property, TG/DTA thermal study, and dielectric studies.

4. RESULT AND DISCUSSION

4.1: Powder X ray diffraction analysis

Powder X ray diffraction analysis was recorded on a XPERT PRO diffractometer using CuK_α radiation for Cd doped KHP crystals. This analysis revealed that the powder crystals of doped KHP crystallize in orthorhombic system. The calculated lattice parameters for Cd doped KHP crystals are a= 9.618 Å, b=13.1312 Å, c=6.487 Å were compared with that of pure KHP from the date base of internal centre for diffraction data (ICDD)[10] and the hkl value were noted. It is reported that the indexed peaks were slightly shifted and some additional peaks, but only change in the intensity of the peaks shows the presence of additional phase due to doping. The powder XRD patterns for $CdCl_2$ doped KHP crystals is shown in fig. 2 , have confirmed that the incorporation of metal ions in KHP crystal lattice does not change the crystal structure though there is a small change in the lattice parameter.

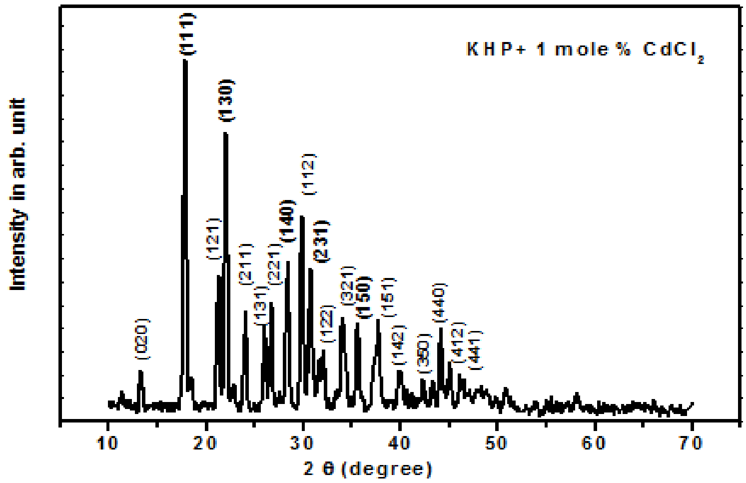

Fig. 2 The powder XRD patterns for CdCl2 doped KHP crystal.

4.3 UV –Vis spectral studies

The UV –Vis spectral study is a special technique tool to determine the transparency, which is on the requirement to be optically active [11]. Optical transmission spectrum of $CdCl_2$ doped KHP single crystals were recorded in the range 200-1500 nm using Lambda -35 UV-Vis 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. It is evident from the spectrum that the $CdCl_2$ doped KHP crystals have very high transmission in the entire visible and IR region and UV cut off wavelength is at 329 nm. The high transmission in the entire visible region and short UV cut off wavelength = 298nm facilitates the grown crystal to be a potential nonlinear optical material for second harmonic of Nd:YAG laser [12].Using the formula $E_g = \frac{1240}{\lambda}$ nm, the band gap energy of the sample was found as 4.161 ev

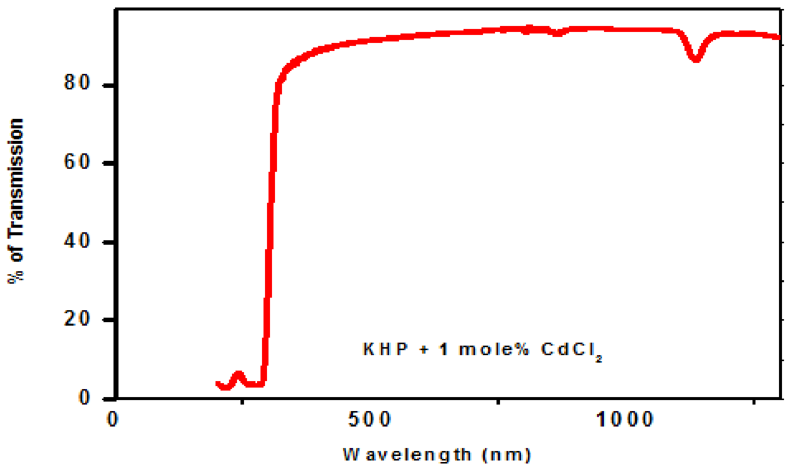

Fig. 3 The UV-Vis spectra of $CdCl_2$ doped KHP crystal

4.4 Thermal Analysis

Using Perkin Thermal Analyser, the Thermo Gravimetric Analysis (TGA) and Differential Thermal Analysis (DTA) were carried out the temperature range of 36-620 ˚C in the nitrogen atmosphere at a heating rate of 10˚C/min . The TG-DTA curves for $CdCl_2$ doped KHP single crystals are shown in fig.4.The TGA curves shows a sharp weight loss at 302˚C without any intermediate stages, which is assigned as melting point of the crystal that is agree with reported values[13]. From the DTA trace, the strong endothermic peak at 302˚C reveals the decomposition of $CdCl_2$ doped KHP structure which is close to the melting point of pure KHP may be attributed to decomposition of $CdCl_2$ doped KHP and it is evident that metal Cd ion does not have influence on thermal stability of KHP crystal. These analysis the material could be used for the fabrication of any optical devices below its boiling point.

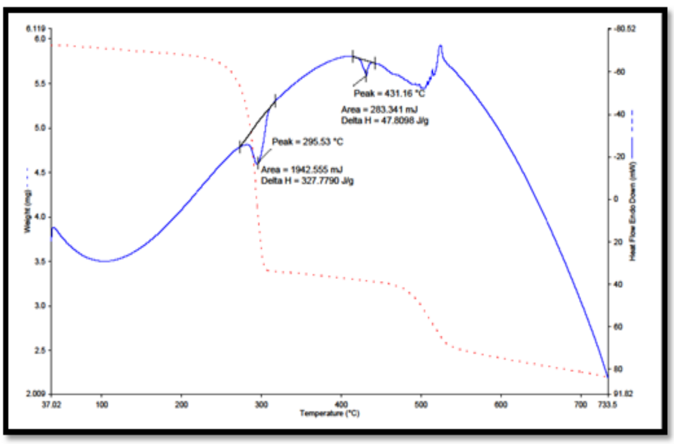

Fig. 4 The TG-DTA curves for $CdCl_2$ doped KHP crystals

4.5 SEM and EDAX

The effect of influence of dopants on the surface morphology of KHP crystal faces the structure defect centres as seen in the SEM images in fig .5. Doping results in defect centres and crystal voids with reduction of grain size which is analysed by reported values [14].Analysis of surface at different sites reveals the incorporation is uniform over the surface. The substitution of bivalent cadmium for the monovalent potassium will result in cation vacancies and crystal defects and it is confirmed that the dopants lead to mosaicity in them.

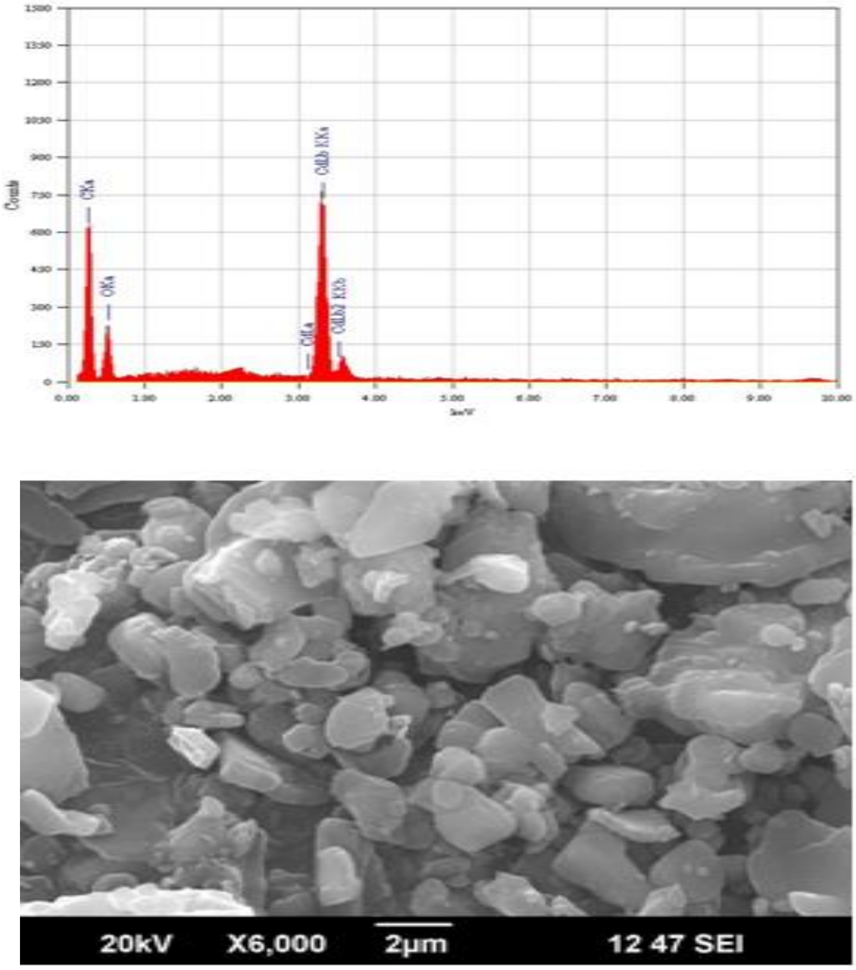

Fig.5. The SEM with EDAX of CdCl2 doped KHP crystal

4.5 Dielectric study

Dielectric measurement provides the information of electrical response in crystalline and ceramic material and it gives the idea about electric fields within the solid materials. Single CdCl2 doped KHP crystals were polished in proper size and for good electrical contact opposite faces of the sample crystals were coated with good quality graphite [15]. The Capacitance(C) and dielectric loss(D) were measured using Agilent 4284A Precision LCR meter in the range of 100 Hz to 1000 KHz from temperature 303 K to 383 K. The dielectric constant was calculated at different temperatures for different frequencies shown in fig.6. For $CdCl_2$ doped KHP crystals. It can be noted that the dielectric constant have high values in the lower frequency, initially increases up to 350 K and then gradually decreases. This denote that $CdCl_2$ doped KHP crystals undergo phase transition from paraelectric to ferroelectric at 353 K which is called Curie temperature. The high value of the dielectric constant at lower frequencies may be due to the presence of all the four polarisations namely, space charge, orientational, electronic and ionic polarisation and its low value at higher frequency may be due to the loss of significance of polarisations gradually. As far as polarisation is concerned, the increase in the dielectric constant with temperature variation of ionic and space charge polarisations and not due to the temperature variation of orientational polarisation [16,17].

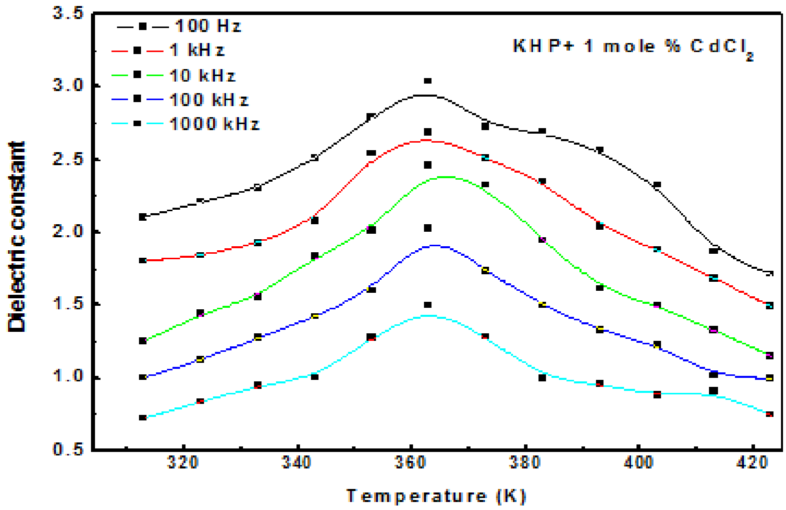

Fig.6. The dielectric constant for CdCl2 doped KHP crystal

The variations of dielectric loss with temperature at different frequencies are shown in fig.7 for $CdCl_2$ doped KHP crystals. The dielectric loss decreases with increase of frequency and decrease of temperature. The low value of dielectric loss at higher frequencies suggests that the crystal possesses enhanced optical quality with lesser defects, and this parameter is of vital role for NLO materials for many applications[18].

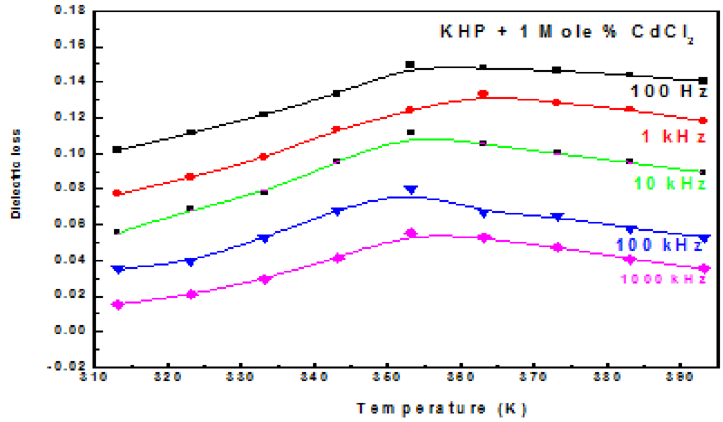

Fig.7. The dielectric loss for CdCl2 doped KHP crystal

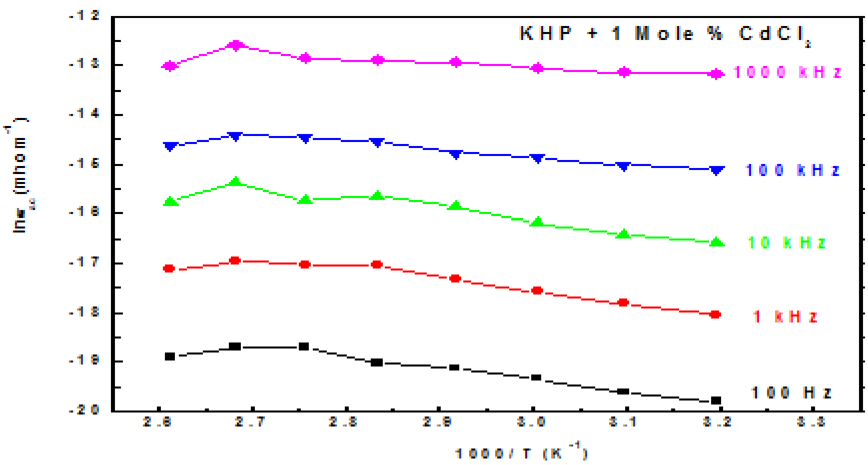

Fig.8. The conductivity values for CdCl2 doped KHP crystal

It is observed from fig. 8 that, AC conductivity increases with increase in temperature. The addition of Cd^{2+} into the lattice of KHP increases the carrier concentration and this leads to increase in conductivity. The AC activation energy for $CdCl_2$ doped KHP crystals are between 0.058 to 0.192 eV. Thus it is clear that the frequency of applied AC voltage is low, more energy is needed to activate the atoms or molecules, but for the same system at higher frequency less energy is enough to activate it. Also it was confirmed that the dopant will increases the activation energy [19].

5. CONCLUSION

Good optical quality single crystals of $CdCl_2$ doped KHP crystals have been grown from solution by slow evaporation method under room temperature. The powder XRD confirms its structure and lattice parameters. The molecular structure was confirmed by FTIR spectral analysis. The optical transmission spectrum shows that $CdCl_2$ doped KHP crystals have high transmission in the entire visible region and have low cut off wavelength. The thermal study reveals that $CdCl_2$ doped KHP crystals is thermally stable up to 302˚C. The temperature dependent dielectric constant dielectric loss measurements show the normal behaviour of ferroelectric properties. SHG efficiency, low value of dielectric constant and dielectric loss are also enhancing the NLO properties. All these studies promising that the $CdCl_2$ doping KHP enhance the thermal, optical and electrical properties of KHP, and thus considered as a potential material for frequency conversion application, electro-optic and optoelectronic devices.

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