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Reconnoitering Sequel of KDP (Inorganic Ligand Potassium Dihydrogen Phosphate) on Characteristics of Cadmium Thiourea Acetate Crystal

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ABSTRACT

Crystals with valuable nonlinear optical properties are exclusively demanded for nonlinear optical device applications. So present communication concentrates on scrutinizing the impact of additive KDP(inorganic ligand potassium dihydrogen phosphate) on non-linear optical properties of CTA (Cadmium Thiourea Acetate) crystal. Both parent & doped crystals were grown from aqueous solution by slow evaporation solution growth technique at 35°C. In Present communication, Kurtz–Perry powder Second Harmonic Generation (SHG) test pointed the towering nonlinearity of KDP-CTA crystal than Parent CTA crystal. TONLO nature of KDP doped CTA crystal was studied via Z-scan technique. The TONLO refractive index (n_2), absorption coefficient (β) and cubic susceptibility (χ^3) of KDP doped CTA crystal has been evaluated using the Z-scan transmittance data. The order of third order nonlinear optical parameters (TONLO) n_2, β and χ^3 is recorded as 10^{-10} cm^2/W, 10^{-5} cm/W, 10^{-4} esu respectively. Determined TONLO parameters vitalize its application for laser stabilization systems.

Keywords— Crystal growth, SHG efficiency, TONLO parameters

1. Introduction

Nonlinear optical (NLO) crystals seek large demand for upgrading the cutting edge technological accessories utilized in data storage, digital communication systems, optical switching, laser fusion, photonics, optoelectronics and laser frequency conversion 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 organo-metallic 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**[7-16].**Potassium dihydrogen phosphate (KDP) is a model system for potential nonlinear optical device applications with high range of thermal stability **[17],** KDP is an excellent nonlinear optical (NLO) crystal with top growth rate and optical homogeneity owing to which it has great demand in the optoelectronics, photonic, frequency conversion devices & UV-tunable laser systems. 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 (χ3) 3.72 $x10^{-14}$esu and 2.04 $x10^{-14}$esu at 1064 nm and 532 nm, respectively **[18].**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 **[19-20]** 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 second and third order nonlinear optical properties (SHG and Z-scan)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 (2 mole) in double distilled de-ionized water according to the reaction as below,

$$Cd(CH_3COO) + 2(CS(NH_2)_2) \longrightarrow Cd(CS(NH_2)_2)_2 + 2(CH_3COO)$$

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 by covering the beaker with perforated coil in a CTB (constant temperature bath) at 35 °C.

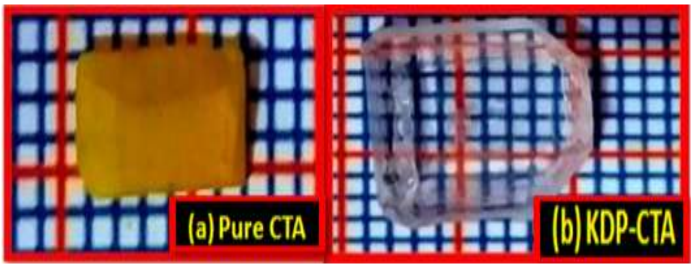

Fig.1. (a) Pure CTA (b) KDP doped CTA crystal

The crystals harvested after 15 days were selected to further characterizations. The harvested CTA and KDP-CTA crystals are shown in **Fig.1.**

3. Results and Discussion

3.1. SHG efficiency

The frequency conversion is the most unique quality of a nonlinear optical (NLO) material and the conversion efficiency has been determined using the standard powder technique developed by Kurtz and Perry **[21].** In the present manuscript, the Q-switched Nd:YAG laser (1064 nm, 10 Hz, 8 ns, 680 mW) has been implemented for the determination of the Second Harmonic Generation (SHG) efficiency. A fine powder of pure and KDP doped CTA crystals was prepared and tightly sieved in a micro-capillary tube of uniform bore. Beam of Gaussian filtered Nd:YAG laser was multi-shot on the said samples and the obtained bright green light output beam was collected via array of the photomultiplier tube. This output emergence confirmed the NLO behaviour of under study grown crystals. The output energy for CTA and KDP-CTA crystal sample was found to be 1.6 mJ **[22]** and 2.37 mJ respectively**.** It is evident that the SHG efficiency of CTA crystal is higher than KDP **[22]**. It is noteworthy that the SHG efficiency of KDP doped CTA crystal is found to be higher as compared to KDP as well as CTA crystal material **[22]**. The observed enhancement in SHG efficiency of KDP doped CTA crystal might have been attributed due to presence of additional phosphate group of KDP **[23]** in addition the semi-organic complexes possess large number of secondary energy bands below band gap which inculcate more electron-phonon interaction that favors enhancement in nonlinearity of the material **[24].** The magnitude of SHG efficiency of KDP doped CTA crystals is systematically organized in **Table1**. The KDP doped CTA crystal confirmed highest SHG efficiency among all the reported doped CTA crystals **[9, 14, 22]** and hence could be the suitable alternative for designing frequency conversion devices **[24].**

Table1. SHG efficiency data

Crystal	**Voltage (mJ)**	**SHG efficiency**		**Reference**
		ReferenceKDP	**Reference CTA**	
KDP	1.35	1	0.84	**[22]**
CTA	1.6	1.18	1	**[22]**
KDP-CTA	2.37	1.75	1.48	**Present work**
LT-CTA	2.1	1.55	1.31	**[22]**
LA-CTA	-	1.24	1.12	**[09]**
G-CTA	-	1.32	1.2	
Mn-CTA	-	1.12	1.01	
LC-CTA	-	1.24	1.35	**[14]**

3.2 Z-scan Analysis

The 3D optical data storage, optical switching, optical limiting, lithography microscopic designing, two photon up conversion lasing applications demand promising third order nonlinear optical (TONLO) crystals **[25-26]** for which KDP doped CTA crystal has been subjected to Z-scan analysis. The Z-scan technique firstly developed by Bahae et al **[27]** facilitated with the He-Ne laser operating at 632.8 nm has been used to explore the TONLO properties of KDP doped CTA crystal. The resolution of Z-scan setup is given in **Table 2.** For the analysis the Z-scan setup has been optically aligned and the sample is placed at the focus (Z=0) position. The sample was gradually translated along the Z direction along the focus position and the transmitted signal was recorded using the photo-detector placed at far field. Initially the aperture was configured to close mode and the respective close aperture Z-scan transmittance is shown in **Fig. 2(a).**

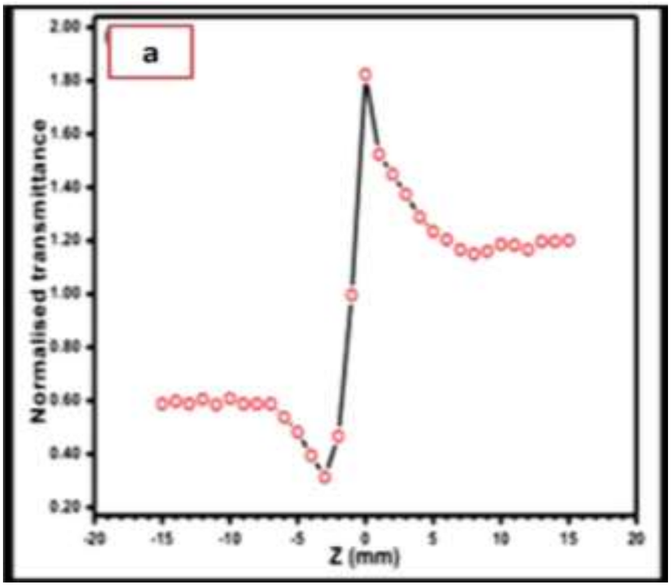

Fig.2. (a) Z-scan transmittance curve with close aperture

It reveals that the KDP doped CTA crystal attributes the pre-focus valley to post-focus peak which is clue of positive nonlinear refraction **[28-29]** while the nonlinear refraction id negative in case of CTA crystal **[13].** The positive nonlinear refraction is the signature feature of material exhibiting self focusing nature **[30].** The material having positive nonlinear refraction also possess the special ability to demonstrate the Kerr lens mode locking effect which is desirable for laser alignment and shorter pulse generation system **[31-32].** The difference between the peak and valley transmission $\Delta T_{p-v} = 0.406(1-S)^{0.25}|\Delta\phi|$, aperture linear transmittance $S = 1-\exp(-2r_a^{\,2}/\omega_a^{\,2})$, nonlinear refractive index $n_2 = \frac{\Delta\phi}{KI_0L_{eff}}$, effective thickness of the sample L_{eff}=[1-exp(-αL)]/α, nonlinear absorption coefficient is estimated as, $\beta = \frac{2\sqrt{2}\Delta T}{I_0L_{eff}}$`, third order nonlinear optical susceptibility $\chi^3 = \sqrt{(\mathrm{Re}\,\chi^3)^2 + (\mathrm{Im}\,\chi^3)^2}$ were determined as mentioned in previous literature **[27-32].**

Table 2. Optical resolution of the Z-scan setup

Parameters and notations	Details
Laser beam wavelength (λ)	632.8 nm
Lens focal length (f)	30 mm
Optical path length (Z)	85 cm
The Beam radius of aperture (w_a)	3.3 mm
Aperture radius (r_a)	2 mm
Incident intensity at the focus (I_o)	26.5 MW/cm²

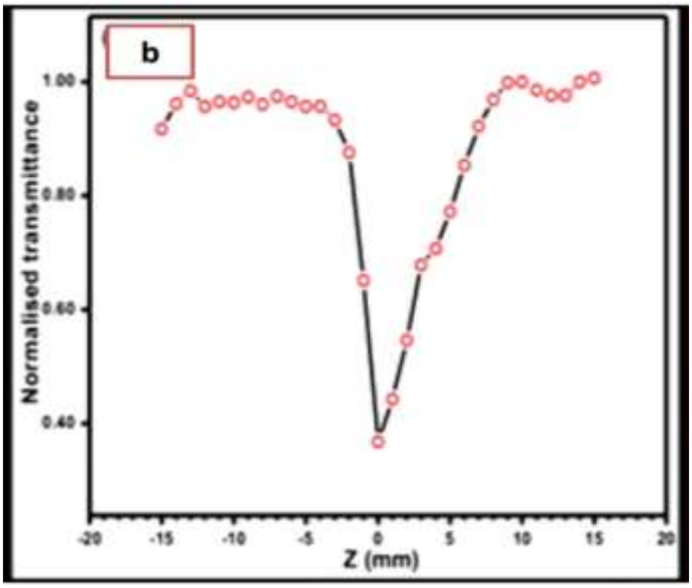

Fig.2.(b) Z-scan transmittance curve with open aperture

The open aperture Z-scan analysis helps to explore the nonlinear absorption behaviour of KDP doped CTA crystal. **Fig. 2(b)** represents the open aperture Z-scan transmittance curve which confirms the transmittance minimum at the focus position. The transmittance falls at the focus indicating the occurrence of reverse saturable absorption (RSA) effect **[33].** The RSA effect is predominantly occurs due to the two photon absorption in excited states assisted with multiphoton absorption **[34-35].** Third order nonlinear parameter (TONLO) susceptibility $\chi^{(3)}$ of KDP-CTA crystal is of the order 10^{-4} esu may be facilitated by photo induced π-electron delocalization along large bonding network also resulting to develop strong polarizing potential in crystal **[36].**

Table 3. Comparison of TONLO parameters

Sample **Crystal**	n_2 (cm²/W)	β (cm/W)	$\chi3$ (esu)	Reference
CTA	8.37 $x10^{-11}$	4.70 $x10^{-6}$	2.58 $x10^{-4}$	**[13]**
LV-CTA	5.06 $x10^{-11}$	9.05 $x10^{-6}$	3.34 $x10^{-4}$	**[13]**
LC-CTA	85 x 10^{-12}	1.19 $x10^{-5}$	6.18 $x10^{-5}$	**[14]**
LT-CTA	4.45 $x10^{-12}$	6.88 $x10^{-5}$	4.81 $x10^{-4}$	**[39]**
KDP-CTA	1.33 $x10^{-10}$	6.13 $x10^{-5}$	4.28 $x10^{-4}$	Present work

The TONLO parameters of KDP doped CTA crystal has been compared with literature in **Table 3**. The KDP-CTA crystal with appealing TONLO properties may find application in optical switching; optical logic gates, calibrating optical distortions and passive laser mode-locking systems and also suggest its suitability for applications in laser stabilization, optical limiting and sensor devices**.**

4. Conclusion and Future Scope

Pure and KDP-CTA crystals have been successfully grown by slow solution evaporation technique at 35°C. The SHG efficiency of CTA-KDP crystal is found to be 1.48 times of CTA and 1.75 times of KDP which is vital for NLO applications. The dopant KDP reinforced the shift in peak maxima of PL emission (481 to 510 nm) of CTA crystal material. The close aperture curve confirmed that KDP-CTA crystal shows the transition from pre-focus valley to post focus peak which indicates the occurrence of positive refraction nonlinearity facilitating the self focusing effect. The magnitude of n_2 is 1.33 $x10^{-10}$ cm²/W for KDP-CTA crystal. The open aperture Z-scan analysis revealed the reverse saturable absorption effect in KDP-CTA crystal and the respective β value is 6.13 $x10^{-5}$ cm/W. The $\chi3$ of KDP-CTA crystal is found to be 4.28 $x10^{-4}$ esu. Dopant KDP offered switching in TONLO 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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References

[1]. Mohd Shakir, S.K. Kushwaha, K.K. Maurya, Manju Arora, G. Bhagavannarayana, J.Cryst. Growth 311 (2009)3871–3875.

DOI:10.1016/j.jcrysgro.2010.01.031

[2]. V. Ganesh, Mohd. Shkir, Rizwan Husain, Rajveer Singh,

T. Bhaskar Rao, K. Kishan Rao, Optik 124 (2013) 6690-6695.**DOI:10.1016/j.ijleo.2013.05.087**

[3]. Mohd Shakir, B. Riscob, K.K. Maurya, V. Ganesh, M.A. Wahab,G. Bhagavannarayana, J. Cryst. Growth 312 (2010) 3171–3177.

DOI:10.1016/j.jcrysgro.2010.07.061

[4].Mohd Anis, Gajanan.G. Muley, Optics & Laser Technology 90(2017)190-196.

DOI:10.1016/j.optlastec.2016.11.020

[5].N.N. Shejwal, Mohd Anis, S.S. Hussaini, M.D. Shirsat, Int. J. Mod. Phys. B 30(2016) 1650159–1650170. **DOI:10.1142/S0217979216501599**

[6].N.N. Shejwal, Mohd Anis, S.S. Hussaini, M.D. Shirsat, Phys. Scr. 89 (2014)125804–125810.

DOI:10.1402-4896/89/12/125804

[7].N.P. Rajesh, V. Kannan,, M. Ashok, K. Sivaji,P. Santhana Raghavan, P. Ramasamy, Journal of Crystal Growth 262 (2004) 561–566.

DOI:10.1016/j.jcrysgro.2003.10.064

[8].R. Geetha Kumaria, V. Ramakrishnana, M. Lydia Carolin b, J. Kumarb,Andrei Saruac, Martin Kuball Spectrochimica Acta Part A 73 (2009) 263–267. **DOI:10.1016/j.saa.2009.02.009**

[9].V.Ganesh, T. Bhaskar Rao, K. Kishan Rao, G. Bhagavannarayana, Mohd. Shkir, Materials Chemistry and Physics 137 (2012) 276-281.

DOI:10.1016/j.physb.2010.10.061

[10].S.Shahil Kirupavathya,S.Stella Marya, P.Mythili,R.Gopalakrishnan, Journal of Crystal Growth 310 (2008) 2555-2562.

DOI:10.1016/j.jcrysgro.2008.01.020

[11]. S.S. Kirupavathy, S.S. Mary, P. Srinivasan, N. Vijayan, G. Bhagavannarayana, R. Gopalakrishnan, J. Cryst. Growth 306(2007)102-110.

DOI:10.1016/j.jcrysgro.2007.03.036

[12].J.Uma ,V.Rajendran, Inter. J. of Computer Applications 30(2011)08-10.

[13].Mohd Anis, S. S. Hussaini, M. D. Shirsat and G. G. Muley, Materials Research Innovations 200(2016)312-316.

DOI:10.1080/14328917.2015.1137693

[14].S.M. Azhar, Mohd Anis, S.S. Hussaini, S. Kalainathan, M.D. Shirsat G. Rabbani, Optics & Laser Technology 87(2017)11-16.

DOI: 10.1016/j.optlastec.2016.07.007

[15].R. Sankar, Cryst. Res. Technol. 41(2006)919-924. **DOI:10.1002/crat.200510696**

[16].Johanan Christian Prasana, Asian Journal of Chemistry 25(2013)969-971.**DOI:10.14233/ajcchem.2013.13274**

[17].Mohd Anis, M.D.Shirsat, GajananMuley, S.S.Hussaini, Physica B 449 (2014)61-66.

DOI:10.1016/j.physb.2014.05.007

[18].Mohd Anis, G.G. Muley, A. Hakeem, M.D. Shirsat, S.S. Hussaini, Optical Materials 46 (2015) 517-521. **DOI:10.1016/j.optmat.2015.04.064**

[19].Mohd. Shakir, V. Ganesh, B. Riscob, K.K. Maurya, K. Kishan Rao, M.A. Wahab, G. Bhagavannarayana, Int. J. of Pure and Appl.Physics7(2011)13-24. **http://www.ripublication.com/ijpap.htm**

[20].Y.B. Rasal, R. N. Shaikh, M. D. Shirsat, S. Kalainathan, S. S. Hussaini ,Materials Research Express(2017). **DOI:10.1088/2053-1591/aa5a66**

[21].S.K. Kurtz, T.T. Perry J. Appl. Phys. 39(1968) 3698-3813. **DOI: 10.1063/1.1656857**

[22].**Rupali B. Kulkarni, Mohd. Anis, S.S.Hussaini, M.D. Shirsat, Materials Research Express (2018). DOI:10.1088/2053-1591/aab2f8**

[23].M.I. Baig, Mohd Anis, G.G. Muley, Optical Materials 72(2017). **DOI:10.1016/j.optmat.2017.05.042**

[24].Mohd Anis, S.P.Ramteke, M.D.Shirsat, G.G.Muley, M.I.Baig, Opt.Mater. 72(2017)590-595. **DOI:10.1016/optmat.2017.07.007**

[25].Ting Bin Li, Ya Li Hu, Chun Lin Ma, Guo Fang He, Ren Gao Zhao,Guo Bing Zhen,Appl. Organometal. Chem. 25(2011)867-870.

DOI:10.1002/aoc.1852

[26].Yali Hu, Tingbin Li, Materials Chemistry and Physics (2014). **DOI:10.1016/j.matchemphys.2014.04.008**

[27].M.S. Bahae, A.A. Said, T.H. Wei, D.J. Hagan, E.W.V. Stryland IEEE J. Quant. Electron. 26 (1990)760-769.**DOI:10.1109/3.53394**

[28].S.P. Ramteke, Mohd Anis,M.S. Pandian, S. Kalainathan, M.I. Baig, P. Ramasamy, G.G. Muley,Optics and Laser Technology 99(2018)197-202. **DOI:10.1016/j.optlastec.2017.09.003**

[29].X. Q. Wang, Q. Ren2, J. Sun, H. L. Yang, T. B. Li, H. L. Fan, G. H. Zhang, D. Xu,J. H. Zhao,Cryst. Res.Technol. 4(2009)657-668.

DOI 10.1002/crat.200900082

[30].Vijender Singh,Praveen Aghamkar,Rajesh Kumar Malik, Appl. Phys. B (2013).

DOI 10.1007/s00340-013-5614-z

[31].Major,J.s. Aitchison,p.w.e. smith,f. Druon,P. Georges,B. Viana, G.P. Aka, Appl. Phys. B 80(2005)199–201.

DOI: 10.1007/s00340-004-1703-3

[32].L.T. Jin , X.Q.Wang, Q.Ren, N.N.Cai , J.W.Chen , T.B.Li , X.T.Liu , L.N.Wang, G.H.Zhang,L.Y.Zhu,D.Xu, Journal of Crystal Growth 356(2012)10-16. **DOI:10.1016/j.jcrysgro.2012.07.005**

[33].Y.B.Rasal, Mohd Anis, M. D. Shirsat,S. S. Hussaini, Materials Research innovations (2017).

DOI: 10.1080/14328917.2017.1327199

[34].N. Vijayan,G. Bhagavannarayana,S.K. Halder,S. Verma,J. Philip,R. Philip,Brijesh Rathi, Appl. Phys. A 110(2013)55–58.

DOI 10.1007/s00339-012-7448-7

[35].Mohd Anis, M.I. Baig, S.S. Hussaini, M.D. Shirsat, Mohd Shkir, H.A. Ghramh, Chin. Phys. B 27 (2018) 27800-27806.

[36].S.P. Ramteke, M.I. Baig, Mohd Shkir, S. Kalainathan, M.D. Shirsat, G.G. Muley, Mohd Anis, Opt. Laser Technol. 104 (2018)83-89.

DOI:10.1016/j.optlastec.2018.02.018