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Actions of Various Amino Acid Additives on the Growth, NLO, Optical and Physical Properties of Potassium Acid Phthalate(Kap) Crystals

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ABSTRACT

Single crystals of potassium acid phthalate (KAP), a semi organic crystal have been grown from aqueous solution by slow evaporation technique by adding non essential, semi essential and essential amino acids L-cystine (CY), histidine (HI) and L-lysine(LY) as additives. Powder X-ray diffraction studies confirmed the phase formation and amino acids doping into KAP crystals. Optical absorption studies reveal that all the doped crystals possess higher absorption of visible ray than pure KAP crystals. Optical transmission is found to be low in case of LY doped KAP than all the other crystals. TG-DTA studies show the onset decomposition temperatures to be 255, 260, 247 and 230˚C for pure, CY, HI and LY doped KAP crystals respectively. All crystals show SHG efficiency. 8.6mV, 6.8mV, 8.6mV and 5.5mV for (28mV for KDP) pure, CY, HI and LY doped KAP crystal. Grown crystals were subjected to FTIR, microhardness and dielectric studies.

Introduction

Potassium hydrogen phthalate also called as potassium acid phthalate [KAP, $K(C_6H_4COOH\text{-}COO)$] is a semi organic salt that belongs to orthorhombic class of alkali acid phthalate series [1]. The crystal structure of KAP is ionic consisting of potassium ions and alkali phthalate ions and it belongs to the $Pca2_1$ space group [2]. KAP crystals are widely used as analyzers in the long wavelength range of the X- ray spectrum and as monochromators in various high- resolution X-ray instruments. At low temperatures KAP crystals are diamagnetic along all the three main crystallographic directions [3] and they exhibit piezoelectric, pyroelectric, ferroelectric, elastic and nonlinear optical properties with long term stability in devices [2, 4, 5]. The metallic ion dopants (Fe^{3+}, Cr^{3+}, Zn^{2+}, Cu^{2+}, etc.) in the KAP crystals are reported to induce significant changes in optical, ferroelectric and non linear optical behaviors [6-8]. Monica Enculescu has studied the effect of rhodamine 6G, coumarine 6 and polyvinylpyrrolidone (PVP) on KAP crystals using solution growth method [2, 9]. It was reported that the dopants enhance the second harmonic generation (SHG) efficiency of KAP. Parthiban et al. [8] also reported that the Zn^{2+} doping into KAP crystals improves its SHG efficiency. Murugakoothan et al [1] have investigated the effect of impurities like potassium dihydrogen orthophosphate, urea and L- arginine phosphate on KAP crystals and concluded that the urea doping yields high mechanical stability and optical transmission than other dopants.

Amino acids contain chiral carbon atoms directing the crystallization in noncentrosymmetric space group and also possess zwitterion nature favoring crystal hardness [10, 11]. Some amino acids by itself have higher SHG conversion efficiency [12]. The addition of amino acids in the semi organic material like KAP could be performing modification or changes in the lattices or crystal behaviors. We already studied the effect of three non essential amino acids like L-alanine ($CH_3CH(NH_2)COOH$), glycine (NH_2CH_2COOH) and L-tyrosine ($C_9H_{11}NO_3$) as additives on KAP crystal as growth, morphology, structural, optical, thermal and mechanical properties of KAP crystals [13]. In the present work we investigate the effect of another three amino acids L-cystine (CY, $C_6H_{12}N_2O_4S_2$), Histidine (HI, $C_6H_9N_3O_2$) and L-Lysine (LY $C_6H_{14}N_2O_2.H_2O$) on the growth of KAP crystal.

Experimental

Pure recrystallised KAP salt (Merck) was used in this work. Saturated KAP solution was prepared by using double distilled water as solvent at room temperature. The prepared solution was filtered by micro filter paper of 0.1µm porosity. The saturated KAP solutions were taken in three different beakers and 0.1 mol % of each dopants CY, HI and LY were added separately. The final solution was stirred well using magnetic stirrer separately. The pH values of all the solutions were found to be 4.0. After a day, tiny crystals were seen at the bottom of the respective beakers and they were used as seed crystals. Transparent and good quality seed crystals were again placed inside the respective mother solutions for even growth of the all surfaces of each crystal. These crystals were allowed to grow for about seven days at room temperature without disturbing the vessels containing solutions and were harvested. The grown crystals were shown in figure1. The pH values of the final solutions after the completion of the crystal growth were found to be 4.0 as that of initial saturated solution.

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Powder X–ray diffraction patterns of all the grown crystals were recorded on Joel 8030 diffractometer (CuKα wavelength λ=1.5406Å). Thermo gravimetric differential thermal analysis (TG-DTA) was carried out between 30°C to 1000°C in nitrogen atmosphere using universal V4.3A instrument (SDT Q 600 V8. 3 Build 101) with the heating rate of 20 /min. UV-NIR spectrum was recorded on a Perkin Elmer Lamda 25 spectrometer in transmission and absorption mode. Fourier transform infrared spectra were recorded in the wave number range of 400-4000 cm^{-1} using the instrument Lambda 35 Perkin Elmer (Spectrum RX1). Dielectric studies were carried out on (010) face of all the crystals using Hioki 3532-50 LCR HiTester. Microhardness measurements were carried out using Shimadzu instrument. The second harmonic generation conversion efficiency of the grown crystals was measured using Kurtz powder technique. The second harmonic generation conversion efficiency of the grown crystals was measured using Kurtz powder technique. A Q switched Nd:YAG laser beam of wavelength 1064 nm was used within an input beam energy of 5.2 mJ/pulse and pulse width of 8 ns, the depletion rate being 10 Hz. The SHG radiations of 532 nm (green light) emitted were collected by a photo multiplier tube (PMT-Philips Photonics model 8563) and the optical signal incident on the PMT was converted into voltage output at the CRO (Tektronix-TDS 3052).

Results and discussion

Crystal growth

KAP crystals grown with and without the addition of CY, HI and LY are shown in Fig. 1. The dopants were not changes the original structure or morphology of the crystal. Even though CY doped crystal was found to have near low growth fronts and appeared to be less transparent (Fig.1b) when compared to the other crystals. The presence of amino acids influences very lowest changes in crystal growth rate and transparent nature of grown KAP crystals.

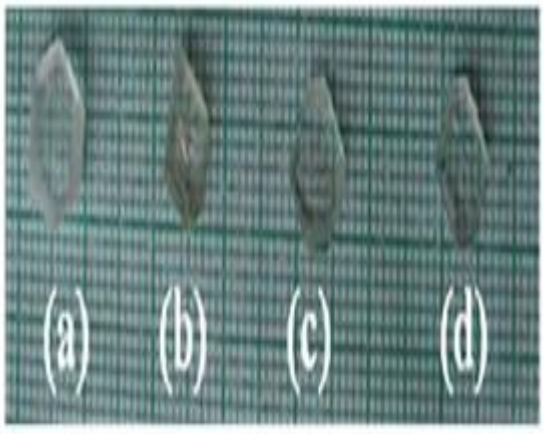

Fig 1. As grown a) pure and doped b)CY,c)HI and d) LY doped crystals

Powder X-ray analyses

X-ray patterns of pure and amino acid doped KAP are shown in Fig.2. The results confirmed that all the crystals grew in orthorhombic structure with space group $Pca2_1$ according to JCPDS data (31 - 1855 and 24 - 1870). The picture of the XRD pattern (Fig.2) shows the peak shifts slightly towards the higher angle side in the amino acid doped samples when compared to the pure KAP. These shifts in peak positions caused a significant change in lattice parameters when compared to the pure KAP (Table1). This result suggests that a certain amount of amino acids have been doped into the KAP system.

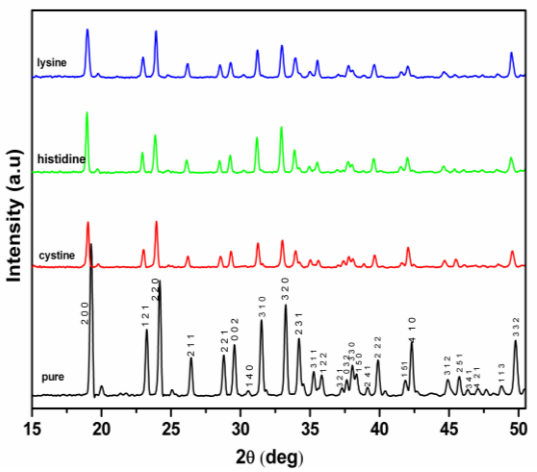

Fig 2. Powder X-ray patterns of Pure and doped KAP crystals

Table 1. lattice parameter values of pure and doped KAP crystals

Lattice Parameter	pure KAP	CY-KAP	HI-KAP	LY-KAP
a(Å)	9.0682	9.440	9.604	9.511
b(Å)	14.371	13.890	14.225	12.998
c(Å)	6.424	6.444	6.239	6.734
volume(Å)	837.169	844.947	852.352	832.484

The lattice parameters of the samples were calculated from the equation for the orthorhombic system using the method of least squares.

$\lambda=2d_{hkl} \sin \theta_{hkl}$

$1/d^2=h^2/a^2+k^2/b^2+l^2/c^2$ and volume V= abc.

Where d is the lattice spacing, h,k,l is the Miller indices , a , b and c is the lattice parameters, λ is the wavelength (CuKα : 1.5406 Å) and 2θ is the diffraction angle. The calculated lattice parameters are presented in Table 1. The results suggest that a certain amount of amino acids have been doped into the KAP crystal.

Thermal analyses

The TGA curves of pure and amino acid doped KAP are shown in Fig.3. Experimentally observed mass loss at various stages of decomposition agrees well with the theoretically calculated values according to the following equations:

$2\ KC_8H_5O_4 \longrightarrow K_2C_8H_5O_4 + C_7H_5O_2 + CO_2$ ….. (1)

$K_2C_8H_5O_4 \longrightarrow K_2CO_3 + C_7H_5O$ …..(2)

The weight loss begins at around 250˚C and about 40% of total mass is lost during the initial decomposition of all the investigated samples. The onset temperature of the decomposition was found to be 255, 260, 247 and 230˚C for pure, CY, HI and LY doped crystals respectively. Newkirk et al [14] and Belcher et al [15] have carried out an extensive studies on thermal behavior of KAP in N_2 and air atmospheres. The authors have reported that the KAP decomposed into K_2CO_3 and char at 800˚C in N_2 atmosphere. The results obtained for pure KAP in the present

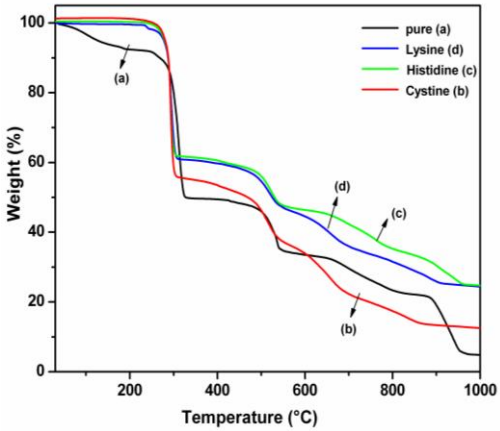

Fig 3. TGA curves of pure and doped KAP crystals

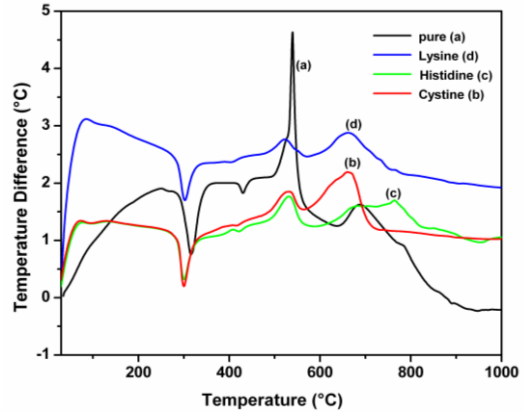

Fig 4. DTA curves of pure and doped KAP crystals

Work agrees well with these reported results. It was noticed that the decomposition temperature of LY doped crystal is much lower when compared to the other crystal. It may be due to the essential nature of lysine. The total mass loss up to 1000˚C was found to be 96%, 88%, 76% and 75% for pure, CY, HI and LY doped KAP crystals respectively. The results again shows a higher mass loss occur for pure KAP.DTA curves (Fig.4) of all the samples correspond well with the TG results. A significant difference in the high temperature region of the DTA curves of the doped samples confirms that the amino acids are doped into KAP crystal.

Optical transmittance studies

The grown crystals of higher quality with thickness of 2.4,2.2,2.3and 2 mm for pure , CY, HI and LY were placed in the crystal holder and the UV-NIR ray of wave length 190 to 1000 nm was allowed to pass through the (010) face of grown crystals. All the crystals have 15% to 40% transmittance in the visible and near ultraviolet region (Fig.5). There was a large absorption in the region of 300 nm. It is due to the n-π transition of the carbonyl group of the carboxyl functions [16]. The transmittance is lower for all doped crystal than pure crystals. On the other hand the transmittance is very low in LY doped crystal than all other.

FTIR analyses

Figure 6 shows the FTIR analyses of the as grown crystals. The observed vibrational frequencies and their assignments are listed in Table 2.The peaks in the region below 900 cm^{-1} appear due to C-H out of plane

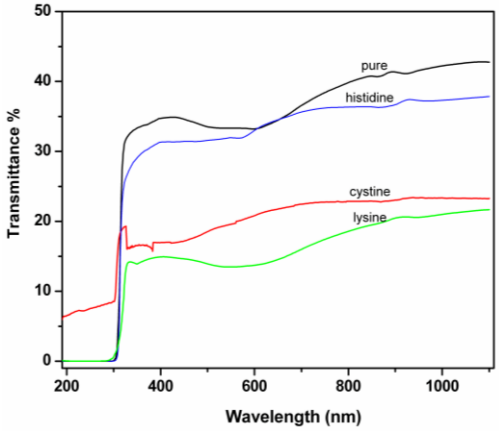

Fig 5. UV-Vis spectrum of Pure and doped KAP crystals

Table 2. Vibrational assignments of pure and doped KAP crystals

Pure KAP cm^{-1}	CY-KAP cm^{-1}	HI-KAP cm^{-1}	LY-KAP cm^{-1}	Tentative assignments
406	411	409	412	C=C out of plane bending
440	441	441	441	C=C out of plane ring bending
548	549	549	550	C=C-C out of plane ring deformation
581	582	581	580	C=C-C out of plane ring deformation
642	642	648	650	C=C out of plane bending
683	682	682	683	C-O wagging
718	718	718	719	=C-H out of plane deformation
762	763	762	764	C-C stretching
802	804	807	805	C=H out of plane bending
848	849	850	850	C-H out of plane bending
891	890	888	892	=C-H out of plane bending
1090	1090	1090	1091	C-C-O stretching
1146	1146	1147	1147	C-C stretching
1280	1281	1284	1284	C-O stretching
1380	1380	1382	1379	-C=O Carboxylate ion =O symmetric stretching
1482	1483	1484	1483	C=C ring stretching
1566	1581	1560	1580	-C=O Carboxylate ion asymmetric stretching
1670	1669	1669	1668	C=C stretching
2480	2482	2481	2483	O-H Hydrogen bonded
2620	2620	2620	2620	O-H stretching
2790	2804	2802	2789	O-H stretching
3431	3430	3425	3433	O-H stretching Hydrogen bond

bending vibrations. The asymmetric stretching modes of vibrations -C-O were observed at 1565, 1569, 1566 and 1564 cm^{-1} for pure, CY, HI and LY doped crystals respectively. On the other hand, symmetric stretching modes of –C-O vibration are observed at around 1380 cm^{-1} for both pure and doped crystals. Aromatic ring group appears in the frequency range 1500 to 1600 cm^{-1}. C-H stretching vibration appears at around 2480 cm^{-1}. The C=C mode of vibration was present between 1480 to 1485 cm^{-1}. The strong hydrogen bonding interaction of C-OH in plane and out of plane bands were observed as week bands at 1470 and 950 cm^{-1} respectively [17]. Marked slight changes in the frequency ranges from 2750 to 3750 cm^{-1} vibration was observed for the doped samples when compared to the pure KAP. The difference in sharpness of multiple bands in this region may also be taken as evidence for the doping of amino acids. The presence of weak bear peak 2300 cm^{-1} in the doped samples corresponds to N-H stretching vibration (19).

KAP got shifted to higher wave numbers of 1569, 1566 and 1564 cm^{-1} for CY, HI and LY doped KAP crystals respectively. This upward shift has been attributed to the interaction of O-H group of KAP with COO group of amino acids [17].

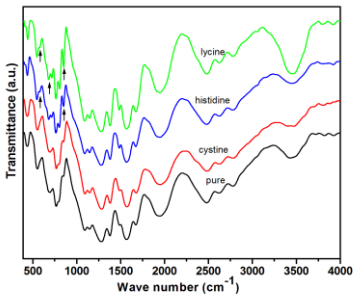

Fig 6. FTIR spectrum of pure and doped KAP crystals

Dielectric studies

A sample with graphite coating on two opposite faces was placed between two copper electrodes and thus a parallel plate capacitor was formed. The capacitance of the sample was measured at various frequencies ranging from 100 Hz to 5 MHz. The dielectric constant is calculated using the relation $\varepsilon_r = Cd/\varepsilon_0 A$, where C is the capacitance, d is the thickness, A is the area of the crystal and ε_0 is the absolute permittivity of the free space. The dielectric constant and dielectric loss for pure and doped crystals measured at 40˚C and 100°C are shown in Figs. 7 to 10 respectively. The dielectric constant has high values in the low frequency region for all the samples. From the graphs, it is clear that dielectric constant (ε_r) decreases as the frequency increases in all cases. The higher values of dielectric constant at low frequencies for all the crystals may be due to the presence of all the four polarizations namely space charge, oriental, electronic and ionic polarization and its low values at high frequencies which might be due to the loss of importance of these polarizations [7,19].

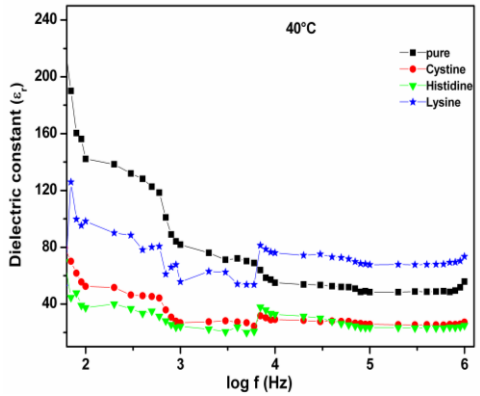

Fig 7. Dielectric constant vs. log frequency of pure and doped KAP crystals measured at 40°C.

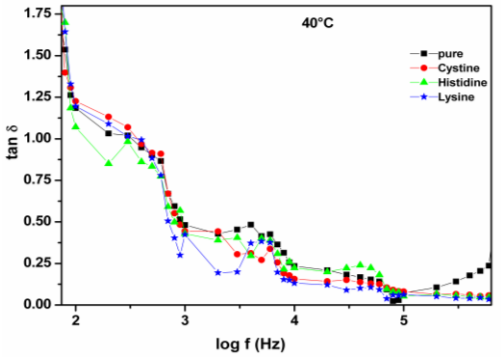

Fig 8. Dielectric loss vs. log frequency of pure and doped KAP crystals measured at 40°C.

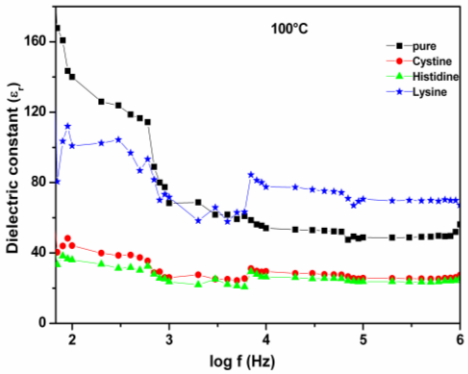

Fig 9. Dielectric loss vs. log frequency of pure and doped KAP crystals measured at 100°C.

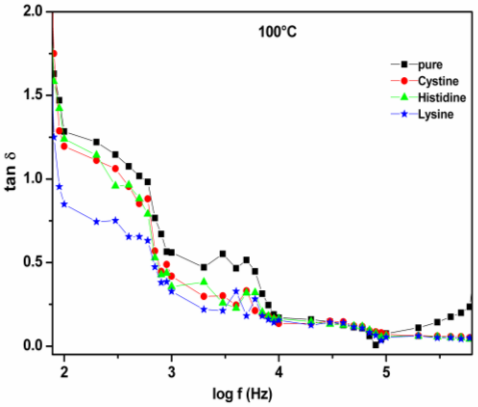

Fig 10. Dielectric loss vs. log frequency of pure and doped KAP crystals measured at 100°C.

Comparison of dielectric constant (ε_r) and dielectric loss for CY,HI and LY doped KAP crystals reveal that the LY doped KAP crystal has the lower values of dielectric constant than all other crystals. This could be attributed to the dielectric material nature of the additive (lysine). The dielectric loss of all crystals was continuously decreases more or less exponentially from 10^2 to 10^5 Hz when frequency increases. The doped crystals seem to undergo some kind of phase transition at around log frequency of 3.75 Hz frequency range. There is a sudden increase at log frequency of 3.75 Hz and slow decrease upto log frequency of 6 Hz in the dielectric constant curve. This occur only in the doped crystals and not in pristine. It is the effect of dopants in the doped crystals. In both pure and doped crystals, dielectric loss decreases with increase in the frequency. This suggests that the dielectric loss is strongly dependent on the frequency of the applied field and very low dielectric loss indicates the high purity of the crystals [7].

Microhardness studies

Microhardness measurements were carried out using Shimadzu tester with test mode of Vickers hardness test. Measurements were carried out on (010) face of all the crystals. Indentations were made at different loads. The microhardness values were calculated from the formula $Hv = 1.8544\ P/d^2$ kg/mm^2, where Hv is the Vickers microhardness number, P is the applied load and *d* is average diagonal length of the indentation. The hardness numbers as a function of load are shown in Fig. 11. The result reveals that the microhardness values are more for all doped crystals up to 50 gram load. When the load increase the hardness also increases for all crystals except LY added crystal. Contrary to this, the hardness values decreased with increase in load for LY doped crystal above 50 gram load. It can be noticed that the hardness value versus load plot for LY and CY doped crystal and CY and HI doped crystals are more or less parallel to each other. The observed changes in the microhardness values of amino acid doped into KAP may be

due to strong interaction of O-H groups of KAP with COO group of amino acids [18]. The result suggests that the LY and CY doped KAP crystals are preferred for device fabrication than the other crystals at higher loads (>100g) significant cracking occurs which may be due to the release of internal stress generated by indentation.

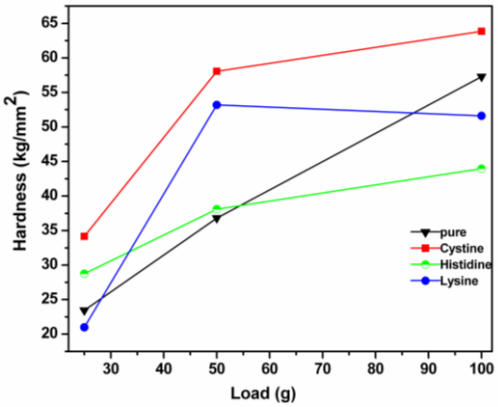

Fig 11. Microhardness number verses load.

SHG measurements

The SHG efficiencies are estimated at 8.6, 6.8, 8.6, 5.5 mV for pure, CY, HI and LY doped KAP crystals respectively. For KDP it was 28 mV. Thus the SHG efficiency for HI doped crystal was same as pure KAP crystal. All the doped crystals show NLO efficiencies.

Conclusions

Single crystals of amino acid doped KAP crystals were grown from the aqueous solutions using slow evaporation solution growth technique. Powder X-ray diffraction results proved that the crystals belong to orthorhombic system. The onset of decomposition begins at 255, 260, 247, and 230˚C for pure, CY, HI and LY doped KAP crystals respectively. These variations have been attributed to the doping of certain amount of amino acids into KAP. CY doped crystal have a higher thermal stability. The FTIR study confirmed the presence of different functional groups of the molecule KAP. The optical transmittance spectra revealed that the transmittance is more for HI doped crystal than all the other doped crystals. The dielectric constant and dielectric loss studies showed that all the doped crystal change the dielectric behavior of KAP crystal significantly. The values of the second harmonic generation efficiencies obtained by Kurtz powder method confirmed that all the doped crystals are suitable for limited level of nonlinear optical applications.

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