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Tuning Structural And Photoluminescence Properties Of Cadmium Thiourea Acetate Crystal Exploiting Inorganic Ligand KDP (Potassium Dihydrogen Phosphate) For NLO Device Applications

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Abstract

Crystals with excellent optical properties are exclusively demanded for NLO device applications. Hence present communication concentrates on to evaluate the impact of KDP on structural & luminescence properties of Cadmium Thiourea Acetate (CTA) crystal. KDP was doped in CTA metal complex and crystal was grown from aqueous solution by slow evaporation solution growth technique at 35°C. Powder X-ray diffraction technique asserted the slight change in crystal system cell parameters and volume of pure CTA. Electronic purity and the color centered emission nature of parent and KDP-CTA crystals were studied by implementing photo-luminescence analysis technique.

Keywords: Crystal growth, Powder XRD, Photoluminescence

1. Introduction

Nonlinear optical (NLO) crystals seek a great demand for developing &upgrading the cutting edge technological accessories applied in frequency modification, optical switching, data storage, digital communication systems,laser fusion, photonics, optoelectronics device applications **[1–4]**. Tremendous efforts have been taken since past few decades for designing a new class of organo-metallic nonlinear optical crystals. In organometallic crystals a large variety of thiourea metal complex crystals have been reported**[5,6]** amongst which the Cadmium thiourea acetate (CTA) deserves more attention due to its orthorhombic crystal structure, appreciable linear-nonlinear optical properties, hardness, electrical and thermal properties as evident in literature **[7-15].**

Potassium dihydrogen phosphate (KDP) is a ideal material for potential nonlinear optical device applications with elevated thermal stability **[16],** Unique features like high growth rate and optical homogeneity increased the demand fof KDP for laser based imaging and remote sensing techniques, industrial photonics and optoelectronics devices. KDP is a well known technological crystal with predominant second order nonlinear optical NLO) response majorly attributed to the phosphate (PO4) group, good SHG efficiency coefficient, interesting third order NLO behavior foreshowing the positive refraction nonlinearity (self focusing tendency), nonlinear cubic susceptibility ($\chi 3$) 3.72 x10-14esu and 2.04 x10-14esu at 1064 nm and 532 nm, respectively **[17].**Therefore large nonlinearities can be achieved in CTA by introducing fascinating KDP as dopant. Due to these potential sites and owing to high technological impetus and appealing research credentials **[18-19]** present research is concentrated on KDP as a preeminent dopant to achieve enhancement in characteristic properties of CTA crystal.

As an output of literature survey, hitherto no other researcher has communicated a report on doping effect of KDP on different traits of Metal complex crystal; hence through this communication authors elaborated and demonstrated the feasibility of the structure and Photo-luminescence analysis of the KDP-CTA crystal for distinct NLO device applications.

2. Experimental procedure

CTA complex has been synthesized by dissolving cadmium acetate (1mole) and thiourea (2mole) in double distilled de-ionized water according to the reaction as below,

$Cd(CH_3COO)+2(CS(NH2)2)Cd(CS(NH2)2)2+2(CH3COO)$

Purity of CTA metal complex salt has been maintained by the repetitive re-crystallization process. The supersaturated solution was prepared and calculated ratio of 1wt% of KDP was added to the supersaturated solution of CTA. Doped solution was allowed to agitate for six hours to achieve the homogeneous doping throughout the solution. The KDP doped CTA solution was then filtered in a rinsed beaker and the filtrate was kept for slow solvent evaporation process at 35°C.

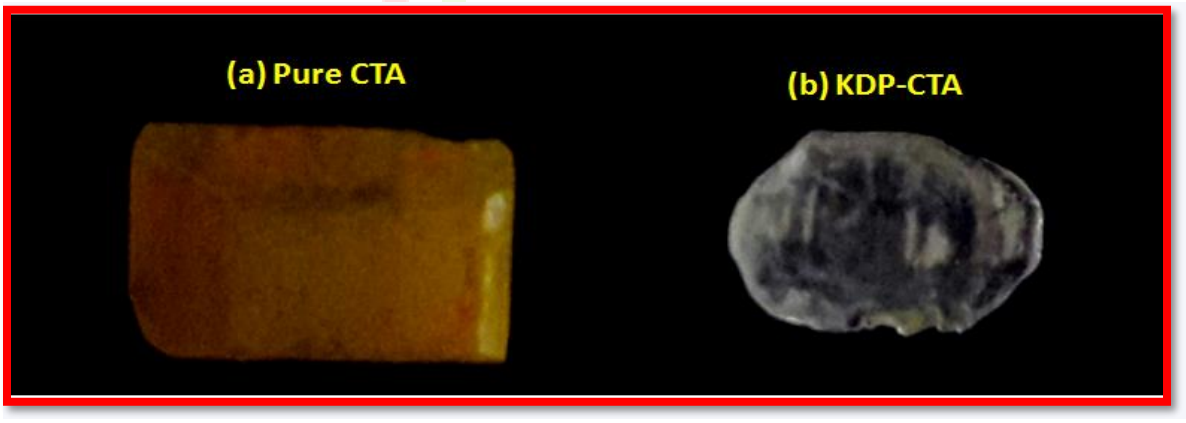

Fig.1. (a) Pure CTA (b) KDP doped CTA crystal

As per the literature survey **[9-15]** and solubility data available in previous literature **[20, 21]** good quality pure and doped CTA crystals were successfully grown in the temperature range 35-41.85˚ **[9-15].**Hence the 35˚C temperature was selected for growth of pure and KDP-CTA crystals shown in **Fig.1.**

3. Results and discussion

3.1 Powder X-ray diffraction (PXRD) analysis

The PXRD pattern of Pure and KDP-CTA crystal has been recorded using the Rigaku Miniflex (II) powder X-ray diffractometer with the scan rate of 0.02 degree/ min in the 2θ range of 10 to 70 degree. The grown CTA and KDP-CTA crystal are confirmed to be oriented with orthorhombic crystal structure. The evaluated cell parameters of Pure and KDP-CTA crystals **(Table 1)** are in close agreement with earlier reported work **[9-15].** Graphical PXRD nature of KDP-CTA material as shown in **Fig. 2 (a) & (b)** was indexed by implementing powderX software (the 2θ error was 0.01), expressed elevated sharp diffraction peaks confirming lesser grain boundaries and excellent crystalline nature **[22]**.

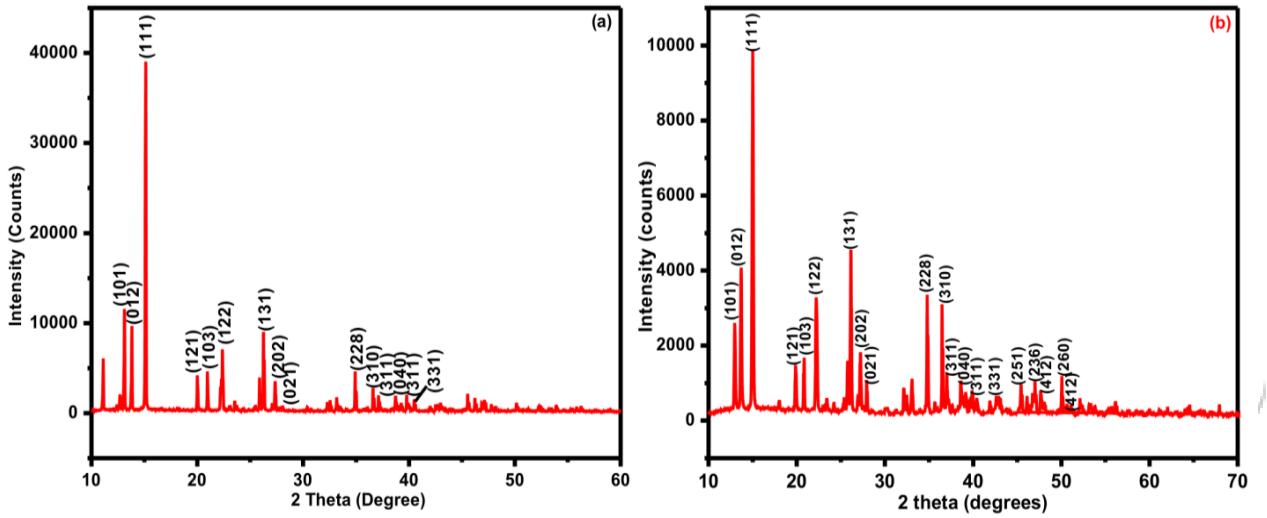

Fig.2 PXRD pattern of (a) Pure CTA (b) KDP-CTA

Table 1. Comparative PXRD data

Crystal	a(A˚)	b (A˚)	c (A˚)	Volume (A˚)^3	Crystal system
CTA	7.54	11.89	15.68	1405.7	Orthorhombic
KDP-CTA	7.56	11.78	15.71	1408.6	Orthorhombic

3.2 Fourier Transform Infrared Analysis

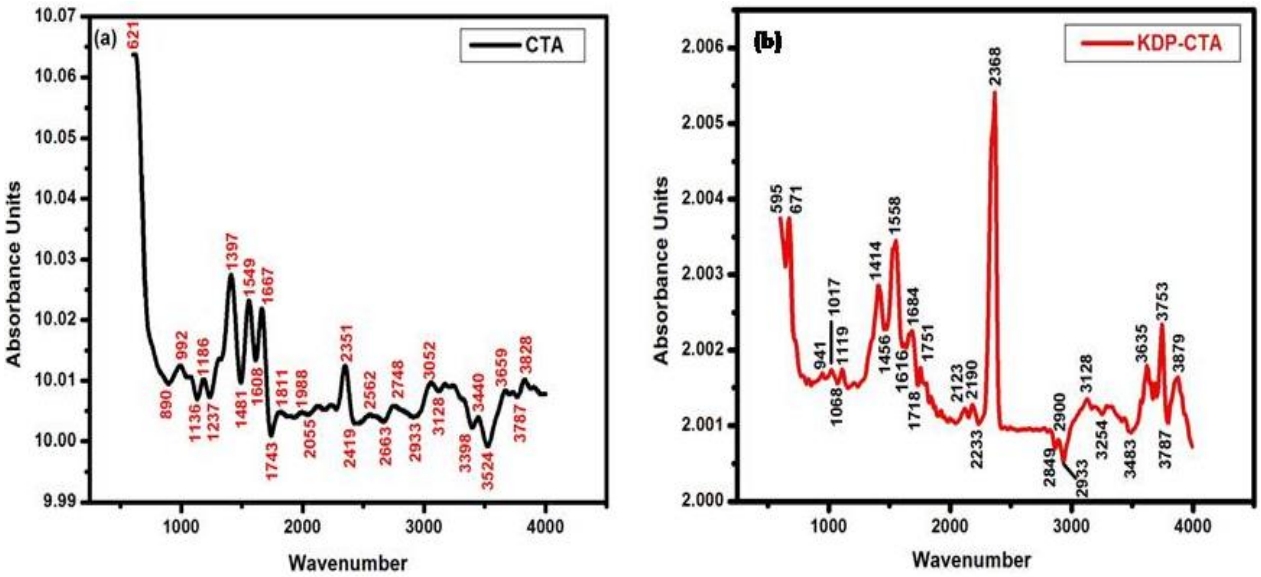

Fig.3. FTIR spectrum of (a) pure CTA (b) KDP-CTA

The qualitative analysis of pure and KDP-CTA crystal has been performed by means of FT-IR spectral analysis using the Bruker α-ATR spectrophotometer. The FT-IR spectrum of both crystals was recorded in the range of 600-4000 cm^{-1} and is plotted in **Fig. 3(a) and (b)** respectively. The CN deformation is observed at 621 and 671 cm^{-1}.The C-H deformation occurred at 992 and 941 cm^{-1}.The P-O-C bond stretching indicating the influence of KDP in CTA crystal lattice is observed at 1017 cm-1.The CH_2 wagging is evident at 1397 and 1414 cm^{-1}. The C-O-O stretching is observed at 1481and 1456 cm^{-1}. Antisymmetric stretching peak of NO_2 in grown crystals is contributed at 1549 and 1558 cm^{-1}. The evidence of C=O bond stretching of carboxyl group is found at 1743 and 1718 cm^{-1}. The characteristic sharp peak attributed at 2351 and 2368 cm^{-1} is an evidence of P-H bond stretching of KDP. The peaks contributed with 3300-4000 cm^{-1} are contributed by NH and OH bond stretching vibrations. The vibration peaks are indexed in FT-IR spectrum and the observed shift in wavenumber of identified functional groups are distinguished in **Table2.** Stretching of PH bond as well as shifting of vibration frequencies of CTA crystal certified the incorporation of KDP in CTA crystal.

Table2. FT-IR spectral assignments

Wavenumber(cm^{-1})		Functional group assignment
CTA	KDP-CTA	
621	671	C-N deformation
992	941	C-H deformation
1009	1017	P-O-C bond stretching
1186	1119	N-C-N stretching
1397	1414	C H_2 Wagging
1481	1456	C-O-O stretching
1549	1558	NO_2 antisymmetric stretching
1667	1684	NH_2 bending
1743	1718	C=O stretching
2351	2368	P-H bond stretching of KDP
3052	3128	N-H stretching
3300-4000		NH and OH stretching

3.3 Photoluminescence

The photoluminescence (PL) study is the worldwide crucial tool to scrutinize the electronic purity, trajectory of electron transition and the recombination rates in the given energy states, discrete energy levels and identify the interface roughness of material which play vital role for detecting different compounds used in biomedical and chemical field of research. The PL process involves the photo-excitation followed by the photo-relaxation of the material. During photo-relaxation the material emits light of specific wavelength and the survey of this emission spectrum reveals various interesting properties of the material **[23-24].**Thus, the PL studies of KDP doped CTA crystal has been accomplished using the Shimadzu spectrophotometer (Model: RF-5301). The excitation spectrum reveals that the pure and KDP-CTA crystal samples were found to have maximum excitation at 354 nm and 383 nm. The pure and KDP-CTA crystal samples were excited at respective wavelengths and the emission spectrum was recorded in the optical range of 380–580 nm. The PL emission spectrum shown in **Fig. 7(a) and (b)** reveals that dopant reinforces the shift in peak maxima of PL emission of CTA crystal material. The KDP-CTA crystals has the maximum emission ate 510 nm which corresponds to the green light. It is noteworthy that the pure CTA crystal attributes the blue colored emission at 481 nm**.** The red shift in PL emission might have been expressed due to charge transfer between the K^+ and COO^- ions of the dopant and host crystal respectively. The modified PL emission of doped CTA crystal thus confirms that the photo-excitation of material at specific energy governs the effective interaction of dopant and host crystal matrix moieties resulting to successful tuning of PL properties of CTA crystal. The materials with peculiar PL property seek huge demand for detection purpose in biomedical and biochemical systems **[25-28].**

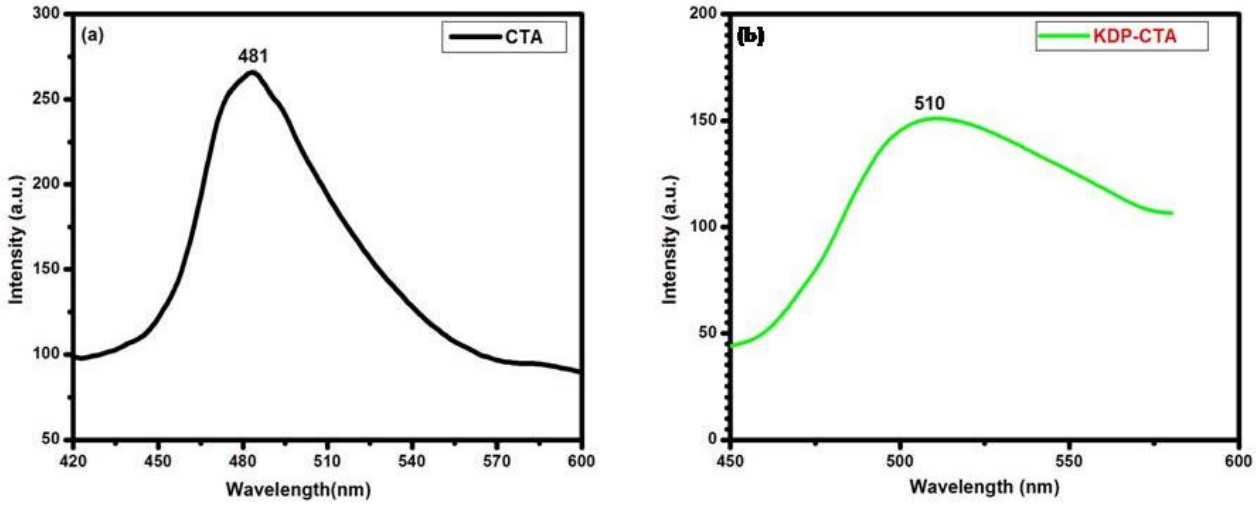

Fig.7. PL emission spectrum of (a) Pure CTA (b) KDP-CTA crystal

Conclusion

Pure and KDP-CTA crystals have been successfully grown by slow solution evaporation technique at 35°C.The PXRD analysis confirmed orthorhombic crystal system of CTA and KDP-CTA crystal. The identified functional groups in FTIR analysis confirmed the presence of KDP in CTA crystal. The dopant KDP reinforced the shift in peak maxima of PL emission (481 to 510 nm) of CTA crystal material. Dopant KDP offered switching in structural and photoluminicence behavior of CTA crystal. Decisive results uncovered in present studies hold strong status of KDP-CTA crystal for technologically vital NLO device applications.

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